Evaluating Spatiotemporal Resolution of Trace Element Concentrations and Pb Isotopic Compositions of Honeybees and Hive Products as Biomonitor for Urban Metal Distribution

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Abstract Assessing metal distributions in cities is an important aspect of urban environmental quality management. Western honeybees (Apis mellifera) and their products are biomonitor that can elucidate small-scale metal distribution within a city. We compare range and variations in trace element (TE) concentrations and lead (Pb) isotopic compositions of honey, bee tissue, bee pollen, and propolis collected throughout Metro Vancouver (BC, Canada). Honey, bee, and bee pollen results have similar TE and isotopic trends; samples collected in urban and industrialized areas exhibit elevated concentrations of anthropogenically influenced TE (e.g., Pb, Zn, V, and Ti) and a less radiogenic Pb isotopic composition (i.e., lower 206Pb/207Pb and elevated 208Pb/206Pb) relative to their suburban and rural counterparts. For example, 206Pb/207Pb, 208Pb/206Pb in honey range from 1.126, 2.131 and 1.184, 2.063; extremes measured in honey from urban and suburban/rural areas, respectively. Except for propolis, measured and interpolated (kriged) results in all materials reflect the immediate zoning or land use setting near the hive, providing kilometer-scale geospatial resolution, suitable for monitoring urban systems. Statistical analysis reveals that no systematic variations or intra- or inter-annual trends exist in TE concentrations or Pb isotopic compositions, including among sampling and field methods (i.e., old vs. new hive equipment and honey from the brood nest box vs. honey super). The results of this systematic study using honeybees and hive products in Metro Vancouver provide a robust, current baseline for future comparison of local land use and environmental policy change.

1. Introduction

Elemental concentrations in bee tissue, honey, and other hive products from Apis mellifera have been used as indicators of anthropogenic metal input to the environment since the 1960s (Svoboda, 1961, 1962). The use of hive media as biomonitor is convenient since A. mellifera is prolific and found on every continent except Antarctica, thus granting accessibility to hives in all parts of the world (van Engelsdorp & Meixner, 2010; Winston, 1987). Humankind’s enormous economic dependency on pollinators, especially A. mellifera, has resulted in widespread hive infrastructure (Bauer & Wing, 2016; Hanley et al., 2015; Klein et al., 2007). Honeybee products represent the ultimate “crowd-sourced” environmental proxy, generated by thousands of foraging honeybees interacting with many environmental domains: air, water, soil, and vegetation (Crane, 1976; Herrero-Latorre et al., 2017; Solayman et al., 2016). Bee products have a chemical composition that reflects the environment within the bees’ typical foraging radius: 2–3 km from their hive (Eckert, 1933) or even as little as 1.5 km in urban areas if floral resources are abundant (Garbuzov et al., 2015; Perugini et al., 2011).

Trace element (TE) concentrations in honey, bee pollen, wax comb, and the bees themselves have been used to assess TE distribution in regions with all types of land use: contaminated areas near obvious or single point sources of pollution (e.g., near mining operations and traffic) (Álvarez-Ayuso & Abad-Valle, 2017; Leita et al., 1996; Losfeld et al., 2014; Satta et al., 2012; Saunier et al., 2013; Zhou, Taylor, Davies, & Prasad, 2018), rural and agricultural areas (Lambert et al., 2012; Ruschioni et al., 2013), and urban centers (de Andrade et al., 2014; Erblir & Erdogan, 2005; Giglio et al., 2017; Zhou, Taylor, Davies, & Prasad, 2018). The most recent studies using bees and hive products in cities (Goretti et al., 2020; Skorbiowicz et al., 2018; Smith et al., 2019; Zarić et al., 2018a) are aligned with the discipline-wide shift
in environmental chemistry to focus more monitoring efforts in urban areas, motivated by the dramatic changes in human and environmental interactions that accompany rapid population growth and urbanization (Chambers et al., 2016). Timescales for pollutant transport are shorter in cities compared to natural (geo)chemical processes due to a higher density of anthropogenic sources in a small area (Chambers et al., 2016; Thornton, 1990). Therefore, biomonitoring that offer effective environmental monitoring in cities must provide information with a geospatial resolution and temporal scale useful for urban contexts. A. mellifera and their products fit these criteria.

“Bee pollen” (also known as “bee bread”) is the pollen that bees store in the brood nest; after foraging, bees return to the hive with pollen and pack it tightly into honeycomb cells with saliva and a small amount of honey. The packed pollen ferments over time, creating a protein- and sugar-rich food source for bee larvae. Compositional monitoring (especially of persistent pollutants: metals and pesticides) of bee pollen is worthwhile, as it reflects the chemistry of surrounding vegetation more directly than by providing a composite pollen sample from various plant species within the foraging radius (Bargińska et al., 2016; Bogdanov, 2006; Formicki et al., 2013; Porrini et al., 2003; Satta et al., 2012). Propolis is a resinous, glue-like substance that bees produce by mixing their wax with natural materials like tree resin or sap, and it is used to seal cracks in the hive. The propolis seal increases security, regulates temperature and moisture, and aids in preventing infection within the hive (Mello et al., 2010). Previous studies have used propolis from urban beehives as a biomonitor for TE distribution in the environment (Bargińska et al., 2016; Conti & Botrè, 2001; Formicki et al., 2013; Matin et al., 2016).

A very recent development in this field is the use of Pb isotopes to improve the pollution source apportionment capability of honey and bees, particularly in urban centers (Smith et al., 2019; Zarić et al., 2018b; Zhou, Taylor, Davies, & Prasad, 2018). The application of Pb isotopes is quite promising so far: Isotopic compositions for honey and bees are well-supported by other environmental monitoring materials or proxies, for example, topsoil and native bees in Sydney, Australia (Zhou, Taylor, & Davies, 2018; Zhou, Taylor, Davies, & Prasad, 2018) and sediments, shellfish, and salmon tissue near Vancouver, BC (Li et al., 2020; Shiel et al., 2012; Smith et al., 2019). While some comparison of TE concentrations between various hive products (honey, bee pollen, and propolis) are available in the literature, for example, in Spain and Poland (Álvarez-Ayuso & Abad-Valle, 2017; Formicki et al., 2013), few comparisons have been made using Pb isotopes. Definitive guidelines in the literature regarding the use of honey and bees as environmental biomonitoring tools are generally lacking (Herrero-Latorre et al., 2017). In this study, we aim to provide some of those missing guidelines through our comprehensive and systematic approach for sampling and comparing the efficacy of honey, bees, bee pollen, and propolis as biomonitoring tools in Metro Vancouver, with the added context of Pb isotopic compositions for all samples.

We present a comprehensive data set of TE concentrations and Pb isotopic compositions of samples (n = 362) representing four hive products: honey, bee tissue (foragers), bee pollen, and propolis. Building on the pilot study in Vancouver, Canada, by Smith et al. (2019) (which only included honey and commenced in 2014), new sampling sites added in 2017 increased the total number of sites to 47. New sites include hives at the University of British Columbia (UBC), near Vancouver International Airport (YVR), and the northern end of the George Massey Tunnel (a four-lane traffic tunnel that runs beneath the south arm of the Fraser River estuary). These sites were selected to expand the geographic coverage and types of land use/zoning districts (i.e., urban, suburban, rural, agricultural, and industrial) included in the study (Figure 1). In 2018, all hives were sampled at least twice throughout the honey production season to assess intra-seasonal variations. We also introduced hives on brand new equipment at four of the sites. Hive boxes, frames, and even the wax honeycomb itself are often reused for years, and apiarists move various structural components between hives as needed. By analyzing samples from colonies raised on new hive structures, we can assess the impact, if any, that older frames and wax may have on the hive products and bees in terms of TE concentrations and Pb isotopic composition. With this data set, we address the following research objectives: (1) compare honey, bee tissue, bee pollen, and propolis and evaluate their efficacy as biomonitoring tools in an urban setting, (2) determine the geospatial resolution of the results using kriging models, (3) determine the temporal resolution of these various hive products, both intra- and inter-annually, and (4) assess relationships among our results and those of other pollution models in Metro Vancouver. Our discussion focuses primarily on Pb, because of its persistent nature as an environmental pollutant with detrimental effects on human health (Landrigan et al., 2018).
2. Materials and Methods

2.1. Field Methods and Sample Collection

This study was conducted in the Metro Vancouver Regional District (formerly “Greater Vancouver Regional District”), a coastal metropolitan area, home to 23 municipalities and ~2.5 million people. Metro Vancouver is uniquely situated between the coast of the Salish Sea and the North Shore Mountains, in the traditional, unceded, and ancestral territory of the Coast Salish peoples (Figure 1). All honeybee colonies sampled in this study are housed in Langstroth\-style hives (Langstroth, 1889), a style of hive equipment widely used in modern apiaries (supporting information Figure S1). Hives were sampled systematically: Brood nest honey and bee pollen were collected from the brood nest (found in the lowest two hive boxes). If the hive had additional boxes for excess honey production (referred to as “honey supers,” usually added as the foraging season...
progressed, Figure S1), honey from those boxes was also sampled to assess potential variations in TE content between honey from the brood nest and the super. The hives were sampled in late summer 2017 and twice in 2018 (once in late May/early June and again in late July/early August, toward the end of peak honey production). At each site, metadata was collected using a field worksheet to record geographic information (e.g., coordinates, address, and street intersection), hive health, notes about veterinary treatments, weather, setting, and land use (Figure S2). To assess intra-season variability, four hives at two sites on the UBC campus (two hives per site, Figure 1) were sampled four times, approximately every 4 weeks between late April and late July 2018.

In spring 2018, four new hives were introduced using the “shook” swarm method (e.g., Guler, 2008; Hansen & Brodsgaard, 2003) (Figure 1). The new hives were also Langstroth-style and contained all new frames, except for the one frame transported with the bees, which contained brood in various life stages in the old wax comb and was necessary for the survival of the newly introduced swarm colony (Figure S3). All hive products described above (honey, bees, bee pollen, and propolis) were collected from these four new hives. Three of the four new colonies survived the 2018/2019 winter; these three hives were re-sampled twice during the 2019 season, following the same sampling protocols, to assess inter-season variation of hives on all new equipment.

2.1.1. Honey
Honey was sampled directly from the hive using the same methods described by Smith et al. (2019). To ensure that the honey was produced during the current season, we identified freshly capped honey by its bright wax caps (Figure 2). Honey samples were collected from both the brood nest and the super (if present).

2.1.2. Bee Pollen
Stored bee pollen was identified on brood nest frames (Figure 2) and sampled using a new wooden spatula (e.g., a coffee stirrer). This tool allowed for the removal of “plugs” of bee pollen from the comb. Several bee pollen plugs were sampled from multiple brood frames to create a composite sample, ensuring that it represented the current bee pollen content of the hive.

2.1.3. Bees
Honeybees were collected from 13 hives starting in 2018. Hives were selected based on location and permission from the hive owner or apiarist responsible for the colony. We attempted to only capture foraging bees since foraging tasks are generally reserved for bees that have reached the end of their lifespan (Huang & Robinson, 1996; Winston, 1987). Foraging tasks commence around 14 days of age, last for about 10 days on average, and end with the death of the bee (Schippers et al., 2006). Foraging bees have therefore had the chance to interact with the environment more extensively than other members of the colony (e.g., Zarić et al., 2016). Bees were collected as they exited the hive, thereby avoiding capture of returning foragers which were likely carrying pollen and nectar. We temporarily blocked the hive entrance for several minutes, compelling the foragers to crawl through a small opening to exit the hive. Wearing disposable gloves, we carefully grasped the exiting bee by the wings and dropped it into a vial containing an isopropanol-soaked laboratory wipe. In this manner, we collected at least 30 foraging bees per hive. Once the bees expired, they were stored on ice in the field and then frozen (and stored at −8°C) upon return to the laboratory.

2.2. Sample Processing
All sample preparation and analyses were completed in Class 1000, or better, clean rooms equipped with Class 100 laminar flow hoods at the Pacific Centre for Isotopic and Geochemical Research (UBC, Vancouver, Canada). All acid reagents were either double-distilled in-house or purchased (as highest purity grade available), and only ultrapure water was used (18.2 MΩ-cm). All plastic and Teflon® materials used in the procedure were pre-cleaned using PCIGR’s in-house cleaning procedure involving sequential leaching with Citranox® (Alconox, Inc. White Plains, NY, USA), 50% HCl, 50% HNO₃, and concentrated HNO₃/HF.
2.2.1. Honey
Honey was digested following the method described by Smith et al. (2019). Briefly, 0.5 g of honey was microwave digested in concentrated HNO₃, evaporated until dry, then reconstituted in 2% HNO₃ for TE and Pb isotope analyses.

2.2.2. Bees and Bee Pollen
Frozen honeybees were lyophilized and powdered. Powdered bee tissue and non-lyophilized bee pollen (0.1–0.4 g) was digested in a manner similar to honey (microwave digested in HNO₃), evaporated, then reconstituted and refluxed in HNO₃/H₂O₂, then finally re-evaporated. The HNO₃/H₂O₂ step was repeated until the content of total dissolved solids in the final sample was less than 0.5% (w/w), then reconstituted in 2% HNO₃ for TE and Pb isotope analyses. For method comparison, four pollen samples were lyophilized and powdered before digestion.

2.3. Trace Element and Pb Isotope Analysis
All samples were analyzed for 22 TE concentrations (Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Zr, Mo, Cd, Sn, Sb, Ba, and Pb) and Pb isotopic compositions following the methods described in detail by Smith et al. (2019). In short, TE concentrations were measured using an Agilent 7700x quadrupole inductively coupled plasma mass spectrometer (ICPMS, Agilent Technologies, Santa Clara, CA, USA), and Pb isotopic compositions were measured using a Nu AttoM high-resolution ICP-MS (Nu Instruments Ltd., Wrexham, UK). All sample batches included procedural blanks, standard reference material (NIST SRM 1568b, Rice Flour), and procedural duplicates. Each analytical session included at least one replicate analysis for every 20 samples analyzed. Trace element and Pb isotope results for NIST 1568b matched previously published data (Smith et al., 2019), and Pb isotopic compositions for this SRM were further verified by multicollector (MC-)ICPMS (Nu Plasma II) and are in agreement with our HR-ICPMS values: 1.21006 ± 0.00001 ²⁰⁶Pb/²⁰⁷Pb, 2.02971 ± 0.00003 ²⁰⁸Pb/²⁰⁶Pb (n = 4) versus 1.215 ± 0.004 ²⁰⁶Pb/²⁰⁷Pb, 2.026 ± 0.006 ²⁰⁸Pb/²⁰⁶Pb (n = 34), respectively (all uncertainties are 2 × standard error). Summaries for SRM and blank analyses can be found in Tables S1a and S1b, uploaded to the Scholars Portal Dataverse database (Smith & Weis, 2020). Procedural duplicates and replicate analyses were averaged (arithmetic mean) before reporting.

2.4. Calculations and Statistical Analysis
We applied an enrichment factor (EF) calculation to our honey concentration results (Zoller et al., 1974). Rather than use local, upper crustal TE values for normalization, we used previously published TE data for honey from Galiano Island (Smith et al., 2019) (an island located southwest of Vancouver in the Salish Sea, Figure 1, with mostly rural and agricultural land use):

\[
EF_{\text{honey}} = \frac{[X]_{\text{sample}}}{[Rb]_{\text{sample}}} \times \frac{[Rb]_{\text{reference}}}{[X]_{\text{reference}}}
\]  

(1)

Where \([X]\) is the concentration of an anthropogenically sourced TE, and \([Rb]\) is the concentration of Rb. For bees, Goretti et al. (2020) proposed the use of a Honeybee Contamination Index (HCI) for comparison of TE concentrations in honeybee tissue between data sets and different studies:

\[
HCI = \log\left(\frac{X_{\text{bees}}}{X_{\text{bees_ref}}}\right)
\]

(2)

Where \(X_{\text{bees}}\) is the concentration of an element, \(X\), in the bees and \(X_{\text{bees_ref}}\) is the reference threshold for that element in bee tissue for that specific region (ideally, previously published, reference values for the study region) (Goretti et al., 2020). Since there are not yet any local reference values for bees in Metro Vancouver, we propose that the maximum, minimum, and median values from our data set could be used to calculate conservative, extreme, and median HCI, respectively, for bee tissue measurements at each site.

The trace element concentration data are nonparametric and strongly tail to the right, toward higher concentrations (lognormal distribution), typical for geospatially constrained environmental data (Filzmoser et al., 2009; Reimann et al., 2011). Thus, any statistical manipulations were completed using tests meant for nonparametric data or after a log₁₀-transformation. To help reduce the number of explanatory variables in the data set (Pirk et al., 2013), a preliminary principal component analysis (PCA) was performed on the
Trace element maps and Pb isoscapes were generated using ArcGIS (v. 10.5.1) (ESRI, 2011). Interpolated data were predicted using an empirical Bayesian kriging (EBK) method (Krivoruchko, 2012). Our data set underwent a log-empirical data transformation (Gribov & Krivoruchko, 2012), and then we selected the best semivariogram model on a case-by-case basis (either exponential or k-bessel model in all instances).

3. Results

3.1. Trace Elements and Pb Isotopes

Trace element concentrations and Pb isotopic compositions of honey (n = 201), bee pollen (n = 121), bee tissue (n = 27), and propolis (n = 13) are reported in the online data set (Tables S3–S6, Smith & Weis, 2020). Trace element concentrations in honey in Metro Vancouver are comparable to or lower than those reported in honey worldwide (Smith et al., 2019; Solayman et al., 2016). In honey, bee tissue, and bee pollen, TEs indicative of anthropogenic activity (those typically elevated near urban centers, relative to local lithogenic values) are generally more concentrated in regions of high-density residential, commercial, and industrial land use (Figures 3, 4, and S5). Most TE concentrations in honey correlate well with Pb concentrations in areas of high urban density and residential/suburban land use, potentially implying similar, anthropogenic sources for these metals nearer to the city center. In agricultural or rural areas, there is moderate or poor correlation between Pb and other TE. Similar correlations are observed in bee tissue but are only somewhat apparent in bee pollen, where Pb is generally more poorly correlated with other TE (Figure S7).

Lead isotopic compositions measured for all matrices in this study are in the range of 1.113–1.187 and 2.063–2.134 for 206Pb/207Pb and 208Pb/206Pb, respectively (Tables S3–S6, Smith & Weis, 2020). Lead isotope ratios measured in honey vary from 1.126 to 1.184 for 206Pb/207Pb and 2.063 to 2.131 for 208Pb/206Pb, similar to the range reported for Metro Vancouver honeys (Smith et al., 2019). For bees and bee pollen, Pb isotopic ratios range from 1.139–1.165 and 2.090–2.121 and 1.120–1.187 and 2.070–2.134 for 206Pb/207Pb and 208Pb/206Pb, respectively.

Lead isotopic compositions of honey, bees, and bee pollen all exhibit a similar geospatial trend: Samples from regions with high-density urban land use have less radiogenic Pb isotopic compositions (lower 206Pb/207Pb and higher 208Pb/206Pb values) (Figures 5 and 6) compared to compositions measured in samples from residential/suburban and agricultural/rural regions. Lead isotopic compositions measured in propolis are 1.133–1.170 206Pb/207Pb and 2.078–2.148 208Pb/206Pb. In contrast to honey, bees, and bee pollen, propolis results show no statistically significant differences between the three land use categories for Pb isotopes or in any of the TEs analyzed (p > 0.05, Kruskal-Wallis test, Figure S5).

3.2. Effects of Sampling Method

There is no significant difference in any of the TE concentrations or Pb isotopic compositions between honey from the brood nest and honey from the super in regions of high-density urban land use. At the same time, we found some variation (the honey super was slightly less concentrated) between the brood nest and super boxes for Pb, Ti, Mo, and Sb in residential/suburban regions. In regions of agricultural/rural land use, there
is variation in concentrations of Mn, As, and Sb; except for Sb, the honey super was slightly more concentrated than the brood honey (Table S2e). Overall, for all types of land use, there are no systematic variations (no consistent or predictable differences) between honey collected from the brood nest box or the super. Similarly, comparison of hive products at three sites that contained both hives made of new...
equipment ("shook” colonies) and old equipment showed no systematic differences in TE concentrations and Pb isotopic compositions for honey, bee pollen, and bees (Table S2f).

### 3.3. Temporal Trends

Inter- and intra-seasonal comparisons were made within the three land use categories determined by preliminary PCA. Overall, there are no systematic temporal trends in the TE concentrations or the Pb isotopic compositions for honey, bee pollen, and bees (Table S2f).

![Figure 5](image.png)

**Figure 5.** Interpolated $^{208}$Pb/$^{206}$Pb isoscape for honey from Metro Vancouver (ArcGIS v. 10.5.1). This map was generated using data from Smith et al. (2019) and this study (2014–2019, $n = 246$). Legends display the minimum and maximum kriged contour values. Corresponding standard error maps can be found in the Figure S8. Inset: Pb/Pb isotope plot for all honey data used to generate the isoscape. Hive site symbol colors are the same as in Figure 1. Shaded land use fields include $\pm 2 \times$ standard error (2SE) of the measurements.

![Figure 6](image.png)

**Figure 6.** Interpolated $^{208}$Pb/$^{206}$Pb isoscapes for bee tissue ($n = 27$) and bee pollen ($n = 121$). Legends display the minimum and maximum kriged contour values. Measured ranges of $^{208}$Pb/$^{206}$Pb for all data used in these interpolations are 2.090–2.121 in bees and 2.070–2.134 in bee pollen. Corresponding standard error maps can be found in Figure S9.
seasonal variation of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ in honey and bee pollen from hives at two sites on the UBC campus. Error bars are 2SE (2 × standard error).

4. Discussion

4.1. Geospatial Trends: Trace Elements and Isoscapes

Spatial dependence as a function of land use of the honey, bee tissue, and bee pollen TE results agrees with previous studies elsewhere in the world, for example, the United States, Serbia, and Australia (Bromenshenk et al., 1985; Zarić et al., 2018b; Zhou, Taylor, Davies, & Prasad, 2018) and locally (Smith et al., 2019). An early study in the Seattle-Tacoma area (Washington, USA) showed increased amounts of As and Cd in bees near the Port of Tacoma (Bromenshenk et al., 1985). In the Serbian studies by Zarić et al. (2016, 2018b), the authors measured higher concentrations of certain TEs in bee tissue within Belgrade (e.g., Sb, presumably from vehicle brake pads) and higher concentrations of Al, Cr, Fe, and Li (constituents of fly ash) in bees collected near thermal power plants, compared to bees from rural and non-industrialized areas. Locally, Pb, V, Sb, and Fe in honey, bees, and bee pollen exhibit geospatial trends in agreement with honey in the pilot study in Vancouver, BC (Smith et al., 2019): higher concentrations in areas of greater urban density and industrial activity relative to suburban and rural samples. Since these other matrices (bee tissue and bee pollen) exhibit similar TE spatial trends as honey, we infer that sources for these metals are similar for all hive matrices. In Metro Vancouver, anthropogenic sources of metals include heavy traffic (especially exhaust and mechanical wear from stop-and-go traffic), continuous urban development and demolition, aging of civil structures, higher instances of water runoff (from the abundance of paved, non- or semi-permeable surfaces), and a large, busy shipping port in Vancouver Harbour near the city center. Potential sources for several TE of interest for pollution studies (e.g., Cd, Cu, Fe, Mn, Sb, Ti, V, and Zn) in Metro Vancouver are discussed at length by Smith et al. (2019).

Less radiogenic (higher $^{208}\text{Pb}/^{206}\text{Pb}$) Pb isotopic compositions measured in samples from the city center likely reflect a combination of various sources. These include modern traffic emissions (unleaded gasoline still contains measurable amounts of Pb, e.g., Chrastný et al., 2018; Shiel et al., 2012), shipping emissions, and legacy sources (Figures 5 and 6) (Smith et al., 2019). Most ships (>70%) arriving at Port of Vancouver originate from Asian ports (Fraser River Port Authority, 2017), where they have taken on bunkering fuel, perhaps derived from Asian geologic endmembers, which generally contain Pb that is distinctly less radiogenic than North American endmembers (e.g., Bi et al., 2017; Mukai et al., 2001). Additionally, since leaded paint and gasoline were used for much of the 20th century in North America, and Vancouver’s Downtown East Side contains brownfields (former commercial or industrial land, currently unused) (Oka et al., 2014), there is likely more legacy Pb in the environment closer to the city center where traffic and historic buildings are most concentrated. Away from the city center, the Pb isotopic compositions of our samples are governed by more radiogenic, natural sources of Pb reflecting the local lithology, for example, Garibaldi volcanic belt and Cascadia basin sediments (Carpentier et al., 2014; Mullen & Weis, 2013). A recent study of several fish and shellfish species from BC’s inland and coastal waters and the northeast Pacific showed that there is indeed a “coastal, anthropogenic” Pb isotopic composition, which overlaps the Pb isotope range reported for all samples in this study (Li et al., 2020). Spatial dependence of the Pb compositions of our samples is in agreement with two other studies (to date) that have measured Pb isotopes in A. mellifera tissue (Zarić et al., 2018b) or tissue and honey (Zhou, Taylor, Davies, & Prasad, 2018). Both studies observed variation in Pb isotopic compositions of hive materials as a function of land use and hive proximity to point sources (e.g., power plants or mining emissions, respectively).
While it may be ideal to place hives in a contrived sampling grid pattern, like that of an urban topsoil survey (Demetriades & Birke, 2015; Smith et al., 2011; Zahran et al., 2013), we have elected to sample hives as they currently exist in Metro Vancouver for several reasons. Mainly, using already existing infrastructure keeps cost low (Wolterbeek, 2002) and makes the study more accessible for citizen scientists (e.g., hobby beekeepers) to contribute samples. The outcome is a sampling distribution in Metro Vancouver that falls somewhere between a "random" and "clustered" classification. Regardless, kriged TE and Pb isoscape maps are coherent and complementary for three hive materials (honey, bees, and bee pollen), and the distribution of TE and Pb isotopic compositions makes sense relative to land use and known TE sources in Metro Vancouver with a resolution that indicates local and regional variance (Figures 1, 3–6), in agreement with other geospatial assessments of hive data (Bromenshenk et al., 1985; van der Steen et al., 2016). Furthermore, our kriged TE maps and Pb isoscapes are in good agreement with mapped distributions of other pollutants in Metro Vancouver. For instance, our concentration maps for TEs associated with traffic emissions (i.e., Pb from today's unleaded fuels, which still contain Pb, and V emissions from heavy fuel oil used in marine shipping, Zhao et al., 2013) show distributions similar to those of land use regression model outputs of traffic-related air pollution: elevated concentrations of NOx and particulate matter near the traffic-heavy city center and busy Port of Vancouver (Abernethy et al., 2013; Setton et al., 2011).

4.2. Enrichment Factors and Indices

To calculate EF (Equation 1), we chose Rb as our normalizing element since it is generally lithogenic (Boës et al., 2011; Grousset et al., 1995), and our data showed no systematic geospatial (or temporal) [Rb] trends in the areas sampled. Strict use of traditional EF for estimating extent of human impact is not ideal for biomonitoring data: Normalization of results to upper crustal TE values may be appropriate for EF calculations in soil or sediment but are not necessarily relevant for EF assessment in biological matrices (Reimann & de Caritat, 2000). We propose that our modified EF is useful since the normalization ratio is measured in the same matrix (honey) and collected locally in a "background" type of land use (rural). Furthermore, geospatial trends for TE concentrations and Pb isotopic compositions are similar and match EF geospatial trends, indicating that there may be utility in developing a standardized enrichment index for honey that can be used in other contexts (Figure 8). Trace element concentrations in honey are quite variable by location throughout the world (Solayman et al., 2016), so an enrichment index relative to locally produced rural or "background" honeys would be particularly convenient for comparing data sets from different studies in other urban centers around the world. Additionally, we agree with others (Pohl

![Figure 8. Left: Lead enrichment factor (EF) in honey from Metro Vancouver (average at each site). This figure includes data from Smith et al. (2019) and this study. Right: Calculated Honeybee Contamination Indices (HCI) (Goretti et al., 2020) for Pb in bee tissue from Metro Vancouver. The plotted HCI values were calculated relative to the median [Pb] concentration in bee tissue at each location. The range of calculated HClmed values is reported in the legend. For plotting purposes only, a + 2 scalar value was added to the calculated HClmed.]
agrees with several previous studies that measured higher TE concentrations in bees and bee pollen relative to honey. This

While TE concentrations in honey, bees, and bee pollen exhibit similar geospatial trends, absolute TE concentration variations.

To calculate the HCl (Equation 2, Goretti et al., 2020), we used the median HCl (HClmed) for Pb in our bees as the reference value. A correlation with land use is present (Figure 8), where a higher HCl indicates enrichment, or potential “contamination” in the case of non-biologically essential TE like Pb, relative to the other measurements in the region. Future studies may find variations on EF or HCl useful for inter-study comparison, and the field may eventually benefit from a standardized approach for both bees and various hive products.

**4.3. Comparison of Bees, Honey, and Other Hive Products**

**4.3.1. Relative Concentrations**

While TE concentrations in honey, bees, and bee pollen exhibit similar geospatial trends, absolute TE concentrations are 4 to 218 times higher in bees and 6 to 47 times higher in bee pollen relative to honey. This agrees with several previous studies that measured higher TE concentrations in fresh pollen (Álvarez-Ayuso & Abad-Valle, 2017; Conti & Botrè, 2001; Lambert et al., 2012; Leita et al., 1996) and bees (Lambert et al., 2012; Porrini et al., 2002; Silici et al., 2016; Zhou, Taylor, Davies, & Prasad, 2018) compared to honey. Measured TE concentrations in bees from Metro Vancouver have similar ranges to bees collected in the Netherlands (150 apiaries) (van der Steen et al., 2016) for As, Cd, Co, Cr, Cu, Mn, Mo, Ni, Sb, Sr, Ti, V, and Zn, similar Pb, Ni, and Cr concentrations in bees from central Italy (Porrini et al., 2002) and generally lower Pb and Cd concentrations than bees from southwestern Poland (Roman, 2010). In our study, some bees exceeded the potential “high threshold” for Pb, Ni, and Cr in bee tissue, calculated by Porrini et al. (2002). Bees from other studies also breach these thresholds, particularly in those collected from a city center (Gutiérrez et al., 2015; Zhou, Taylor, Davies, & Prasad, 2018), indicating that a threshold defined by a specific study is highly dependent on local factors, including land use, climate, pedology, and lithology.

Bee bodies will sequester some metals more than others (e.g., Cd, Cu, and Pb) (Di et al., 2016; Hladun et al., 2016; Satta et al., 2012). In controlled feeding studies, others have observed detrimental effects on hive vitals (e.g., honey production, brood surface area, and queen weight) accompanied by metal accumulation in live foragers (Di et al., 2016; Hladun et al., 2016). Our bee tissue concentrations do not exceed those measured in control hives for Cd, Cu, and Pb in these feeding studies (Di et al., 2016; Hladun et al., 2016). The bees in Metro Vancouver are not consuming and are not accumulating, anywhere near enough of these three metals to harm the colony.

**4.3.2. Sample Preparation and Treatment**

Researchers that collected fresh pollen at the entrance of the hive using pollen baskets needed to dry and homogenize the sample before analysis (Álvarez-Ayuso & Abad-Valle, 2017; Conti & Botrè, 2001; Lambert et al., 2012; Leita et al., 1996). Our method of collecting packed bee pollen from multiple frames in the brood nest removes the need for pollen traps and subsequent lyophilization of the sample, since bee bread is fermented (due to storage with small amounts of honey and bee saliva) and has a somewhat controlled moisture content if sampled from the same region (De-Melo & de Almeida-Muradian, 2017; Fuenmayor et al., 2014). Indeed, our comparison of lyophilized versus non-lyophilized samples of bee pollen is within error for Pb isotopic compositions except for pollen from one site (Figure S10). Compared to honey, bee pollen may be subject to more sampling bias in the field, leading to homogeneity issues. The quality of the bee pollen aliquot is highly dependent on the sampling approach: collecting enough pollen plugs from several brood nest frames to create a composite sample that is representative of the hive. We suggest that bee pollen might be most useful as a biomonitor for metals when analyzed in conjunction with honey and/or bees.

Honey and bee tissue results showing similar geospatial trends in TE and Pb isotopic compositions in this study are in contrast with others that concluded honey was unsuitable or less suitable than bees or pollen as a biomonitor for TE distribution (Al Naggar et al., 2013; Conti & Botrè, 2001; Fakhimzadeh & Lodeniús, 2000; Lambert et al., 2012; Silici et al., 2016). These other studies, however, used atomic absorption methods (less sensitive than ICPMS by a factor of 10 to 1,000, depending on the analyte), so they could only measure a few metal concentrations in honey (usually Pb, Cd, and Cr) and could not detect subtle TE concentration variations.
While there is some utility in bee pollen and bees as biomonitors, using honey simplifies the field methods and makes sample collection more accessible for citizen scientists. Honey has the advantage of being simple to collect, ship internationally, and store indefinitely (bees and pollen will eventually spoil if not lyophilized or kept frozen). Through collecting honey, we introduce a certain degree of standardization by avoiding the debate of how to collect and prepare other hive samples: dried versus fresh pollen, dead bees versus live foragers, rinsed versus unrinsed bee bodies (e.g., Leita et al., 1996; Sadowska et al., 2019). Conversely, the higher concentrations of specific TE in bee pollen and bees may allow for the use of other isotope systems if the concentrations are high enough. These include Zn, Cd, or Cu isotopes, all potentially useful for identifying anthropogenic processes by observing isotopic compositions that deviate from geologic ones. While Pb isotopic compositions of environmental samples are overwhelmingly governed by the two major end-members (Broken Hill and southeast Missouri ores) of the global gasoline mixing line, use of another isotope system can aid in source apportionment by revealing other potential point sources of pollution (e.g., Araújo et al., 2019). Furthermore, bee pollen and bee tissues may be more suitable for laboratories without access to mass spectrometers, since the higher TE concentrations will result in less challenging concentration measurements (e.g., by ICP-AES) for specific low-level TE useful in anthropogenic sourcing studies (e.g., Cd, Sb, and Sn).

4.3.3. Propolis
In urban settings that lack nearby access to natural saps or resins, bees will substitute anthropogenic materials like asphalt or road tar to make propolis (Alqarni et al., 2015; Matin et al., 2016). However, our propolis results do not appear to reflect the environment surrounding the hive, in contrast to previous studies that observed geospatial variation in propolis (Conti & Botré, 2001; Formicki et al., 2013). Propolis is less processed by bees than honey, so it is perhaps not sufficiently homogenized within the hive for use as a reliable biomonitor. Or perhaps plenty of sap and resin is available for Metro Vancouver bees, so they are not reliant on human-made resins, and the sap-producing plant species may be less sensitive to local land use than other environmental domains that bees encounter (i.e., topsoil and aerosols). There is limited published TE data available for propolis (Bogdanov, 2006), but the Metro Vancouver propolis has lower concentrations of Pb, Cd, and Zn than those reported by Leita et al. (1996), which were collected ~25 years ago near a busy traffic intersection in Italy when leaded gasoline was still in use. The Ni concentrations measured in Metro Vancouver are lower than those observed in propolis more recently by Formicki et al. (2013), collected near Karków, Poland, but Pb, Cd, and Fe concentrations are comparable (within the same orders of magnitude). Therefore, propolis may offer some utility as a biomonitor over several decades as large-scale anthropogenic changes are made (e.g., nearly a worldwide ban of leaded gasoline), but the reliability of the results may be highly dependent on local plant species as sap and resin sources.

4.3.4. Implications for Hive Management
This is the first hive products-as-biomonitor study to complete a detailed investigation of the effects of sampling methods and colony management. Our findings show that as long as freshly capped honey is collected, the results are not affected by the age of the equipment or which frame or box the honey came from within the hive. These results bode well for future, multi-year studies using hive products as biomonitors of metals in the environment, indicating that apiarists can continue their “business-as-usual” practices: reusing comb and frames from year to year and between hives (e.g., when splitting a hive) at the same apiary (same site).

4.4. Temporal Trends and Future Implications
The non-systematic, minor seasonal variations in bee pollen and bee TE concentrations could be attributable to changes in floral nectar and pollen sources as the season progresses or to cyclical variations in bee life spans: shorter in the spring and longer in the autumn as the colony prepares for over-wintering in temperate climates (Pirk et al., 2013). Also, a swarm or new shook colony will have a slightly lower average bee age than an established colony (Pirk et al., 2013). In general, hive tasks are dictated by the life-stage of each bee, so there is some flexibility in age-related task assignments within the hive, potentially causing variation in cumulative environmental exposure among foragers (Huang & Robinson, 1996; Pirk et al., 2013; Zarić et al., 2018a). We suggest that the solution for assessing inter- and intra-annual variabilities is statistical evaluation to determine if the temporal differences are significant and systematic (i.e., if the TE or isotope results increase, decrease, or cycle consistently seasonally, or year to year). The non-systematic variability can therefore be ignored, and more focus can be given to TE ratios and Pb isotopic compositions if the goal of the project is to assess relative spatial differences of these analytes.
Combined with previous honey data for Metro Vancouver (Smith et al., 2019), the results from this study indicate temporal and spatial reproducibility both in TE concentration and Pb isotopic compositions for at least 6 years and as a result can serve as a robust baseline, representing the current combination of local geogenic (background) and anthropogenic (legacy and modern) metal compositions of honey (Johnson & Demetriades, 2011; Matschullat et al., 2000). Additionally, the 3 years of bee pollen and 2 years of bee tissue data presented in this study represent the current baseline for those materials. Hive biomonitor with a decadal temporal scale will be useful for assessing upcoming and ongoing changes to urban settings. For instance, two multyear studies using honeybees in Serbia reported decreased metal loadings in honeybee tissue when a local steel plant ceased production (Zarić et al., 2017) and a shift in Pb isotopic composition in bee tissue over 3 years due to Serbia’s relatively recent (2011) discontinuation of leaded gasoline usage (Zarić et al., 2018b). In Metro Vancouver and surrounding regions, examples of city-scale, baseline changes include the continuous development of former industrial and low-density residential areas for high- and medium-density housing to facilitate “ecodensity” (Weiss, 2016). Metro Vancouver also has “urban greening” initiatives to increase numbers of public green spaces and urban gardens (City of Vancouver, 2019; Metro Vancouver, 2015); this trend is observed in cities worldwide, as access to green space in urban settings provides positive impacts on human social connectivity and species diversity for plants and pollinators (Egerer et al., 2020; Grimm et al., 2008; Lanner et al., 2020). Additionally, the expansion of Canada’s Trans Mountain Pipeline was approved in 2019 and will require an increased capacity of the Westridge Marine Terminal in Burnaby, BC. This will cause an approximate 14% overall increase in shipping traffic through Vancouver Harbour once the expansion is complete (Trans Mountain Pipeline ULC, 2020).

Globally, changes in industrial regulation policies have decreased metal loadings in the environment (European Environment Agency, 2019; Pacyna & Pacyna, 2001), evident in measured concentrations of Pb in ocean surface waters (Pinedo (European Environment Agency, 2019; Pacyna & Pacyna, 2001), evident in measured concentrations of Pb in ocean surface waters (Pinedo-González et al., 2018) and Pb and other heavy metals in air particulate and air pollution biomonitor like mosses and lichen in and around metropolitan centers, including Vancouver (Pott & Turpin, 1996; Simonetti et al., 2003). Variations of Pb isotopic compositions in temporally constrained proxies like peat (Kamenov et al., 2009; Kamenov & Gulson, 2014; Shotyk et al., 1998) and sediment records (Andrade et al., 2017; Michelutti et al., 2009) reflect changes in source and extent of anthropogenic Pb inputs throughout history, particularly in the last century. Biomonitor will continue aiding researchers in the future as policies and industrial practices further evolve. For global Pb sources, increasing the use of electricity-centric, rather than coal-centric, infrastructure is creating a higher demand for Pb-containing batteries. The largest modern input of Pb into the environments of many developed nations comes from the recycling of these batteries (Ettler et al., 2004; Wilburn, 2014) which may cause a systematic shift of the average isotopic composition of industrial Pb as more recycling occurs (Ayuso & Foley, 2018). This is a likely scenario as our increasingly urbanized world requires a circular economy (i.e., more recycling and reuse of materials) to be sustainable (Sauvé et al., 2016). Global changes like these will indeed be reflected in bees, hive products, other biomonitor, and the environment worldwide.

### 5. Conclusions

Honey, bee tissue, and to some extent, bee pollen are well suited as biomonitor of metals in Metro Vancouver. These three matrices can effectively reveal TE concentration distributions and variation of Pb isotopic compositions (isoscapes) in hive products at a kilometer-scale in a metropolitan region. The data are spatially and temporally reproducible, even as apiarists manage hives normally by moving equipment among sites and splitting colonies. Combined with the data from Smith et al. (2019), this study provides useful, geospatially constrained TE concentrations and Pb isotopic compositions for Metro Vancouver and will be valuable for comparison against future chemical surveys of hive products as this region grows and changes over the next century. Some standardization would greatly benefit this field of study, including the development and use of certified reference materials for bees and various hive products and adoption of a standardized enrichment factor (or another index) for ease in comparing results between studies and hive matrices.

As the world becomes more urbanized (United Nations World Population Prospects, 2019), biomonitor will become especially useful in areas that do not have established environmental monitoring programs (e.g., topsoil survey) or data for public health biomarkers (e.g., blood lead levels). Instances of urban...
greening may promote hive infrastructure and citizen science opportunities, making city-scale environmental surveys easier and less costly. We therefore are confident that honey, bees, and bee pollen will likely remain useful as biomonitors in the next century, perhaps offering some insight into biogeochemical cycling of metals in urban environments (e.g., Kaye et al., 2006), ultimately aiding policymakers, urban ecologists, city planners, and public health officials.

Conflict of Interest

The authors declare no conflict of interest relevant to this study.

Data Availability Statement

Data for this study (Tables S1–S6) are available on the Scholars Portal Dataverse (doi: 10.5683/SP2/Y9MKTN).

Acknowledgments

Funding for this work was provided by a Solutions Award from the Peter Wall Institute for Advanced Studies and by a Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant, both awarded to D. Weis. Additional support for K. Smith was provided by the University of British Columbia’s International Doctoral Fellowship and NSERC’s Multidisciplinary Applied Geochemistry Network. The UBC Office of the Vice-President, Research and Innovation provided funding for community networking and outreach events, via the BeeHIVE Research Excellence Cluster. The authors give special thanks to PCIGR scientists M. Amini, V. Lai, and K. Gordon and to Hives for Humanity chief apiarist J. Common and her collaborators: S. Common, A. Green, and D. Cross.

Thank you to A. McAfee and L. Foster for access to hives on UBC rooftops and Hives Research Farm. The authors wish to thank community members for offering samples from their backyard hives: K. Parry, L. Holstein-Sjärdal, L. Taylor, L. Williams. Finally, the authors thank R. McMillan for initial manuscript editing and feedback, and W. Shotyk and an anonymous reviewer for constructive peer review.

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