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Quantifying the elemental composition of mosses in western Washington USA

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HIGHLIGHTS

- Two species of moss were used to evaluate atmospheric deposition of major and trace elements.
- Major and trace elemental concentrations were higher in urban moss samples than those in rural western Washington.
- Pb isotope analyses suggest Seattle mosses receive metals from various industrial sources.
- Most trace metal concentrations were correlated with traffic rates.

GRAPHICAL ABSTRACT

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ABSTRACT

Major and trace element deposition across western Washington, USA was assessed in 2016 and 2017 by analyzing tissue metal concentrations in the epiphytic mosses *Isothecium stoloniferum* (Bridel) and *Kindbergia praelonga* (Hedw.) Ochyra. We used an intensive, vertically stratified sampling approach in *Acer macrophyllum* canopies in the Hoh Rainforest on the Olympic Peninsula, WA and in Seattle, WA to collect 214 samples of *I. stoloniferum*. An extensive, ground-based sampling approach was used across an urban-to-wildland gradient to collect 59 *K. praelonga* samples. Intensive samples were collected four times (April, July, and October of 2016 and in January 2017) and extensive samples three times (April, July, and October 2016) to assess seasonal differences in metal concentrations across sampling locations. A total of 273 moss samples were analyzed for Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, Ti, and Zn concentrations. Elevated concentrations of these elements were found in moss samples from both intensive and extensive sampling efforts across all seasons. Sampling location for both intensive and extensive sampling efforts was found to be a significant factor in determining moss metal concentrations. Metal deposition in and around Seattle appears to be derived from the regional transportation sector and other industrial sources. Ten *I. stoloniferum* samples from Seattle and the Hoh Rainforest were analyzed for Pb and Sr isotope ratios to help differentiate between natural and industrial-based emission sources. Hoh Rainforest Pb isotopes appear to be explained by a mixture of long-range Asian Pb influences and natural Pb sources, whereas Seattle Pb isotopes appear driven by industrial and road dust sources.

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1. Introduction

Elevated metal deposition in urban areas of the Pacific Northwest (PNW) has been recorded in Portland and Seattle (Armitage, 2012; King County, 2015); however, until recently, few studies used epiphytic mosses in the region as indicators of metal pollution (Donovan et al., 2016). Outside of the PNW, mosses have long been used as bioindicators of air quality and atmospheric pollution (Ruhling and Tyler, 1968; Pott and Turpin, 1996; Reimann et al., 2001; Cloquet et al., 2006; Aboal et al., 2010; Ćujić et al., 2014). Unlike vascular plants, mosses lack roots and absorb most nutrients from the atmospheric (Bates, 1992). Moss leaves are only one cell-layer thick, lack a protective epidermis and demonstrate ion exchange properties, all of which allows for the absorption of water, organic compounds and inorganic ions that are deposited on their surfaces (Gjengedal and Steinnes, 1990; Tyler, 1990; González and Pokrovsky, 2014).

Hylocomium splendens and *Pleurozium schreberi* are two moss species that have successfully been used as bioindicators of metal deposition across Europe (Berg et al., 1995; Berg and Steinnes, 1997a; Reimann et al., 2001, Harmens et al., 2015). These studies show a highly significant positive correlation between moss tissue metal concentrations and wet metal deposition values. The time period represented for pollutant accumulation in moss tissue consistently ranges from several months to a maximum of three years. The limited recycling of metals from senescent tissue in mosses (Brown and Bates, 1990) results in the metals being concentrated in the upper two-thirds of the moss shoots, which allows the green tissue to be used to infer metal deposition over a three year or less time period (Berg and Steinnes, 1997b; Fernández and Carballeira, 2002; Couto et al., 2003).

The PNW is a region generally considered to have high air quality (e.g. SO_2, O_3) among regions of the United States (NADP/NTN, 2015), in part due to a lack of coal-fired power plants and a small industrial base. However, rapid increases in population and consequent growth in automobile, bus and truck transportation threatens to decrease air quality within the region (Geiser and Neitlich, 2007). In the Puget Sound Region alone, the population is expected to grow by roughly one million people from 2010 to 2040, which will in turn increase demand for travel throughout the region by 25% (Puget Sound Regional Council, 2014). As evidence of this increase, Seattle highways and roads were recently ranked the 10th most congested urban areas in the United States (Cookson and Pishue, 2017).

This region-wide expansion in the transportation sector has impacted the amount of metal pollutants entering western Washington ecosystems. Brake and tire attrition, as well as lubricant degradation produce high rates of metal pollution in highly congested areas (Garg et al., 2000; Apeagyei et al., 2011; Hulskotte et al., 2014). Brake bands and tires contain heavy metals, including Cr, Cu, Fe, Ni, Pb, Sr, Ti, and Zn, that are released with disintegration, potentially leading to adverse human health and wildlife effects (U.S. Government, 2001; Perrenoud et al., 2010; Denier van der Gon et al., 2013). These transportation pollutants as well as long-range atmospheric transports originating from Asia (Jaffe et al., 1999) also have the potential to negatively affect ecosystem health through their inimical effects to bryophyte communities (Davies et al., 2007; Aničić et al., 2009; Zvereva and Kozlov, 2011).

To date there have been no prior assessments of metal deposition using epiphytic moss as a bioaccumulator of atmospheric pollutants in Washington State. In this set of studies, we sought to quantify the extent and magnitude of metal accumulation in two species of moss commonly found in urban, suburban, and rural areas in western Washington utilizing an extensive (broad spatial sampling) and an intensive (two primary locations with high density sampling and sampling of multiple layers of the tree canopy) sampling approach described below. We also assessed the Pb and Sr isotopic ratios in moss tissue in urban and rural sampling locations as a means of identifying the potential source of the metal deposition.

2. Materials and methods

2.1. Study area & sampling design

We collected moss samples for major and trace elemental analyses by using two approaches. The first was an intensive, vertically-stratified sampling in bigleaf maple (*Acer macrophyllum* Pursh) canopies in the Hoh Rainforest on the Olympic Peninsula, WA, USA and in the urban center of Seattle, WA, USA. The second was an extensive, broad ranging sampling across an urban-to-wildland gradient in western WA. We chose *A. macrophyllum* because it is widely distributed across the urban-to-wildland gradient and hosts abundant growth of a variety of moss species on its branches and trunk. The study sites (Fig. 1) and the two sampling approaches are detailed below.

2.1.1. Intensive approach

We collected samples from one stand located on Hoh River Trust land in the Hoh Rainforest (47°49′14.6″N, 124°12′01.2″W) on the Olympic Peninsula, WA, and from three *A. macrophyllum* stands located in Seattle city parks: Seward Park (47°33′16.0″N, 122°15′01.2″W), Interlaken Park (47°38′07.5″N, 122°18′29.8″W), and Ravenna Park (47°40′15.1″N, 122°18′10.0″W). Replicate moss samples were collected from a total of 18 *A. macrophyllum* trees: nine from the Hoh Rainforest, WA (106 samples), and nine from three city parks in Seattle, WA (108 samples), over the course of four seasons (April, July and October 2016, and January 2017). Trees were selected based on several safety criteria and sampling needs. The samples trees had to have a least three accessible branches below a solid anchor point so that we could obtain samples from three different heights throughout the crown. The average branch heights across all 18 trees were 17 m for the high point, 12 m for the middle point, and 9 m for the lowest point. Trees were ascended using the Single Rope Technique (Coffey and Andersen, 2012) employing the Singing Tree Rope Wrench and a friction hitch to gain access to the canopy. The 18 trees were instrumented with ionic resin lysimeters (UNIBEST Ag Manager, Walla Walla, WA) and installed over the 12-month sampling period (January 2016 – January 2017) at the three sampling heights within the canopy to evaluate wet deposition throughfall rates (Susfalk and Johnson, 2002; Klopatek et al., 2006; DeLuca et al., 2008). As moss metal concentrations are not reliable integrators of metal deposition rates (Aboal et al., 2010), the lysimeters provide an estimate of annual wet deposition levels. Cat's tail moss (*Isothecium stoloniferum*) was chosen as the target species for the intensive design as it was the only species we found available to sample across all sites and at all points in the canopy, and it has also been used previously for biomonitoring studies conducted in the Georgia Basin, British Columbia, Canada (Pott and Turpin, 1998; Raymond and Pott, 2003; Raymond and Bassingthwaighte, 2010).

2.1.2. Extensive approach

To extend the spatial coverage of the intensive sampling approach, we also sampled moss using ground-based sampling techniques across an urban-to-wildland gradient in western Washington. Replicate field samples were collected from a total of 20 primarily *A. macrophyllum* stands across western Washington: five sites from the western side of the Olympic Peninsula (15 samples), five suburban sites in the Cascade foothills collected east of Seattle and along Interstate 90 (15 samples), and 10 urban sites in Seattle, WA (29 samples) (see Fig. 1). Samples of *K. praelonga*, were collected from the bole of *A. macrophyllum trees* ~1 m above the ground. Extensive samples were collected within five days of the intensive sample collections for April, July and October 2016. We chose *K. praelonga* as a monitoring species because it is a common feather moss that is consistently found in urban, suburban, rural and pristine settings throughout western Washington and commonly found on the trunk of the tree thereby not requiring tree climbing which would have been prohibitively time consuming for extensive sampling.

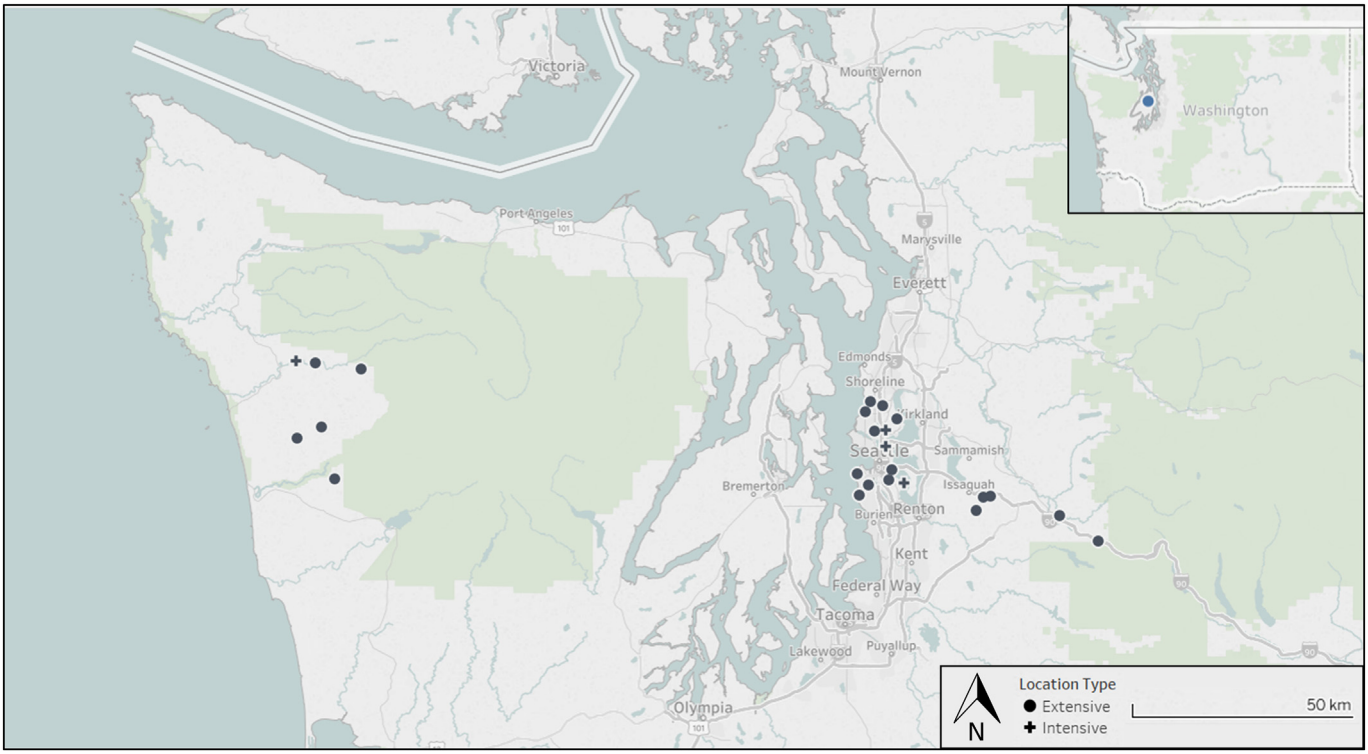

Fig. 1. Map of the location of intensive and extensive sampling sites across western Washington, USA. Asterisks represent intensive sampling sites and circles indicate extensive sampling sites.

2.2. Laboratory analysis

2.2.1. Major and trace element concentrations in moss tissue

Prior to analysis, all debris and necrotic tissue were removed with sterilized plastic forceps from the base of moss samples keeping only the upper two-thirds of the shoots (Gatziolis et al., 2016). We did not wash the moss samples prior to drying because previous studies have shown that it is ineffective in removing particulates (Aboal et al., 2011) and that some elements such as Cd and Zn may increase in concentration after washing (Fernández et al., 2010).We also wanted to retain particulates adhered to the moss surface in order to compare results to similar sample preparation methods used in other western North America moss biomonitoring studies (Pott and Turpin, 1998; Donovan et al., 2016; Gatziolis et al., 2016).

Moss samples were dried for 24 h at 40 °C and ground to a fine powder while immersed in liquid nitrogen. The HNO_3 + H_2O_2 digestion method (Jones, 1989) was used to prepare the dried and ground samples for analysis. A total of 0.3 g of ground moss tissue was placed into 50 mL graduated digestion tubes and treated with 4.0 mL of concentrated reagent-grade HNO_3. The tubes were covered with Pyrex watch glasses and left overnight at ambient temperature in a fume hood (approximately 18 °C) to allow some initial oxidation of the samples. Samples were digested at 95 °C for 90-min in borosilicate tubes heated evenly in a 36-tube graphite block digester. Following cooling to ambient temperature, 4 mL of reagent-grade 30% H_2O_2 were added to each tube followed by a 30-min digestion at 95 °C and allowed to cool. Next, an additional 4 mL of H_2O_2 were added to each sample and heated again at 95 °C. After cooling, deionized water was added to each tube to the 20-mL mark. To remove any undigested particulates not dissolved in the HNO_3 and H_2O_2, the samples were filtered through 0.45-μm membrane syringe filters. Digests were analyzed for a suite of metals (Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, Ti, and Zn) using inductively coupled plasma optical emission spectrometry (ICP-OES). Instrument performance tests were carried out daily to ensure proper calibration. After calibration, quality control samples consisting of reagent and method blanks, independent check standards were analyzed. The accuracy of the digestion and analysis protocol was checked using certified standards pine needles SRM-1575 and peach leaves SRM-1547 for moss samples. The measured values for the certified standards were within the certified ranges.

2.2.2. Wet deposition analysis

The ionic resin from the canopy lysimeters was collected in January 2017 six months after installation. Elements adsorbed in the resin capsules were extracted with by shaking the resins with 10 mL of 0.5 M HCl for 30 min, decanting, and repeating that process two additional times to create a total volume of 30 mL (DeLuca et al., 2002). Resin extracts were then analyzed for Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, Ti, and Zn by ICP-OES.

2.2.3. Lead and strontium isotopic analysis

Isotopic ratios of Pb and Sr were used as a tool to distinguish between natural and anthropogenic source inputs (Åberg, 1995; Komárek et al., 2008; Sherman et al., 2015). Utilizing the HNO_3 + H_2O_2 digestion method described above, we analyzed 10 moss samples collected in January 2017 from the intensive sites for Pb and Sr isotopes. Five samples were collected from the Hoh Rainforest site on the Olympic Peninsula, WA, five samples from Seattle, WA (Ravenna, Interlaken, and Seward) and run alongside aliquots of an internal laboratory standard (UW BCR-1). All reagents used for isotopic analysis were purified by a double sub-boiling distillation in Teflon.

2.2.3.1. Lead separation and analysis. Immediately following the HNO_3 + H_2O_2 digestion method, samples were dried down at 93–107 °C on a hot plate overnight and redissolved in 2.5 mL of 6 N HCl. Samples were dried down once again and purified for Pb and Sr using standard ion chromatography procedures (Kayzar et al., 2014). Lead isotopes ($^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$) were analyzed on a Multicollector Inductively-Coupled-Plasma Mass Spectrometer (MC-ICP-MS). Prior to isotopic analyses, a small aliquot of the sample

solution was measured for concentration in order to adjust sample intensity to within 10% of the intensity of the Pb isotope standard (SRM 981) (Kayzar et al., 2014). Samples and standards were spiked with NIST Thallium (Tl) isotopic standard (SRM 997) to correct for Pb isotope instrumental mass fractionation. Unknowns were normalized to SRM 981 by sample-standard bracketing using values of Todt et al. (1996).

2.2.3.2. Strontium separation and analysis. Strontium separation was achieved using 0.3 mL of a Sr-specific crown ether resin (Eichrom Sr-SPEC resin). The Sr-bearing elutions from the previous Pb column procedure were collected and dried down at 107 °C and then redissolved in 0.4 mL of 4 N HNO_3. This solution was loaded onto the Eichrom resin column and rinsed with 3.2 mL of 4 N HNO_3 to elute Ca, Na, Rb, and Ba. Strontium was eluted with 3 mL of 0.05 N HNO_3. Samples were dried and redissolved in 3 mL of 2% HNO_3. Concentrations were adjusted to within 10% of the bracketing NIST-987 Sr standard. The procedure for MC-ICP-MS Sr isotope analysis follows that of Brach-Papa et al. (2009). The IAPSO seawater standard was run after every three samples to verify analytical accuracy.

2.3. Statistical analysis

Descriptive statistics (minimum, maximum, and median) were calculated for each element across intensive and extensive moss samples. We also estimated the Pearson correlation coefficient between moss metal concentrations and average daily traffic counts across the intensive sampling sites. Annual average daily traffic volumes were gathered from Washington State's Department of Transportation traffic counters near the four intensive sites (WSDOT, 2016).

Major and trace elemental concentrations, represented as mg kg^{-1}, were transformed using a centered log-ratio (from the rgr package). We used a permutational multivariate analysis of variance (perMANOVA) to test if moss metal concentrations significantly differed across site types for both intensive and extensive sites. The subsequent test of multivariate homogeneity of groups (DISPER) was used to calculate significant multivariate dispersions in variables among the site types for intensive and extensive moss samples. Euclidean distance was chosen for the perMANOVA, and significance of the perMANOVA was determined based upon 1000 random permutations.

Principal component analysis (PCA) was selected as the appropriate ordination method where dissimilarity was calculated as Euclidean distance (Legendre and Legendre, 1998). PCA was performed on the data matrix 'site type x metal concentration parameters' for both intensive (*I. stoloniferum* for urban and peninsula) and extensive (*K. praelonga* for urban, suburban, and peninsula) sampling sites. Twelve major and trace elemental concentration parameters (Cd, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Sr, Ti, and Zn) were introduced as the analysis variables. PCA was performed to assess the dominant patterns in moss metal concentrations across sites. The loadings of variables to each Principal Component (PC) were examined by converting eigenvector coefficients to structure correlations.

Linear regression models were used to determine the relationship between metal concentrations in *I. stoloniferum* tissue collected in January 2017 with average annual wet deposition measured using resin lysimeters across intensive sampling sites. Linear regression analyses were only carried out on moss samples from January 2017 as they were exposed to the full 12-months of wet deposition captured by the canopy lysimeters. All statistical analyses were conducted in the RStudio (RStudio Team, 2016).

3. Results

3.1. Major and trace element concentrations in moss tissue

Descriptive statistics for intensive (*I. stoloniferum* at peninsula and urban sites) and extensive (*K. praelonga* at peninsula, suburban, and urban sites) collected moss samples are reported in Table 1a–b. Within the intensive sites, urban *I. stoloniferum* samples exhibited higher metal concentrations compared to peninsula *I. stoloniferum* samples (e.g. 0.68 mg kg^{-1} median Pb concentrations in peninsula samples vs. 9.41 mg kg^{-1} median Pb concentrations in urban samples). For the extensive sites, *K. praelonga* metal concentrations were generally highest in the urban sites and lowest in the peninsula sites, with intermediate values measured from suburban areas (e.g. median Pb value of 6.99 mg kg^{-1} for urban, 3.06 mg kg^{-1} for suburban, 0.75 mg kg^{-1} for peninsula). Both intensive and extensive samples lacked exceptionally high metal concentrations. Estimate of Pearson correlation coefficients revealed several significant relationships between some elemental concentrations and daily traffic counts across the intensive sites (Table 2).

A two-way perMANOVA was initially run for the intensive samples for the matrix: site type * canopy height. Canopy height was not a significant driver of metal concentrations ($F = 0.56$, $p = 0.77$). For the intensive canopy samples, elemental concentrations were significantly different between peninsula and urban *I. stoloniferum* samples ($F = 93.19$, $p < 0.001$). Considering the site type term for the intensive samples, the DISPER results show no significant differences in between-site variation ($F = 1.38$, $p = 0.19$). For the extensive moss samples, a one-way perMANOVA showed that metal concentrations were significantly different across the three site types ($F = 8.81$, $p < 0.001$). Considering the site type term, the DISPER results showed no significant differences in between-site variation ($F = 2.44$, $p = 0.11$).

Much of the variability in the 'site type x element concentration parameters' for both intensive and extensive samples were explained by their first two PCs. The total amount of variance explained by the first two PCs in the intensive data (PCA 1) were PC1 (55.26%) and PC2 (14.12%) (Fig. 2). For the major axis representing 55.26% of the data variance in PCA 1, Fe, Pb, and Ti were positively and heavily loaded to PC1 (loading scores 0.877 to 0.930) and K, Mg, Mn, Ni, and Zn were negatively and heavily loaded to PC1 (loading scores −0.766 to −0.914). For the secondary axis representing 14.12% of the data variance in PCA1, Cr, Cu, and Sr were positively and heavily loaded to PC2 (loading scores 0.872 to 0.956), and Cd was negatively and heavily loaded to PC2 (loading score −0.922).

The total amount of variance explained by the first two PCs in the extensive data (PCA 2) were PC1 (53.98%) and PC2 (14.21%) (Fig. 3). For the major axis resenting 53.98% of the variance in PCA2, K, Mg, Mn, Sr and Zn were positively and heavily loaded to PC1 (loading scores 0.846 to 0.954), and Cr, Fe, and Ti were negatively loaded to PC1 (scores −0.713 to −0.852). For the secondary axis, Cd, Cu, and Pb were positively and strongly loaded to PC2 (scores 0.807 to 0.998), and Ni was negatively loaded to PC2 (score −0.956).

3.2. Wet deposition concentrations

No significant differences in wet deposition values, as collected with the resin lysimeters, were observed across the canopy heights ($p = 0.62$); therefore, we used an average annual precipitation-weighted wet deposition value per tree (Chance et al., 2015; Wetherbee et al., 2010). The moss metal concentration values are the arithmetic mean of metal concentrations per tree from the January 2017 collection. Of the twelve elements measured, Cr, Cu, Fe, Ni, Pb, Ti, and Zn showed correlation ($R^2 > 0.30$, $p < 0.05$) between intensive *I. stoloniferum* moss tissue concentrations and annual average wet deposition rates (Fig. 4). No strong correlations were found for Cd, K, Mg, Mn and Sr.

3.3. Lead and strontium isotope composition

Table 3 reports the trace element concentrations and isotopic compositions for the ten *I. stoloniferum* samples analyzed in this study. In general, elemental concentrations for Cu, Pb, Sr, and Zn were found to be elevated in the Seattle samples compared to those from the Hoh Rainforest. Elemental concentrations are also expressed in term of

Table 1
Summary statistics for the 12 elements analyzed in moss tissue samples collected from both intensive (a) and extensive (b) sampling sites in western Washington. BDL = below detection limit.

a

	Peninsula intensive *I. stoloniferum* (mg kg^{-1}, $n = 106$)				Urban intensive *I. stoloniferum* (mg kg^{-1}, $n = 107$)			
	Min	Max	Median	Samples BDL	Min	Max	Median	Samples BDL
Cd	BDL	3.44	0.07	41	BDL	0.50	0.18	17
Cr	0.08	1.93	0.49	0	0.35	5.91	2.32	0
Cu	0.52	11.97	3.21	0	1.78	21.71	11.48	0
Fe	33.79	316.3	86.89	0	78.11	1396	565.8	0
K	2373	10,170	5109	0	2290	12,482	8155	0
Mg	1254	3721	1903	0	809.1	4415	2318	0
Mn	16.10	373.8	76.66	0	9.62	290.5	100.4	0
Ni	BDL	4.28	1.35	11	0.34	98.91	2.73	0
Pb	BDL	5.79	0.68	5	0.62	64.06	9.41	0
Sr	11.42	149.17	46.08	0	24.15	300.00	116.6	0
Ti	1.39	16.99	4.94	0	3.58	60.51	25.6	0
Zn	17.62	162.67	38.45	0	15.42	191.82	76.12	0

b

	Peninsula extensive *K. praelonga* (mg kg^{-1}, $n = 15$)				Suburban extensive *K. praelonga* (mg kg^{-1}, $n = 15$)				Urban extensive *K. praelonga* (mg kg^{-1}, $n = 29$)			
	Min	Max	Median	Samples BDL	Min	Max	Median	Samples BDL	Min	Max	Median	Samples BDL
Cd	BDL	0.31	0.08	5	BDL	0.27	0.13	5	BDL	1.48	0.19	2
Cr	BDL	2.21	0.50	4	0.24	3.09	1.34	0	0.61	6.69	2.90	0
Cu	1.82	6.81	3.96	0	4.69	10.88	7.85	0	6.79	21.7	10.79	0
Fe	20.54	994.4	154.8	0	162.8	1097	502.7	0	212.9	2029	1007	0
K	3394	1150	5011	0	4561	9356	5620	0	4791	13525	7986	0
Mg	1282	2831	1722	0	1175	1935	1581	0	1495	2918	2021	0
Mn	41.01	278.8	104.3	0	41.25	286.2	85.93	0	73.52	411.8	141.4	0
Ni	BDL	5.20	1.56	5	BDL	4.36	1.45	5	BDL	5.95	2.94	8
Pb	BDL	1.89	0.75	1	1.20	9.90	3.06	0	1.22	35.47	6.99	0
Sr	23.64	102.8	45.25	0	18.92	68.16	34.72	0	34.46	232.4	96.29	0
Ti	1.57	50.13	5.64	0	7.87	62.32	25.25	0	10.06	99.46	54.57	0
Zn	21.18	90.82	36.75	0	33.29	108.92	68.54	0	37.17	196.5	69.33	0

metal/metal ratios for Cu/Pb vs. Zn/Pb, and Fe/Sr vs. Ti/Sr (Fig. 5). Samples from Seattle contain lower ratios of Cu/Pb and Zn/Pb ratios and less radiogenic Pb isotope values ($^{206}Pb/^{207}Pb = 1.1751–1.1859$), suggesting an industrial source input for Pb. Samples from the Hoh Rainforest are characterized by higher ratios of Cu/Pb and Zn/Pb ratios and more radiogenic Pb isotope values ($^{206}Pb/^{207}Pb$ generally >1.1849). Possible source patterns emerged by plotting $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ (Fig. 6). Measured Pb isotope compositions show that

Table 2
Estimates of Pearson's correlation coefficients between annual average daily traffic counts (AADT) and metal concentrations in *I. stoloniferum* samples collected the intensive sampling sites in western Washington. Darker cell color indicates higher correlation values.

	AADT	Cd	Cr	Cu	Fe	K	Mg	Mn	Ni	Pb	Sr	Ti	Zn
AADT	•	−0.01	0.75	0.81	0.78	0.65	0.36	0.14	0.19	0.59	0.67	0.75	0.55
Cd		•	0.00	0.01	0.01	0.00	−0.05	0.24	0.01	0.07	0.03	0.02	0.08
Cr			•	0.90	0.97	0.64	0.45	0.33	0.22	0.82	0.75	0.94	0.70
Cu				•	0.90	0.76	0.55	0.38	0.20	0.78	0.79	0.86	0.82
Fe					•	0.64	0.42	0.37	0.18	0.83	0.76	0.98	0.69
K						•	0.71	0.23	0.06	0.51	0.70	0.61	0.62
Mg							•	0.25	0.08	0.34	0.57	0.38	0.53
Mn								•	0.08	0.30	0.22	0.29	0.54
Ni									•	0.28	0.16	0.18	0.22
Pb										•	0.73	0.81	0.73
Sr											•	0.72	0.70
Ti												•	0.66
Zn													•

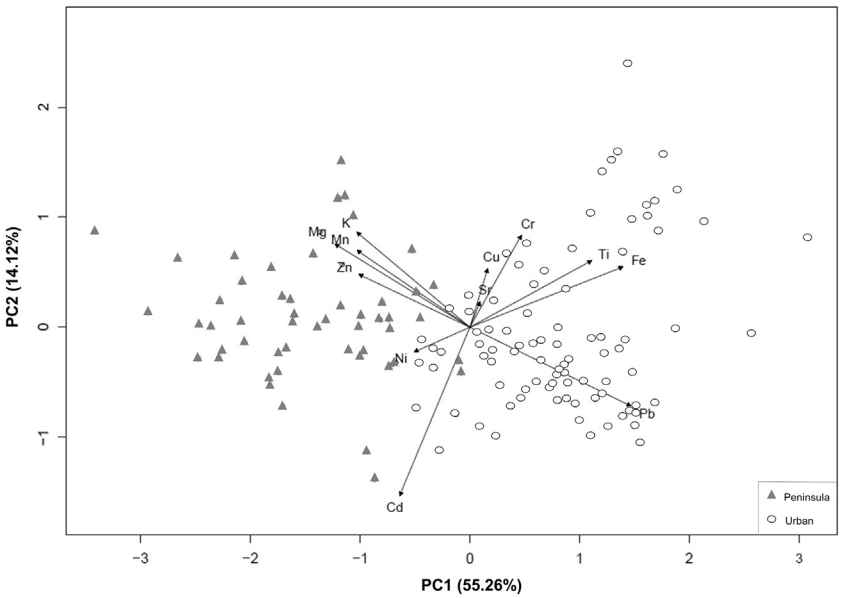

Fig. 2. Principal component analysis (PCA) ordination of *I. stoloniferum* samples collected at intensive sampling sites in western Washington, USA. The open circles represent urban samples and gray triangles are samples collected from the Olympic Peninsula.

Western U.S. natural geologic samples are more radiogenic than Seattle or West Coast industrial sources, making them distinct from the Seattle and Hoh Rainforest moss samples analyzed. Two linear trends were identified: (1) the first trend includes Pb isotopic signatures from a variety of North American sources, and (2) a second trend corresponding with the Pb isotopic signatures from Asian sources. From the North American trend line, Seattle samples are grouped near similar isotopic signatures for road dust samples from mainland British Columbia, Canada and metallurgy dust from Asian industrial sources.

Hoh Rainforest isotopic signatures identify possible trans-pacific mixing from Asian sources (e.g. Chinese Loess) given the location on the parallel trend lines. Samples from the Hoh Rainforest moss samples had higher $^{87}Sr/^{86}Sr$ values (0.7051–0.7067) and higher 1/Sr concentrations (0.011–0.026 mg kg^{-1}) compared to Seattle samples (0.7047–0.7052 and 0.005–0.011, respectively) (Fig. 7). Both Seattle and Hoh Rainforest Sr isotopic signatures were distinct from other natural sources identified (e.g. seawater and rocks).

4. Discussion

Metal deposition and accumulation in *I. stoloniferum* and *K. praelonga* were higher in urban sites in Seattle than in suburban and rural sites near Seattle. Among intensive sampling sites, concentrations of Cr, Cu, Fe, Pb, Ti, and Zn are positively correlated with heavier daily traffic rates (Table 2). Traffic density is highest in Seattle relative to our other sampling locations, and Seattle has a mean daily traffic volume of 1,010,000 vehicles (WSDOT, 2016) in areas where metal concentrations are among the highest recorded. In contrast, daily traffic counts from the western side of the Olympic Peninsula are ~1300 vehicles per day and metal concentrations are notably lower (WSDOT,

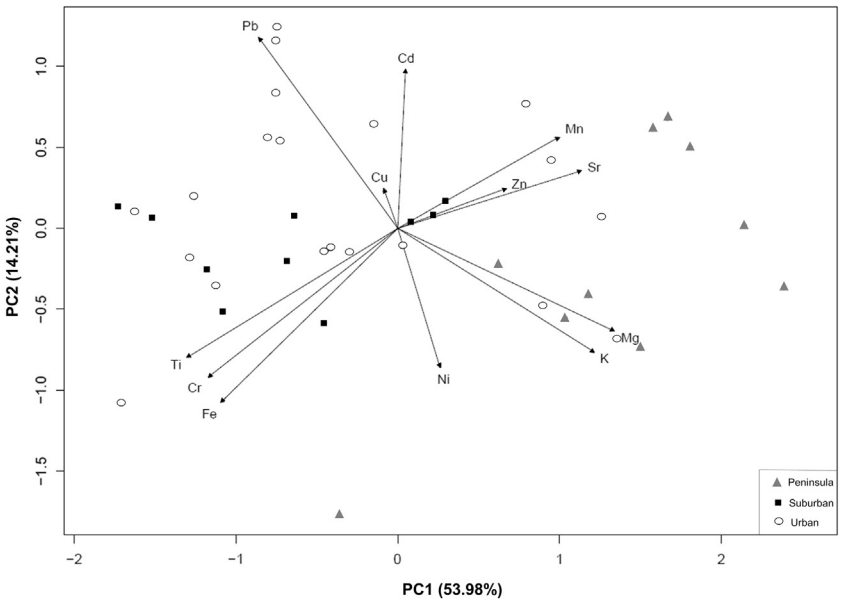

Fig. 3. Principal component analysis (PCA) ordination of *K. praelonga* samples collected at extensive sampling sites in western Washington, USA. Urban, suburban, and peninsula samples are represented by open circles, black squares, and gray triangles, respectively.

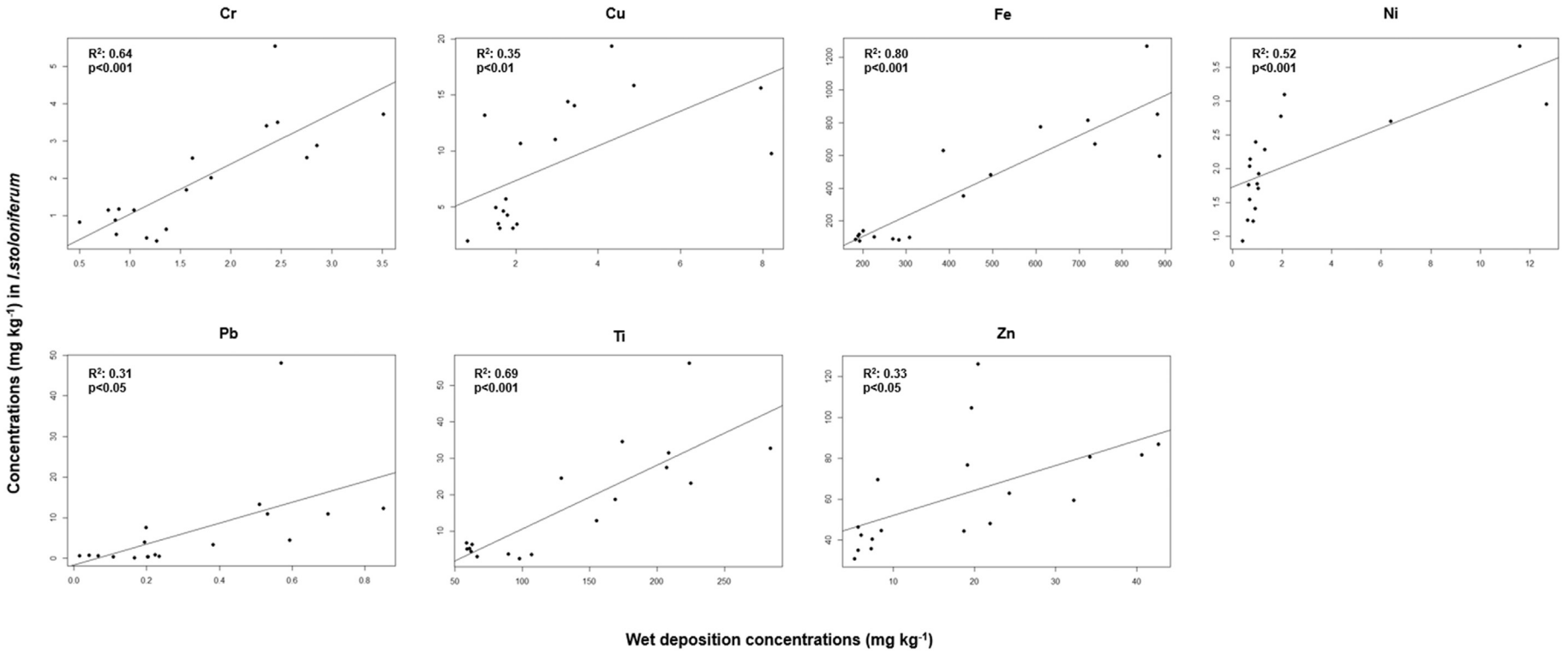

Fig. 4. Trace element concentrations in intensive *I. stoloniferum moss* tissue (mg kg^{-1}) versus annual atmospheric wet deposition of trace elements (mg kg^{-1}) in western Washington, USA.

Table 3
Isotopic composition and elemental concentrations at the intensive moss sampling sites in the Hoh Rainforest on the Olympic Peninsula and in Seattle.

Sample	Elemental concentration (mg kg^{-1})						Isotopic composition					
	Cu	Fe	Pb	Sr	Ti	Zn	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{87}Sr/^{86}Sr$
Hoh rainforest												
HRT3-M	2.14	68.45	0.48	53.4	3.54	31.95	18.6965	15.6597	38.3131	1.1939	2.0508	0.70518
HRT5-L	2.83	64.07	0.52	51.42	3.3	37.61	18.5447	15.6504	38.3434	1.1849	2.066	0.70578
HRT6-L	5.81	76.04	0.79	47.38	5.86	55.45	18.2967	15.618	38.182	1.1715	2.0868	0.70679
HRT7-T	3.43	48.22	0.34	38.1	3.73	48.22	18.616	15.6521	38.3293	1.1894	2.0589	0.70618
HRT8-L	2.2	57.42	0.36	86.2	5.86	33.13	18.6073	15.6473	38.3133	1.1892	2.059	0.70592
Seattle												
INT1-T	1.11	622.90	16.40	135.1	27.36	77.45	18.523	15.6192	38.1316	1.1859	2.0586	0.70518
INT2-L	15.55	876.63	34.63	191.63	35.98	122.03	18.3654	15.6031	38.0268	1.177	2.0706	0.70526
RAV2-T	9.86	504.59	10.76	87.82	42.25	54.89	18.3343	15.6022	37.9992	1.1751	2.0726	0.70500
SEW3-M	9.31	433.82	5.77	94.18	17.66	54.33	18.4321	15.6127	38.0886	1.1806	2.0664	0.70501
SEW3-T	9.92	282.53	2.85	105.68	19.92	59.48	18.505	15.6272	38.1558	1.1842	2.0619	0.70470

*2 sigma analytical precisions are: Sr = ±40 ppm; Pb ± 125, 150 and 200 ppm for 206/204, 207/204 and 208/204, respectively. *Five contemporaneous analyses of the IAPSO seawater standard yielded an average 87Sr/86Sr = 0.709190 (accepted value = 0.709166).

2016). As the Puget Sound region is expected to experience significant population growth by 2040, increasing pressure from construction and the transportation sector is likely lead to higher levels of metal pollutants in the region. Specifically, we observed a significant positive correlation between daily traffic rates and concentrations of Cr, Cu, Fe, Pb, Sr, Ti, and Zn, suggesting these come from a common class of pollution sources (Table 2). In a prior study, Apeagyei et al. (2011) reported that the most abundant element in automobile tires was Zn (17,720 mg kg^{-1}), followed Ca > W > K > Fe > Ti > Cr > Mo > Cu > V > Sr > Zr > Pb. Fugitive dust from tire attrition is a potentially substantial source of Zn entering the environment (Councell et al., 2004). Elevated levels of Zn were found in the intensive and extensive urban sites close to major roadways such as Interstate 5 and WA State Route 99.

Of the plant essential nutrients examined in this study, the correlation between K and Mg for intensive samples were substantial (r = 0.71). In PCA 1, K, Mg, Mn, and Zn were grouped together suggesting this is due to natural processes such as internal nutrient cycling. Iron and Ti also exhibited a strong correlation (r = 0.98) and were clustered together in PCA1 and PCA2. Elevated Fe and Ti concentrations were found in intensive urban (565.81 and 25.59 mg kg^{-1}, respectively median concentrations) and extensive urban (1007.1 and 54.57 mg kg^{-1}, respectively median concentrations) samples. Mineral dust from construction activities is a potential source of these two elements observed in this study (Coz et al., 2010).

Although Cu, Fe, and Zn are essential plant micronutrients, Cu is of particular concern in the PNW as it can be hazardous to wildlife in high concentrations in the environment. This is particularly a problem in road runoff where Cu concentrations ranging from 1 to 30 μg/L have been shown to produce sublethal neurotoxicity in salmon (Linbo et al., 2006; Sandahl et al., 2004; Sandahl et al., 2007; Baldwin et al., 2003). To regulate sources of Cu entering waterways by surface runoff and dust deposition, Washington State passed the Better Brakes Law (Chapter 173-901 WAC) in 2010. The law will be fully implemented in 2025, but until then brake pads will be a source of Cu pollution in Washington State. In this study, Cu concentrations measured from *I. stoloniferum* were significantly positively correlated with daily traffic rates (r = 0.81, $p < 0.001$), and with annual average Cu deposition rates (R^2 = 0.35, $p < 0.01$). This suggests that Cu released as fugitive dust from brake pads along major roadways and arterials, such as Interstate 5 and Washington State Route 99, could account for the higher levels of Cu we observed from both intensive and extensive urban moss samples.

Lead is an obvious trace metal of environmental concern given that it is not an essential nutrient and it is toxic to living organisms even in

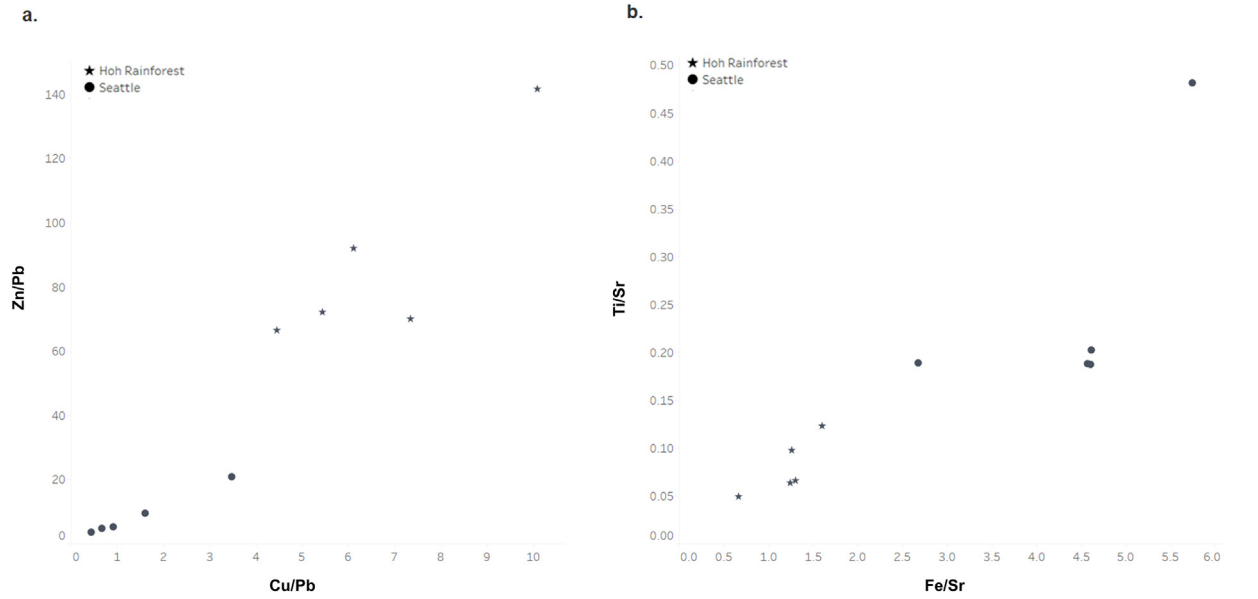

Fig. 5. Trace element signatures in *I. stoloniferum* samples analyzed for isotopic composition. (a) Variation between Zn/Pb versus Cu/Pb ratios, and (b) variation between Zn/Sr versus Cu/Sr ratios.

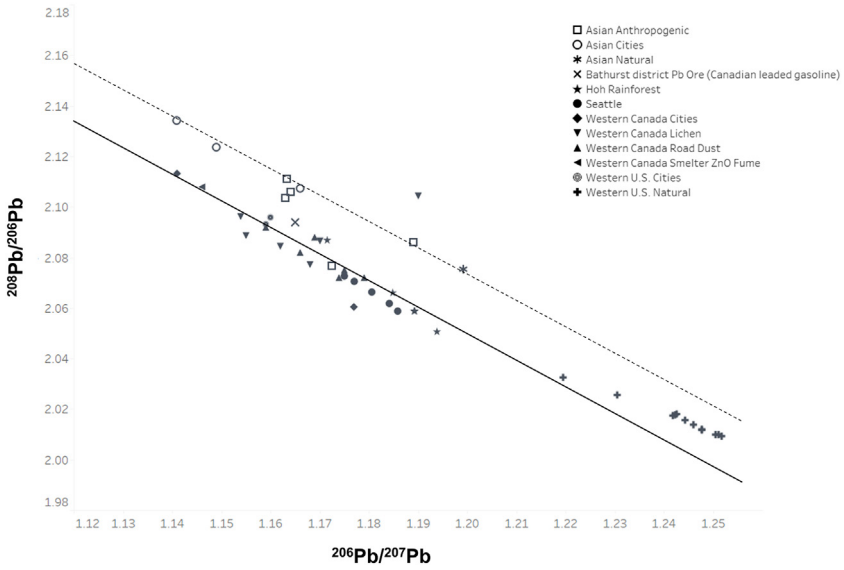

Fig. 6. $^{208}Pb/^{206}Pb$ vs. $^{206}Pb/^{207}Pb$ for samples collected from the Hoh Rainforest and Seattle. Also shown are the compositions for samples representative of cities in Western U.S., Western Canada, and Asia (Bollhöfer and Rosman, 2001); Asian natural sources (representing Chinese loess) (Jones et al., 2000); Asian industrial sources (including coal combustion, metallurgy dust and PM10) (Tan et al., 2006); Bathurst district ore (representing British Columbia leaded gasoline) (Sangster et al., 2000); road dust from mainland B.C. (Preciado et al., 2007); B.C. smelter ZnO fume (Shiel et al., 2010); lichen samples from Vancouver Island, B.C.(Simonetti et al., 2003); and Western U.S. natural geologic influences (Chan et al., 2012). The solid black line represents the North American array and the dashed gray line represents the Asian array of isotopic ratios. Analytical error is smaller than the data symbols.

relatively low concentrations, and many studies have reported on the effects of Pb pollution to human and wildlife health (e.g., Lanphear et al., 2005; Nevin, 2000; Needleman and Gatsonis, 1990; Holcombe et al., 1976; Spehar et al., 1978).

We observed that *I. stoloniferum* collected from Seattle have less radiogenic isotopic composition, which is consistent with the anthropogenic Pb composition of other west coast cities (Fig. 6). In the intensive samples from this study, Pb were positively correlated with average daily traffic counts ($r = 0.59$, $p < 0.001$) (Table 2) and had similar isotopic signatures to Pb measured in road dust from mainland British Columbia, B.C. (Preciado et al., 2007). This suggests that a possible source of Pb in Seattle samples may be from brake pad and tire abrasion (Apeagyei et al., 2011). Hallock (2010) reported that Pb is likely to be transported as particle-bound fugitive dust rather than in the dissolved phase as Pb has a high affinity for particulate matter. Existing studies suggest a significant positive relationship between bulk deposition levels and the concentrations of Pb in moss (Ross, 1990; Berg et al., 1995; Thöni et al., 1996; Berg and Steinnes, 1997a, 1997b; Schintu et al., 2005; Fowler et al., 2006), which is supported in our findings (Fig. 4). As for possible sources of Pb in the Hoh Rainforest samples, emissions from

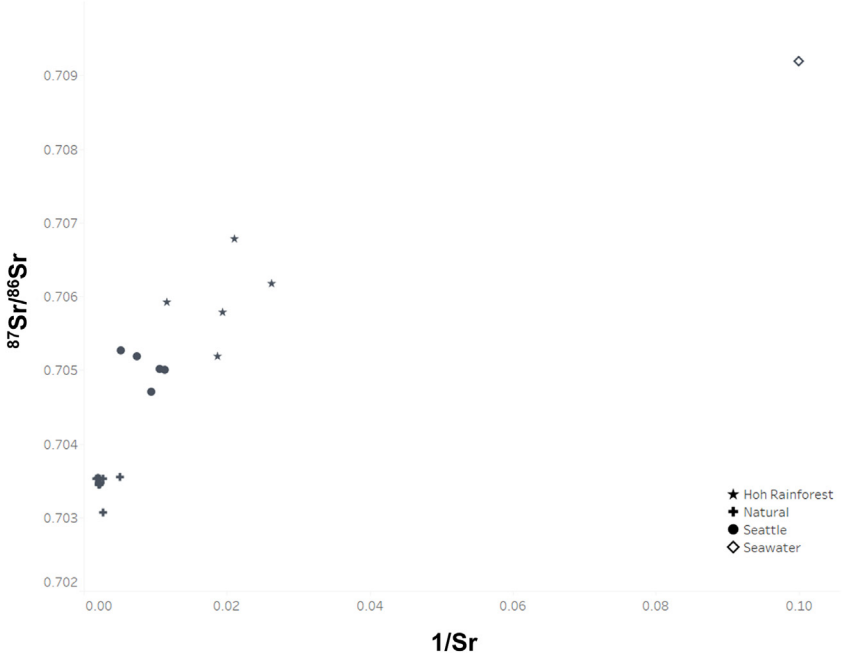

Fig. 7. $^{87}Sr/^{86}Sr$ vs. 1/Sr concentrations (mg kg^{-1}) for moss samples collected from intensive sampling sites in the Hoh Rainforest and Seattle. Also shown are the compositions for samples representative of seawater influence (IAPSO certified standard) and natural geologic sources from Washington State, USA (Chan et al., 2012). Analytical error is smaller than the data symbols.

Asia are known to reach the western U.S. within 10 days (Jaffe et al., 1999), and Chinese aerosol is enriched in ^{208}Pb (Bollhöfer and Rosman, 2001; Ewing et al., 2010). The Pb isotopic compositions for Hoh Rainforest samples indicate potential trans-Pacific contamination by Asian emissions (i.e. inputs from long-ran Chinese loess).

Approximately 1.0 Mg yr^{-1} of Cd is released from anthropogenic sources in Puget Sound, which includes leaching from roofing materials, release from agricultural fertilizer, air emissions for industrial facilities, and road-related sources such as tire and brake pad wear (Ecology and King County, 2011). The sampling sites in the current study were located in the Hoh Rainforest, along I-90, or in Seattle city parks; therefore, they are unlikely to experience Cd leachate from roofing materials. Spectrum Glass was the only known industrial facility in the Puget Sound region reporting fugitive air releases of cadmium in the last 10 years, but they ceased production in July 2016. We note that we did not observe significantly high levels of Cd in either intensive or extensive samples. Also, because Cd was not significantly correlated with daily traffic rates ($r = -0.01$, $p = 0.98$), it is unlikely that tire and brake wear were the source of cadmium detected in *I. stoloniferum* and *K. praelonga* samples across the sampling locations.

Elevated levels of Sr were observed in urban areas in *I. stoloniferum* and *K. praelonga* samples (116.57 mg kg^{-1} and 96.29 mg kg^{-1}, median concentrations respectively) compared to rural samples (46.08 mg kg^{-1} and 45.25 mg kg^{-1}, median concentrations respectively). Strontium is an alkaline earth element with an average concentration of 370 mg kg^{-1} in the earth's crust and 240 mg kg^{-1} in soil minerals (Sposito, 1989). The $^{87}Sr/^{86}Sr$ isotope ratio has been used extensively to measure atmospheric inputs of Sr to soils and vegetation (Graustein and Armstrong, 1983; Graustein, 1989; Miller et al., 1993; Capo and Chadwick, 1999). The source of the levels of Sr associated with Seattle and Hoh Rainforest samples is not clear. One possible source for Sr in Seattle could be from tire attrition associated with traffic along major corridors in Seattle, given the positive correlation with daily traffic rates ($r = 0.67$), and significant relationship with other metals commonly found in tires (see Table 2 for relationships with Cr, Cu, Fe, K, Pb and Zn).

A comparison of mean element concentrations in mosses obtained from this study with recent moss monitoring studies in the PNW region is presented in Table 4. A study from Portland, Oregon (Gatziolis et al., 2016) used the moss *Orthotrichum lyellii* Hook & Taylor to monitor pollution patterns, whereas this study and the one conducted in British Columbia, Canada (Pott and Turpin, 1998), used *I. stoloniferum*. While interspecies variation may affect the comparison of metals levels to some extent, when the same sample preparation procedure is used it is unlikely to cause the differences in metal levels between urban and rural environments. Mean metal concentrations in the urban *I. stoloniferum* samples in this study were higher than values previously reported in the PNW, with the exception of Cd reported from Portland (Gatziolis et al., 2016), and Cd and Pb reported from British Columbia (Pott and Turpin, 1998). The higher levels of Cd and Pb reported in British Columbia, Canada in 1993 (Pott and Turpin, 1998) may be attributed to legislative policies that did not remove leaded gasoline from the Canadian market until December 1990. Several other studies have attempted to address the time over which metals are present in moss tissue (Boquete et al., 2013; Fernández et al., 2013), but none of them used *I. stoloniferum*, *K. praelonga*, or *O. lyellii*. The metal range captured in these three studies presented in Table 4 likely represents a maximum of a three-year exposure period (Gatziolis et al., 2016) as only the top two-thirds of the moss shoot was analyzed. The sources of the Cd levels reported by Donovan et al. (2016) were identified as industrial atmospheric deposition originating from two stained-glass manufacturers. Except for Cd, both Ni and Pb levels found in the urban *I. stoloniferum* from this study were 1.42 and 1.74 higher, respectively, than the *O. lyellii* levels reported in Portland (Donovan et al., 2016).

Table 4
Comparison of mean trace element concentrations (mg kg^{-1}) in mosses obtained in this study with those collected in British Columbia, Canada (Pott and Turpin, 1998) and Portland, OR, USA (Gatziolis et al., 2016). The Hoh Rainforest and Bridal Veil Falls represent rural sites, whereas Seattle, Vancouver, and Portland represent urban sites.

	Washington, USA[a]		British Columbia, Canada[a]		Oregon, USA[b]
	Hoh Rainforest, Olympic Peninsula	Seattle	Bridal Veil Falls Provincial Park	Vancouver	Portland
Cd	0.23	0.17	0.17	0.42	0.31
Cr	0.65	2.49	1.30	0.90	2.38
Mn	93.61	110.40	35.00	184.00	87.65
Ni	1.42	4.04	1.10	3.00	2.83
Pb	0.86	12.34	2.50	20.06	7.09
Sr	51.19	122.89	n.a.	n.a.	35.77
Zn	44.47	79.46	19.30	43.20	71.94

n.a. = concentration not measured.
[a] *I. stoloniferum*.
[b] *O. lyellii*.

5. Conclusion

We used two common moss species across western Washington to evaluate major and trace elemental concentrations and compared them with wet deposition values. The values found in this study cannot be treated as an absolute measure of wet deposition, but rather used as a comparative index of metal deposition and as a screening tool to assess areas of metal pollution. In the Puget Sound region, the public is increasingly concerned with the effect of the growing rate of urbanization on regional air quality (Gould and Cummings, 2013). Moss metal concentrations and isotopic source analysis presented in this study showed that: (1) Urban moss samples were elevated in metal content primarily from transportation inputs and other industrial sources; (2) Rural moss samples were influenced by natural variability and long-range pollutant sources from Asia. Expanding existing USFS Forest Inventory assessment lichen monitoring networks to include moss sampling could improve our understanding of the regional distribution patterns of transportation-based pollutants.

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