ABSTRACT

PROVIDING NEW ENVIRONMENTAL HEALTH CONTEXTS FOR NATIVE AMERICAN POPULATIONS: A GEOCHEMISTRY, SEM, AND GEOSPATIAL INVESTIGATION OF AIRBORNE URANIUM AND METAL PARTICULATE IN TREE BARK NEAR THE MIDNITE MINE AND DAWN MILL, SPOKANE RESERVATION, WA, USA

by Lonnie Elizabeth Flett

The uranium boom in the United States from the 1940's to the 1980's was a period of extensive uranium mining on Native American lands. However, detailed environmental investigations of the resulting uranium pollution are sparse. The Midnite Mine is an abandoned open pit uranium mine located on the Spokane Indian Reservation, where approximately 35 million tons of ore and waste rock were left behind in stock piles. Although investigations of water and soil contamination have been conducted, there have been no investigations of associated airborne particulate matter. Bulk elemental analyses of tree bark from 31 Pinus ponderosa trees throughout the study area show that significant levels of U, moderate levels of Th, and low levels of Pb and As contamination are present in particulate matter on the reservation. SEM investigations confirm that U and Th particulate matter exist in the inhalable size range while geospatial analyses indicate that U, Th, and As contamination are centralized along the Midnite Mine access road and at the nearby Dawn Mill. These findings indicate that airborne particulate matter from the Midnite Mine and Dawn Mill may be a cause for concern to local health and provides context for future health and environmental studies.

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PROVIDING NEW ENVIRONMENTAL HEALTH CONTEXTS FOR NATIVE AMERICAN POPULATIONS: A GEOCHEMISTRY, SCANNING ELECTRON MICROSCOPY, AND GEOSPATIAL INVESTIGATION OF AIRBORNE URANIUM AND METAL PARTICULATE IN TREE BARK NEAR THE MIDNITE MINE AND DAWN MILL, SPOKANE RESERVATION, WA, USA

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Dedication

This work is dedicated to the Spokane Tribe of Indians. May our culture, language, health, and environment remain strong.

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1.Introduction

1.1 Minewaste and the Midnite Mine

Mine waste and its resulting pollution is of significant environmental concern both globally (e.g., Srafi et al., 2019; Cymes et al., 2017; Bian et al., 2012; Bian et al., 2009; Meck et al. 2006, Hancock and Turley, 2006) and in many regions of the United States (e.g., Schellenbach and Krekeler, 2012; Geise et al., 2011; Krekeler et al., 2010; Krekeler et al., 2008; Brown 2005). The negative impacts from mine waste on socio-economically disadvantaged communities worldwide has been comprehensively documented (e.g., Pal and Mandal, 2019; Babayan et al., 2019; Aires et al., 2018; Jiang et al., 2015; Garvin et al., 2009; Dambacher et al., 2007). Within the context of the United States, this is particularly true with respect to Native American communities (Moore-Nall, 2015; Lewis et al., 2017). However, compared to other regions of the U.S., detailed studies of mine waste and its potential environmental and/or health impacts are uncommon (e.g., Credo et al., 2019; Zota et al., 2009). The Spokane Indian Reservation is only one example of a Native American community that has been deeply impacted by mining operations.

The Midnite Mine is a 350-acre inactive open pit uranium mine located on the Spokane Indian Reservation in eastern Washington (Figure 1). In 1954 when uranium was discovered 9 km west of the main village of Wellpinit, the land was leased by the Spokane Tribe to the Dawn Mining Company (a subsidiary of Newmont USA Limited). Uranium was mined from 1955 to 1965 under contracts with the Atomic Energy Commission (AEC) and from 1969 to 1981 under contracts with the energy industry. In total, 5.3 million tons of ore were mined averaging a concentration of approximately 0.2% uranium oxide (U3O8).

At the abandoned mine site, 2.4 million tons of ore and 33 million tons of waste rock were left behind in stockpiles, and concurrently utilized as gravel for access and haul roads. The majority of the open pits have been backfilled with waste material, however two of the pits remain open and have accumulated water. There are three natural drainages from the mined area that converge and flow into Blue Creek and then into the Spokane River arm of Lake Roosevelt (Figure 1). Ponds and seeps in the mined area are pumped to the largest open pit where a water treatment plant uses barium chloride and lime to precipitate radium, uranium, and other heavy metals. The resulting radioactive sludge is hauled to the Dawn Mill for processing and disposal. The Dawn Mill is the Dawn Mining Company's mill site located adjacent to the reservation border about 20 km east of the Midnite Mine (Figure 1). During mining operations, ore was hauled in open bed trucks across the reservation to the Dawn Mill for processing. From 1955 to 1982, the Dawn Mill produced approximately 11 million pounds of yellow cake (finely milled uranium oxide). A tailings pond, several tailings disposal areas, and approximately 16 acres of stockpiled ore were subsequently left behind at the mill site.

In 1999, the U.S. Environmental Protection Agency (EPA) investigated surface water, groundwater, aquatic sediments, surface materials, sub-surface materials, and airborne radon activity at the Midnite Mine (U.S. EPA, 2005a; U.S. EPA, 2005b). These investigations identified 22 contaminants of potential concern (COPC) including uranium (U), manganese (Mn), arsenic (As), lead (Pb), radium (Ra), vanadium (V), nickel (Ni), cobalt (Co), chromium (Cr), and cadmium (Cd). The largest identified cancer risk was determined to be derived from inhalation of contaminated groundwater used in sweat lodge ceremonies, and consumption of local plants and meat. In May 2000, the Midnite Mine was designated as a Superfund Site. Remediation began in 2009 and is expected to continue through 2025.

1.2 Local Concerns

The estimated population on the Spokane Indian Reservation is 2,145 with 32.9% of this population living below the poverty level. This is more than twice the national average of 13.1% (US Department of Commerce, 2017; U.S. Department of Commerce, 2019). Members of the Spokane Tribe living on the reservation rely on the land for subsistence and traditional ceremonial activities. For example, wild game, fish, roots, and berries are regularly consumed for subsistence, while surface and groundwaters are used for drinking and sweat lodge ceremonies. Various plants across the reservation are also used for medicinal and ceremonial purposes. Individual members of the tribe are allowed, and encouraged to, partake in these activities anywhere on the reservation. This traditional lifestyle makes tribal members susceptible to exposure of environmental contaminants through multiple pathways.

The Spokane Tribe has worked with an environmental company to create the basis for a reasonable maximum exposure (RME) that fits their traditional subsistence lifestyle better than the standard RME used by the EPA (Harper et al., 2002). The EPA used the tribal RME when calculating exposure hazards in the health risk assessment, however, it was noted during their study that the risks and hazards associated with the mine were significantly above their target health goals no matter which RME was used (U.S. EPA, 2005a).

The main concerns of tribal members, as communicated to the Agency for Toxic Substances and Disease Registry (ATSDR), were: perceived high rates of disease on the reservation that they worry could be attributed to exposure to mine contaminants; the loss of a large portion of the reservation which can no longer be used for hunting, fishing, gathering, and ceremonial use; and the social changes and stress experienced by the tribe (ASTDR, 2010). The EPA and others have thoroughly investigated the water, sediments, and soils surrounding the mined area. However, no studies have been conducted which focus on investigating the nature of airborne particulate matter and the associated inhalable size fractions, both of which have the potential to significantly impact the health of the population of the reservation. Despite these long-standing concerns, no health studies have ever been conducted which investigate the impacts uranium mining has had on health on the reservation.

1.3 Previous Work

Land use on the reservation is primarily for timber, forestry, livestock grazing, and agriculture. Hence, local sources of environmental pollution are predominantly from vehicular exhaust products and abandoned mines. Precaution must be taken when establishing an accurate natural background level because some contaminants, such as U, As, Pb, Mn, and copper (Cu) are naturally elevated in various environmental media due to the unique bedrock composition of the area (Ames et al., 1996; U.S. EPA, 2005a; U.S. EPA, 2005b; Church et al., 2007). Natural background levels alone present risks above the EPA's target health goals, however, this contribution is not identified as dominant when establishing overall risk (U.S. EPA, 2005a). Various processes associated with mining and milling work to increase the rate of weathering and transport of contaminants which otherwise would have remained buried and contained within the bedrock.

Previous studies of the mined area have documented elevated levels of U, Pb, As, and molybdenum (Mo) in soils (Boudette and Weis, 1956; Stroud and Droullar, 1995), elevated levels of U, Ra, sulfate, Mn and other metals, in surface and groundwater (Marcy et al., 1994; Schultze et al., 1996; Suzuki et al., 2002), elevated levels of U, As, Mn, Ni, Co, Cu, Cd, and Pb in aquatic sediments (Church et al., 2007), and high doses of gross gamma radiation in the mined area (Stroud and Droullar, 1995; U.S. EPA, 2011). Several studies have also suggested microbial remediation and ion exchange as feasible options to treat contaminated water at the site (Marcy et al., 1994; Suzuki et al., 2002; Schultze et al., 1996).

1.4 Purpose

Historic and to a lesser degree, current dust inhalation near the mine site is of potential environmental health concern. In addition to drilling, blasting, and other mining practices at the pit, ore and waste rock in past and current stockpiles, use of haul trucks, and mine materials used in graveled roads can become airborne. Dispersion occurs through past or to a much lesser degree current, drilling and detonations, natural wind currents, and vehicular traffic. However, little work has been carried out that focuses on comprehensively characterizing this airborne particulate matter. There is no understanding of the dispersal of dust from the time the mine began or during the period of operation, which likely would have been much higher when the mine was active than the current remediation state. The EPA investigation focused on radon gas as the most pertinent threat to inhalation exposure, so no COPCs were determined for dust inhalation. Since 2016, the Dawn Mining Company has been using total suspended particulate (TSP) monitors at the mine site to monitor fugitive dust caused by remediation activities (Dawn Mining Company, 2016). No studies to date have characterized the mineralogy or geochemistry of the airborne particulate matter. Specifically parameters such as of concentrations of elements associated with the mine in airborne particulate in any environmental media, or size and mineralogical constraints of the nature of particulate matter determined from electron microscopy have never been conducted. There has also been no attempt to constrain the geospatial distribution of atmospheric particulate matter in any way specifically associated with the Midnite Mine.

Environmental media choices for reconstructing the depositional history of airborne particulate matter derived from the Midnite Mine are highly limited. The surrounding area is heavily forested with Pinus ponderosa (Ponderosa Pine) which occurs on hilly to mountainous terrain. There are no nearby lakes or ponds distributed such that they could spatially and temporally capture particulate matter in fine-grained sediment. To our knowledge there is no systematic sampling of airborne particulate matter derived from the Midnite Mine while in operation. Owing to these constraints other environmental media that meet the spatial distribution requirements, and that have the potential to capture airborne particulate matter derived from the Midnite Mine over the time period in question is needed.

Tree bark has been effectively used in other environmental monitoring studies to investigate the distribution of particulate and metal pollution. The porous texture of the surface of tree bark passively entraps particles from the air over extended periods of time, potentially throughout the life of the tree at that height (Martin and Coughtrey, 1982; Chrabaszcz and Mroz, 2017). This permits tree bark to be a widespread, easily accessible, and cost-effective biomonitor of past and present airborne particulate matter. For example, tree bark has been effectively used to investigate U in airborne particulate matter from pollution sources such as nuclear reactors and U processing facilities in the UK, Japan, and Ohio (Bellis et al., 2000; Bellis et al., 2001a; Conte et al., 2017). Pine tree bark in particular has been shown to be one of the most effect barks for environmental biomonitoring applications (Schulz et al., 1999; Saarela et al., 2005). Pinus sp. have been used extensively as biomonitors in numeorus localities globally. Examples include that of Austrian pine (Pinus nigra Arnold.) (Coskun, 2006); Italian stone pine (Pinus pinea L.) (Oliva and Mingorance, 2006); Masson pine (Pinus massoniana Lamb.) (Kuang et al., 2007); Pinus eldarica Medw. (Kord and Kord, 2011); Scots pine (Pinus Sylvestris L.) (e.g., Laaksovirta et al. 1976; Dogan et al., 2010, and many others); Turkish red pine (Pinus brutia Ten.) (Dogan et al. 2007). In addition, several recent studies have used tree bark biomonitoring in conjunction with Geographic Information Systems (GIS) methods to investigate spatial trends in airborne particulate matter (Bellis et al., 2001b; Kousehlar and Widom, 2019; Gueguen et al., 2011; Schelle et al., 2007).

The objective of this study is to use Pinus ponderosa (Ponderosa Pine) tree bark to: (1) characterize the nature of airborne particulate matter on the Spokane Indian Reservation with respect to concentration of elements of environmental concern and size and mineralogy of particles; (2) assess the level of contamination that exists through the establishment of geoaccumulation indices and; (3) determine if concentration of elements of environmental concern that are associated with airborne particulate matter are spatially related to the Midnite Mine.

2.Methods

2.1 Sampling

Tree bark samples (n = 31) were collected in the study area in November 2017 (Figure 1). The tree species sampled was kept constant in order to reduce variability in the data. Accordingly, only Ponderosa Pine trees were sampled. The concentrations of heavy metal contaminants in tree bark have been shown to vary significantly across the height of a tree and peak concentrations tend to occur between 1-2 m (Ward et al., 1974; Barnes et al., 1976) A sampling height of 1.5 m has been a long-running standard across most tree bark studies (Hamp and Holl, 1974; Schulz et al., 1999; Gueguen et al., 2012; Birke et al., 2018).

The ages of sampled trees ranged from 70-139 years. This was calculated based on circumference measurements and a growth factor of 4. Tree bark samples taken on the reservation (n = 24) were sampled in the direction facing the Midnite Mine in order to capture and document the highest concentration of windblown contaminants. Similarly, samples taken at the Dawn Mill (n = 3) were taken in the direction facing the mill. Samples taken at the 2 background locations to northwest and southeast of the reservation (n = 4) were sampled in the direction that faced away from any roads in order to minimize contamination. A chisel was carefully used with gloved hands to undercut and remove a large chunk of bark from the tree, which was then stored in a heavy-duty Ziploc bag. At each sampling location, GPS coordinates were taken using a Trimble Geo 7x handheld GNSS system. Soil samples were taken at 4 of the bark sampling locations and street sediment samples were taken at the mill, the mine access road, and at Wellpinit High School.

2.2 Geochemistry

The tree bark samples were dried at 100°C for 24 hours to remove most of the moisture. Samples were then coarsely crushed and ashed in a Thermo Scientific Thermolyne 6028 furnace, in batches of 5-6 at 350°C. Time spent ashing varied from approximately 2-5 weeks as samples were periodically weighed and were only considered complete when mass was no longer being significantly lost (less than 1% change in 48 hours). Repeat dissolution of two international standards (NBS 1632a; coal, and NIST 1547; peach leaves) were prepared throughout the ashing process in addition to 5 total procedural blanks. Ashed samples were digested in a Mars 6 Microwave Digestion System (CEM Corporation) at the Stable Isotope Laboratory facility at the University of Arkansas. Specifically, samples were digested in a mixture of concentrated nitric acid (16 ml) -hydrochloric acid (4 ml). Digested sample solutions were made up to 50 ml with the addition of high purity MilliQ H2O. Solutions were centrifuged after which a 0.5 ml aliquot was taken and diluted at 20x through the addition of 9.5 mls of 2% HNO3. Sample dissolution procedures were monitored through the repeat analysis of NBS 1632a and NIST 1547 which were treated identically to all unknowns (samples) throughout the sample preparation procedure.

Sampled tree bark, standards, and total procedural blanks were analyzed for their elemental compositions via a Thermo iCap Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the Trace Element and Radiogenic Isotope Laboratory (TRAIL) at the University of Arkansas. The ICP-MS was calibrated by using two multi-element standards (68A and 71B, High Purity Solutions). Calibration curve measurements were made using a series of seven dilutions with concentrations ranging from 1 ppb to 1000 ppb. The elements measured were: V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Nb, Sn, Sb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Tl, Pb, Th, U. Sample data is reported in Table 1 in supplemental data. Repeat analysis of the NBS 1632a and NIST 1547 standards are reported in Table 2 in supplemental data.

2.3 Geoaccumulation Index (Igeo)

To determine which elements are enriched relative to background samples, geoaccumulation indices (Igeo) were calculated for each element in all samples. Igeo was specifically calculated using the following approach (after Barbieri, 2016):

$$Igeo = \ln [(concentration)/(1.5*background\ concentration)]$$

Background concentration was constrained by the mean concentration of the background tree bark samples. The resulting Igeo indices represent the level of contamination where Igeo > 0 is characterized as potentially contaminated, Igeo > 1 is characterized as moderately contaminated, Igeo > 3 is characterized as heavily contaminated, and Igeo > 5 is characterized as extremely contaminated.

2.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed using a Zeiss VP35 model field emission scanning electron microscope (FESEM) at the Center for Advanced Microscopy and Imaging (CAMI) at Miami University. Subsamples of tree bark were dried and were then cut to 1-2 mm thick pieces, mounted on aluminum stubs, coated with carbon, and grounded with colloidal silver. Ashed tree bark, soil, and street sediment samples were mounted onto aluminum stubs using carbon sticky tabs and were left uncoated. Samples were scanned for particles of high atomic weight and density using backscatter detection (BSD) mode. Particles of interest were imaged using secondary electron detection (SED) and BSD modes. Energy dispersive spectrometry (EDS) was used to detect elements present using an EDAX2000 system with a detection limit of approximately 0.1 wt. %. In total, 9 tree bark samples were investigated via SEM including 1 from each background site, 1 from the Dawn Mill, 3 from the Midnite Mine access road, and 3 along Wellpinit-Westend Road. Also investigated were 8 tree bark ash samples (1 access road, 2 mill, and 5 along Wellpinit-Westend Road), 4 soil samples (1 south of the mine and 2 along Wellpinit-Westend Rd), and the 3 street sediment samples (mine access road, mill, and high school).

2.5 Geospatial Analysis

Geochemical and GPS point data were imported into ArcGIS Pro for spatial analyses of airborne uranium and metal particulates (deLemos et al., 2009). Graduated symbology maps of the concentrations of select elements (those of environmental health concern) identify and assess their spatial distribution. Additionally, inverse distance weighting (IDW) interpolation maps of Igeo indices were created to estimate contamination levels throughout the study area. IDW interpolation was chosen due to the non-Gaussian nature of the data, aligning with established spatial analysis protocols for geology (Setianto and Triandini, 2013).

3.Results

3.1 Bulk Geochemical Data

The concentrations of the 32 elements analyzed in tree bark ash are summarized in Table 1 of the supplemental data. Within the context of this study, only those identified as being of potential environmental concern are further considered here. In general, concentrations of U are highest along the Midnite Mine access road (min = 29.74 ppb, max = 179.94 ppb, mean = 78.75 ppb) and at the Dawn Mill (min = 4.94 ppb, max = 281.78 ppb, mean = 154.01 ppb) and are lowest at the two background sites (min = 0.37 ppb, max = 0.83 ppb, mean = 0.61 ppb). Similarly, Th, As, yttrium (Y), and heavy rare earth elements also have highest concentrations along the mine access road and at the mill.

When linear regressions are applied to the data (Figure 2), U correlates positively with Y ($R2=0.80$, $p < 0.001$), Nb ($R2=0.76$, $p < 0.001$), and heavy rare earth elements such as ytterbium (Yb) ($R2=0.89$, $p<0.001$). U also positively correlates moderately well with Th ($R2=0.59$, $p < 0.001$) and As ($R2=0.56$, $p < 0.001$). Strong to moderate positive correlations also exist among all combinations of As, Co, Ni, and iron (Fe) (R2 varying from 0.50 to 0.88 and all at $p < 0.001$) and all combinations of U, Th, As, Nb, Y, and Yb (R2 varying from 0.56 to 0.95 and all at $p < 0.001$).

3.2 Geoaccumulation Indices (Igeo)

The range of geoaccumulation indices (Igeo) from minimum to maximum for each element are shown in Figure 3. There are 7 elements with at least one quartile of samples extending above 0. They are as follows: As (min = -1.28, max = 0.75, mean = -0.14), Y (min = -0.78, max = 1.15, mean = 0.19), barium (min = -1.20, max = 0.79, mean = -0.07), La (min = -0.84, max = 0.49, mean = 0.04), Pb (min = -1.77, max = 0.89, mean = -0.01), Th (min = -0.99, max = 1.69, mean = 0.43), and U (min = -0.30, max = 5.73, mean = 1.84). Additionally, Th is at moderate contamination levels in 4 samples (1.14 to 1.69), while U is at moderate contamination levels in 8 samples (1.03 to 2.95), heavy contamination levels in 7 samples (3.17 to 4.93), and extreme contamination levels in 3 samples (5.26 to 5.73). All of the remaining elements analyzed are at uncontaminated levels in the majority of samples. Elements of further interest were selected based on the distribution of Igeo indices in conjunction with the potential toxicity of the element. Using these two criteria, the elements of interest chosen for further characterization in this study are U, Th, Pb, and As.

3.3 Scanning Electron Microscopy (SEM)

3.3.1 Uranium

In total, 6 uranium-rich particles were found using SEM. Three particles were in tree bark or tree bark ash, and three occurred in street sediment. All the U-rich particles contained significant amounts of Fe, most of them were Nb-rich (4 out of 6), one was Th-rich, and one was Y-rich. All of the observed uranium-rich particles were found in samples from the mine access road or the mill. The diameters of these particles varied from 1.0 µm to 5.5 µm. Select U-rich particles are shown in Figure 4.

3.3.2 Thorium

A total of 11 thorium-rich particles were found, two particles were in ash, two were in street sediment, and seven were in soil samples. These particles were found near the mine, the mill, the main village of Wellpinit, and at various locations throughout the reservation. All thorium-rich particles also contained detectable phosphorous (P), calcium (Ca), and Fe. Two of the particles were also cerium (Ce)-rich, 1 was U-rich (indicated above), and 5 of the particles contained small amounts of light rare earth elements. Diameters varied from 1.1 µm to 8.5 µm. Select Th-rich particles are shown in Figure 5. Additionally, Th as a trace element in REE phosphates was ubiquitous throughout all sample types and locations.

3.3.3 Arsenic and Lead

One As and Fe-rich particle was found using SEM. It occurred in a tree bark sample from the mine access road. The particle was a flake approximately 8.5 µm wide and 1 µm thick. Two Pb-rich particles were found in tree bark and tree bark ash. One Pb and iron-rich particle was identified in a sample from the mill site and one Pb and Cr-rich particle was in a sample 5 km south of the mine. The diameters were 9.1 µm and 11.4 µm respectively.

3.4 Geospatial Analysis

3.4.1 Concentration Maps

In general, the highest U and As concentrations appear to concentrate along the mine access road and at the mill (Figure 6). Thorium is a little more broadly distributed, but the highest concentrations are located at the mill, on the mine access road near its intersection with the main road, and in one sample to the southwest of the mine on the main road. Lead concentrations are the most diffuse with the highest concentrations occurring along the main road throughout the study area and localized at the mill. Also of note, some of the lowest Pb concentrations occur along the mine access road.

3.4.2 Igeo Interpolation Maps

The Igeo indices of the elements of U, Th, Pb, and As, are interpolated throughout the study area in Figure 7. By these estimations, the level of U contamination is highest at the mill and on the mine access road, with contamination levels decreasing with distance away from these identified hotspots. Only one small area north of Wellpinit is estimated to be uncontaminated with U (Igeo<0, Figure 7). Levels of Th contamination are estimated to be the highest at the mill and at the intersection of the mine access road and main road, with thorium contamination near the mine access road extending to the south. Wellpinit, the central portion of the study area, and the western side of the study area are estimated to be uncontaminated by Th. The interpolated levels of Pb contamination are highest at four points along the main road to the east and west of the mine. Another area of relatively high estimated Pb contamination occurs in Wellpinit. The mine access road is estimated to be uncontaminated by Pb, but there is the potential for low Pb contamination levels near the mill. The level of As contamination is highest at the mill and along the mine access road. The area surrounding Wellpinit is also potentially contaminated with As. Arsenic contamination is estimated here to be restricted to the vicinity of the mine access road, Wellpinit, and the mill, while the rest of the study area is estimated to be uncontaminated.

4.Discussion

4.1 Potential for Inhalation of Particulate Matter

It is well established that a connection exists between exposure to toxic airborne particulate matter and short-term and long-term adverse health effects (e.g., Nel, 2005; Pope and Dockery, 2006; Valavanidis et al., 2008). Particulate matter is known to be the most significant aspect of air pollution with direct negative health outcomes well established (e.g., Valavanidis et al., 2008). In general, the smaller the diameter of airborne particulate matter, the more potential impact on human health as the smaller the particle the higher the probability penetrating the deep lung. The commonly used distinctions are PM10 (diameter less than 10 µm) and PM2.5 (diameter less than 2.5 µm). PM10 is small enough to be inhaled, however PM2.5 is known to have a stronger correlation with negative health effects because it can penetrate deeply into the lung, it has more surface area per volume, and is more commonly retained in lung tissue than PM10 (e.g., Seaton et al., 1995; Valavanidis et al., 2008). Tree bark as a proxy of potentially harmful airborne particulate matter, may be therefore an effective way to predict negative health outcomes. For example, a recent study found strong correlations between the concentrations of Al, S, Mn, Fe, Cu, and Zn in tree bark and mortality rates from both lung cancer and COPD (Carvalho-Oliveira et al., 2017). While it is acknowledged that the toxicity and health effects of airborne particulate matter can vary based on the chemical composition, radionuclides and heavy metals such as those identified as contaminants in this study (U, As, Th, Pb) do have the potential to be damaging to human health (e.g., Duruibe et al., 2007; Tchounwou et al., 2012).

4.2 Uranium

Uranium concentrations in bulk chemical analyses are interpreted to be from uranium particulate and not from dissolved uranium absorbed by tree bark. There is a reasonably strong correlation of niobium and uranium in bulk chemical data and there is ample evidence of uranium-niobium mineral particles entrapped in the bark as indicated by SEM data. Although there is extensive literature on pinus ponderosa, as well as extensive literature on micronutrients, there is no mention in any of this body of literature of niobium serving as a micronutrient for pinus ponderosa, or any other organism. Uranium concentrations in bulk chemical analysis of bark are therefore interpreted to be from particulate.

Uranium is the most highly concentrated element in tree bark relative to background values. Uranium in particulate matter along the Midnite Mine access road and at the Dawn Mill occurs at statistically extreme levels of observed contamination. The east mine access road is of particular concern within the context of environmental health because it was the primary access road used to haul ore off site when the mine was in operation. Ore was hauled in open bed trucks which have been documented to spill ore on roadways between the Midnite Mine and the Dawn Mill (Dawn Mining Company, 2005). The access roads are also known to have been resurfaced using waste materials from the mine (U.S. EPA, 2005b).

While uranium contamination does not appear to be significant in the main village of Wellpinit, geospatial studies of the health effects from environmental pollutants on Indian reservations need to incorporate knowledge of tribal culture in order to truly assess and represent risks. On the Spokane Indian Reservation, the Midnite Mine is located in the unpopulated center of the reservation, however, the traditional subsistence lifestyle entails utilizing the entire reservation for hunting, fishing, gathering, and ceremonial use. Residents on the Spokane Indian Reservation could be reasonably expected to be partaking in these outdoor activities near the mine where inhalation of uranium in airborne particulate matter is a potential risk. Moreover, low to moderate levels of uranium contamination in airborne particulate matter extend throughout most of the study area, including Wellpinit. Previous studies have shown that uranium is also a contaminant in groundwater, surface water, soils, and aquatic sediments associated with the Midnite Mine (Marcy et al., 1994; Ames et al., 1996; Church et al., 2007; U.S. EPA 2005a; U.S. EPA 2005b).

The uranium-rich particles observed in tree bark are considered small enough to be inhaled (aerodynamic diameter smaller than 10 µm). Uranium-rich particles in the fine and ultra-fine size fractions were not observed in tree bark or tree bark ash but could still be present as these fractions are below the detection limit of the SEM. The SEM methods used cannot observe nanoscale particles and biases in visually scanning samples for atomically dense particles in BSD mode may translate to larger particles being more commonly identified and investigated. Furthermore, challenges exist with SEM investigations of granular materials, or materials where particles may be embedded in other media, as particles present at lower abundances may simply be obscured by matrices of other materials or particles.

4.3 Thorium

Thorium is at low to moderate levels of contamination in the analyzed tree bark samples. Thorium contamination appears to be concentrated around the Dawn Mill and at the opening of the Midnite Mine access road near its intersection with Wellpinit-West End road. Thorium is a decay product of the major site contaminant, uranium, which may partially explain the correlation between the two elements. Furthermore, uraninite (one of the major ore minerals at the Midnite Mine) is known to contain significant amounts of Th, Y, and REEs (Boudette and Weis, 1956; Barrington and Kerr, 1961; Nash and Lehrman, 1975) which could explain some of the observed correlations between all of these elements. The EPA also designated thorium as a COPC in haul road soil (U.S. EPA, 2005a). The thorium-rich particles observed in tree bark and tree bark ash had diameters of 1.1 and 3.9 µm, indicating that there are PM2.5 thorium-rich particles present.

4.4 Arsenic

Arsenic was observed in airborne particulate matter on the Spokane Indian Reservation at low levels of contamination. Clusters of high arsenic concentrations and Igeo indices are found adjacent to the Dawn Mill and the main Midnite Mine access road. This observed arsenic contamination is likely sourced from uranium mining and processing. At the Midnite Mine, arsenic is known to be geologically related to the uranium ore deposits (Boudette and Weis, 1956; Barrington and Kerr, 1961). Uranium ore at the mine is closely associated with arsenopyrite and various iron sulfides which can commonly contain arsenic as an impurity (Majzlan et al., 2014). One of the most common uranium minerals at the Midnite Mine, coffinite, also commonly contains arsenic (Steiff et al., 1956; Boltsov and Kaikova, 1964; Majzlan et al., 2014). Arsenic has been identified as a contaminant in sediments directly downstream from the Midnite Mine and the EPA designated it as a COPC in surface sediments of the mined area (Church et al., 2007; U.S. EPA, 2005a). Only one particle containing arsenic was found using SEM, however it is possible that arsenic exists as a trace element in particles smaller than the resolution of the SEM and is not within the detection limits of the EDS system.

4.5 Lead

Throughout the Spokane Indian Reservation, there are potentially low levels of lead contamination in airborne particulate matter. Although lead has been found as a contaminant in other environmental media associated with the Midnite Mine (Church et al., 2007; U.S. EPA, 2005a), and some of the uranium minerals of the mine are known to be rich in lead (Nash and Lehrman, 1975; Ludwig et al., 1981), the spatial distribution of lead contamination in airborne particulate matter does not appear to be related to the Midnite Mine or the Dawn Mill. The highest areas of lead contamination are instead located along Wellpinit-Westend Road. Lead particulate matter is most commonly sourced from vehicular exhaust (Valavanidis et al., 2008) which would be consistent with what is observed on the Spokane Reservation as well. Also of note, several past lead mining operations including Queen, Providence, and Fouress, were located directly to the north and southeast of the Spokane Reservation (Campbell and Loofbourow, 1962; Becraft and Weis, 1963). Although lead airborne particulate matter does not appear to be related to the Midnite Mine, it is still present and is a potential concern for local health – even at low concentrations (Valavanidis et al., 2008).

4.6 The Dawn Mill

The Dawn Mill is a more prominent source of contaminants in airborne particulate matter than originally anticipated. In this study, the areas surrounding the Dawn Mill were not extensively sampled, however the samples taken at the mill had some of the highest concentrations of uranium, thorium, and arsenic. Unlike the mine, the Dawn Mill is not a Superfund Site. Its cleanup, which began in 1995 and is still ongoing, is overseen by the Washington State Department of Health. While the Dawn Mill is not located on the Spokane Indian Reservation, it is directly adjacent and sits above up gradient groundwater. No known studies on the Dawn Mill have been published. Based on these findings, further investigations on the health and environmental impacts of the Dawn Mill are warranted.

4.7 Disparities in Health among Native American Populations

Uranium mining pollution on Indian reservations is common. During the uranium boom from the 1940s to 1980s, mining and production of uranium heavily affected Native American lands, which tend to be rich in mineral deposits. The Navajo Nation alone had over 1,000 mines and four uranium mills on their lands (Moore-Nall, 2015). During this time, many Native American workers were eager to have employment at uranium mines, but they were not made aware of the hazards associated with radiation exposure.

Throughout the scientific literature there is a general lack of health studies on Native American populations. One potential reason for this is that they are usually small communities that cannot provide the large sample sizes desired by researchers. However, there are numerous studies which show high levels of toxic pollutants from mines on Indian reservations (e.g., Marron, 1989; Ong et al., 2014; Hund et al., 2015) and there are well documented disparities in the health and mortality rates of Native American populations (e.g., Lewis et al., 2017). Greater inclusion of Native American communities in toxicological studies is greatly needed. Correspondingly, no health studies have ever been conducted on the Spokane Indian Reservation. Given the results of this study, and the results of previous investigations at the Midnite Mine, and the concerns of the Spokane Tribe regarding disease rates on the reservation, future studies are needed on the health of residents in relation to local uranium mining and milling activities.

5. Conclusions

The findings presented in this study demonstrate that airborne particulate matter pollution containing U, Th, Pb, and As occurs on the Spokane Indian Reservation. Although challenging to detect, SEM investigations confirm that uranium and thorium particles on the surface of tree bark occur in size fractions that can be inhaled and interact with the deep lung. Geospatial modeling indicates the source of U, Th, and As airborne particulate matter are likely centered around the Midnite Mine access road and the Dawn Mill and therefore provides a basis for more detailed future sampling. Geospatial analyses work to validate the long-standing concerns that airborne particulate matter pollution from the Midnite Mine indicates there is potential concern for the health of populations throughout the reservation.

Future systematic medical studies to investigate the health impacts on the reservation resulting from particulate matter pollution from the Midnite Mine and the Dawn Mill are warranted. The results of this study have provided the material and geospatial contexts to guide these future landscape-level investigations of disease on the Spokane Indian Reservation.

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7. Figures

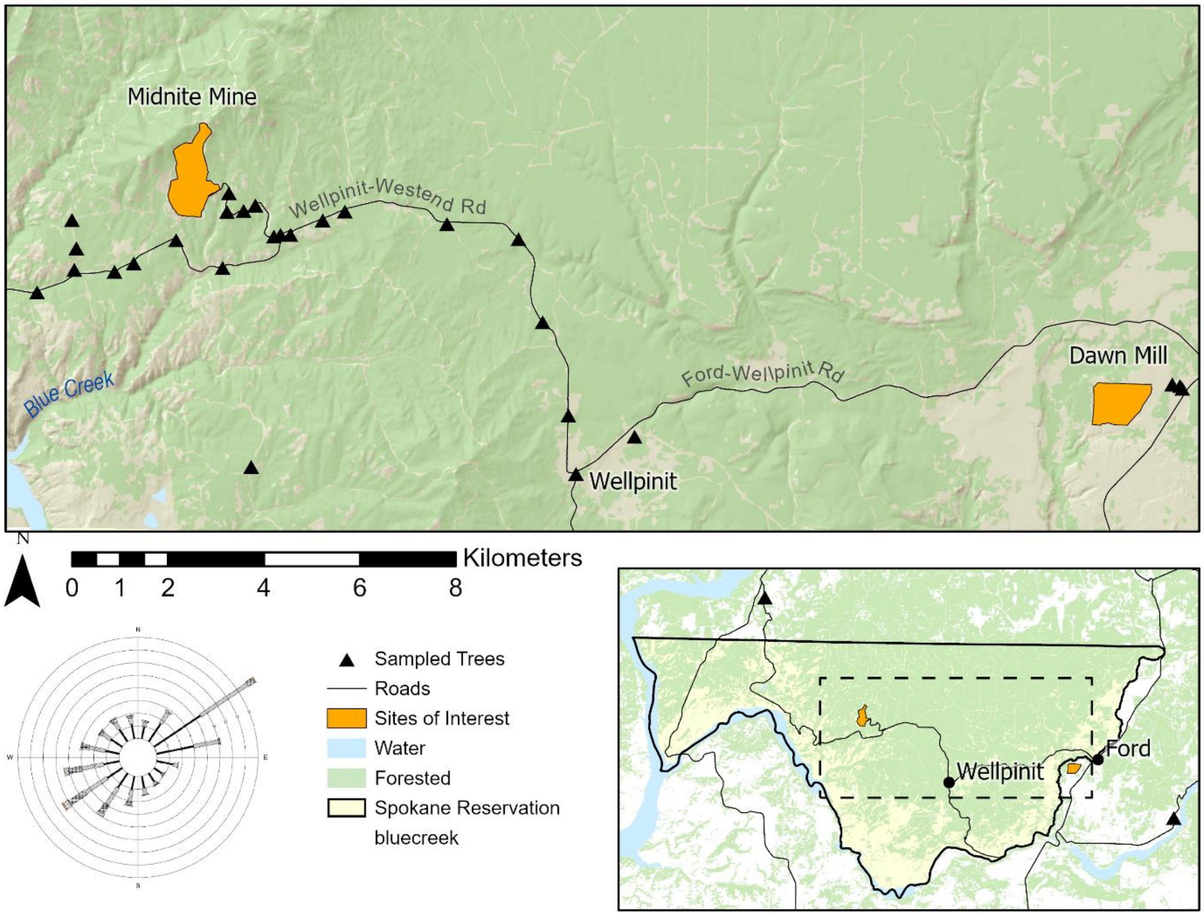

Figure 1. Map of study area. Black triangles represent locations of sampled tree bark. The inset map shows the location of the study area within the Spokane Indian Reservation and the NW and SE background locations. The bottom left shows the dominant wind direction at the Midnite Mine is to the NE and secondary wind direction is to the SW (wind rose adapted from EPA 2005b).

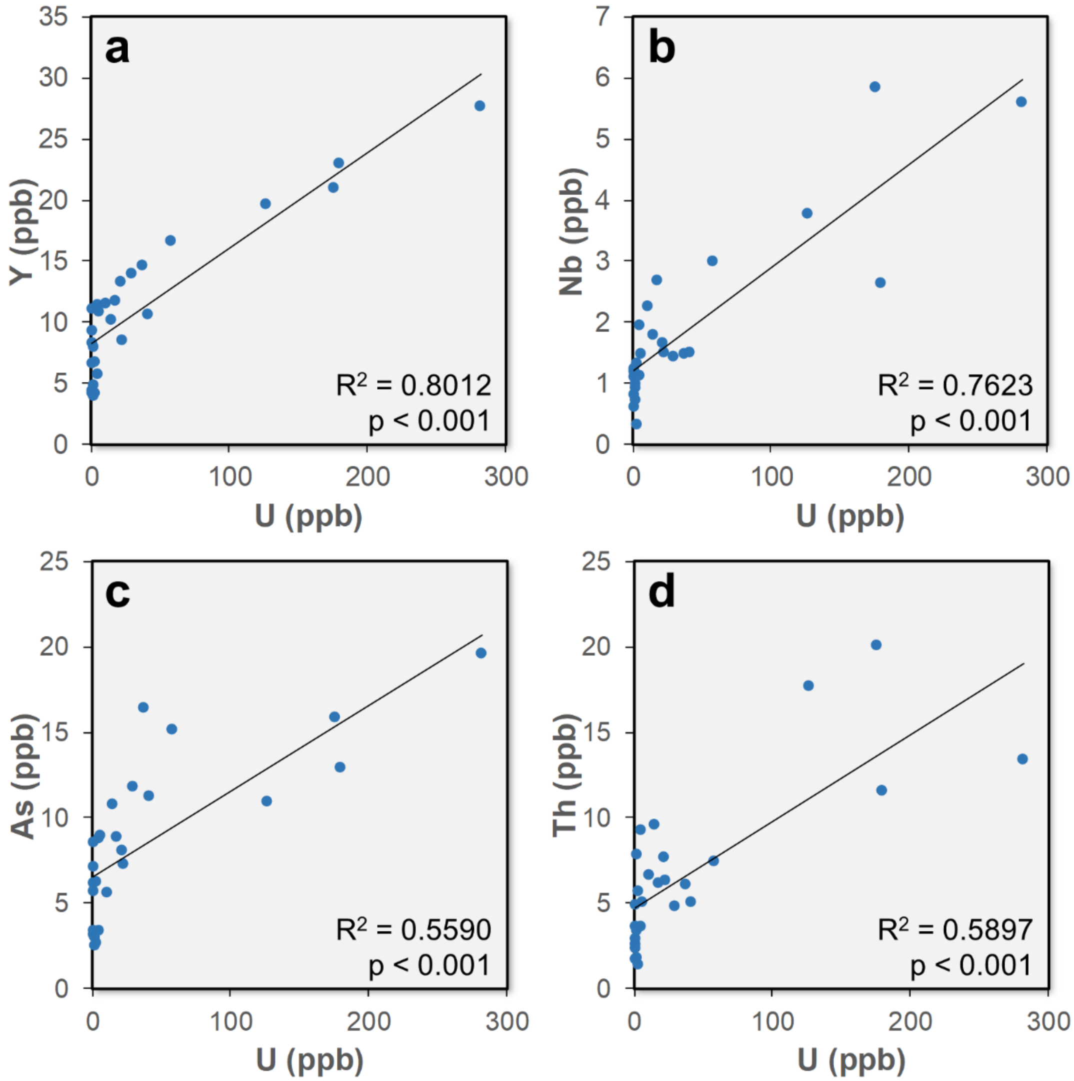

Figure 2. Linear regressions of bulk geochemical data showing the correlations between elemental concentrations in tree bark ash among all samples (n=31).

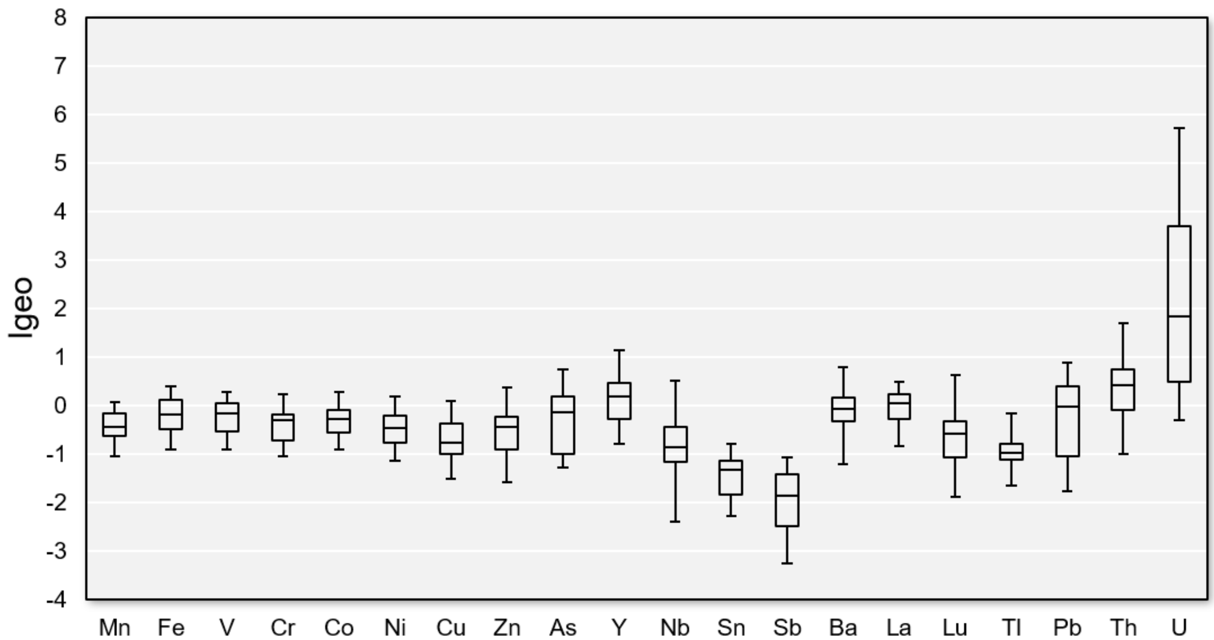

Figure 3. The distribution of geoaccumulation (Igeo) indices of select elements in all non-background samples (n=27) with no outliers. The middle line represents the median, the boxes represent the 2nd and 3rd quartiles and the whiskers represent the 1st and 4th quartiles.

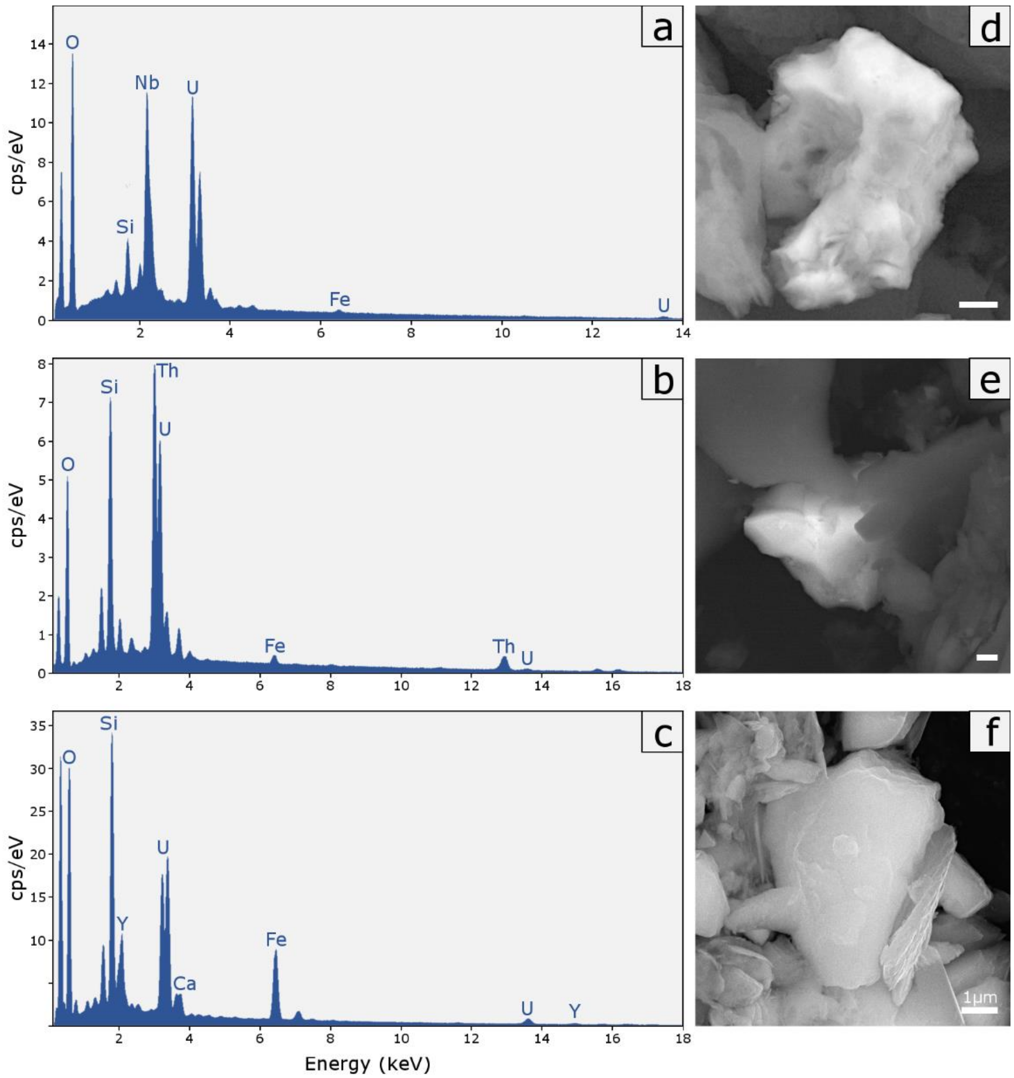

Figure 4.

EDS spectra (a-c) with paired micrographs of select U-rich particles (d-f). (**a**) Major peaks indicate U (3.164 and 13.612 keV), Nb (2.166 keV) and O (0.525 keV) are the major constituents. Si (1.739 keV), Fe (6.398 keV), and Al (1.486 keV) also present. (**b**) Prominent peaks indicate Th (2.991 and 12.967 keV), U, Si, O, Al, and Fe are present. (**c**) Dominant peaks indicate U, Y (1.992 and 14.931 keV), Si, O, Fe, and Ca (3.690 keV) are present. (**d**) U-Nb-rich particle of approx. 5.5 µm diameter from a mill tree bark sample. Imaged in secondary electron detection mode (SED) at 15.00 keV. (**e**) U-Th-rich particle of approx. 4.6 µm diameter from street sediment of the mine access road. Imaged in backscatter detection mode (BSD) at 25.00 keV. (**f**) U-Y-rich particle of approx. 4.8 µm diameter in the ash of tree bark from the mill. Imaged in SED at 25.00 keV.

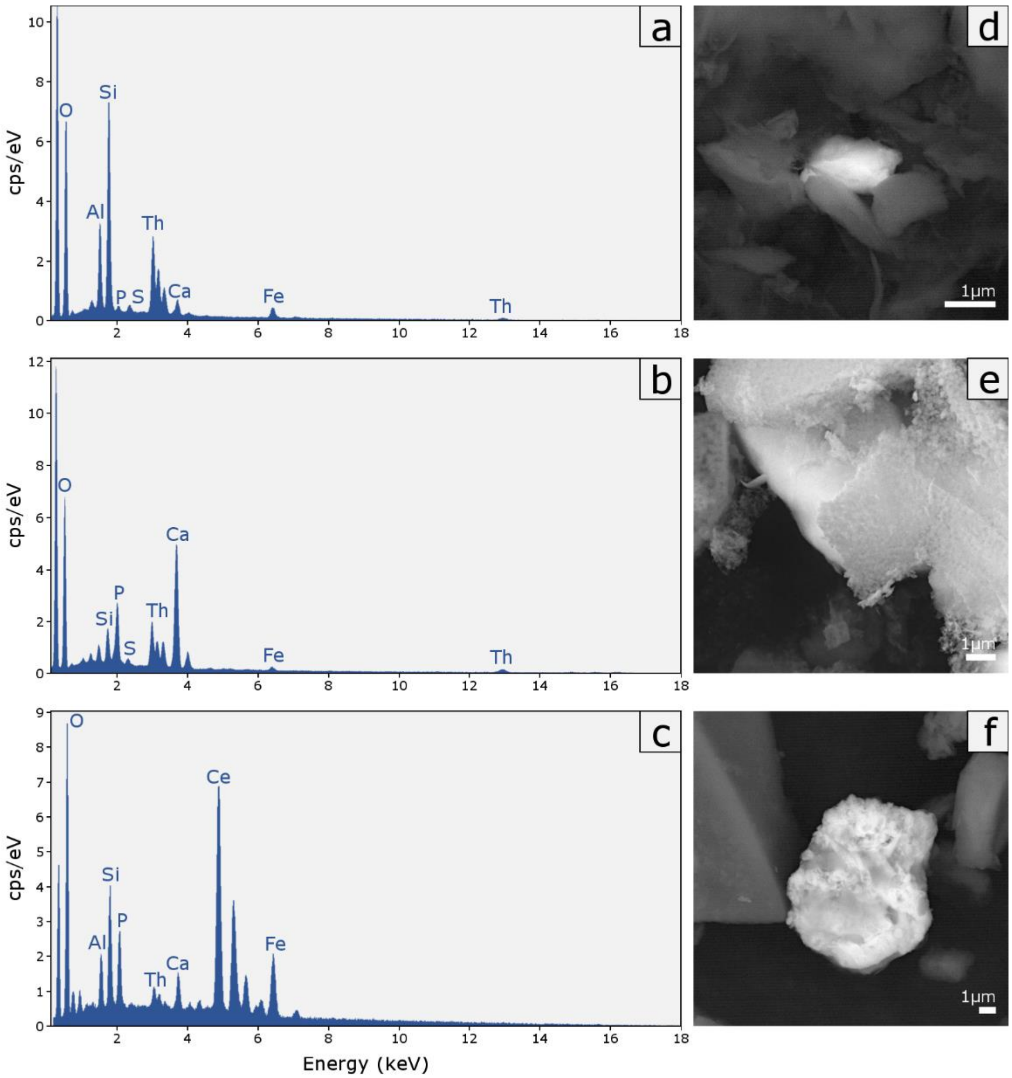

Figure 5.
EDS spectra (a-c) with paired micrographs of select Th-rich particles (d-f). (a) Major peaks indicate Th, Si, O, Al, Fe, Ca, P (2.103 keV), and S (2.307 keV) are present. (b) Peaks indicate Ca, P, O, Th, Si, S, and Fe are present. (c) Peaks indicate Ce, Th, O, Si, Al, P, Ca, and Fe are present. (d) Th-rich particle of approx. 1.1 µm diameter in tree bark ash from the mill. Imaged in BSD at 20 keV. (e) Th-rich particle (the smooth particle behind the flakey textured particle) of approx. 3.9 µm diameter from mine access road tree bark ash. Imaged in SED at 25.00 keV. (3) Ce-Th-rich particle of approx. 8.5 µm diameter in a soil sample 5 km south of the Midnite Mine. Imaged in BSD at 20.00 keV.

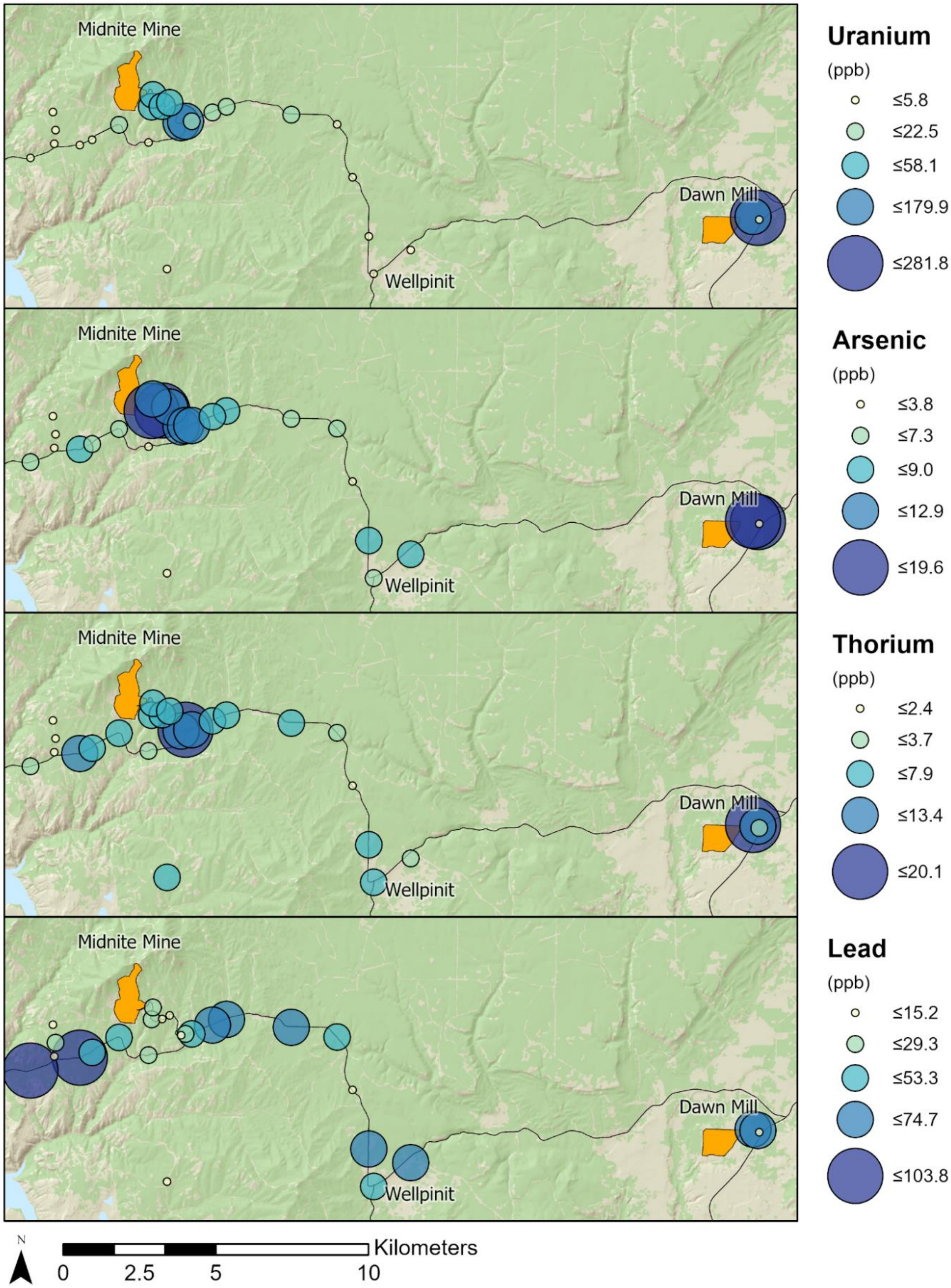

Figure 6. Concentration maps of U, As, Th, and Pb in non-background samples (n=27). Symbology classes based on Jenks natural breaks.

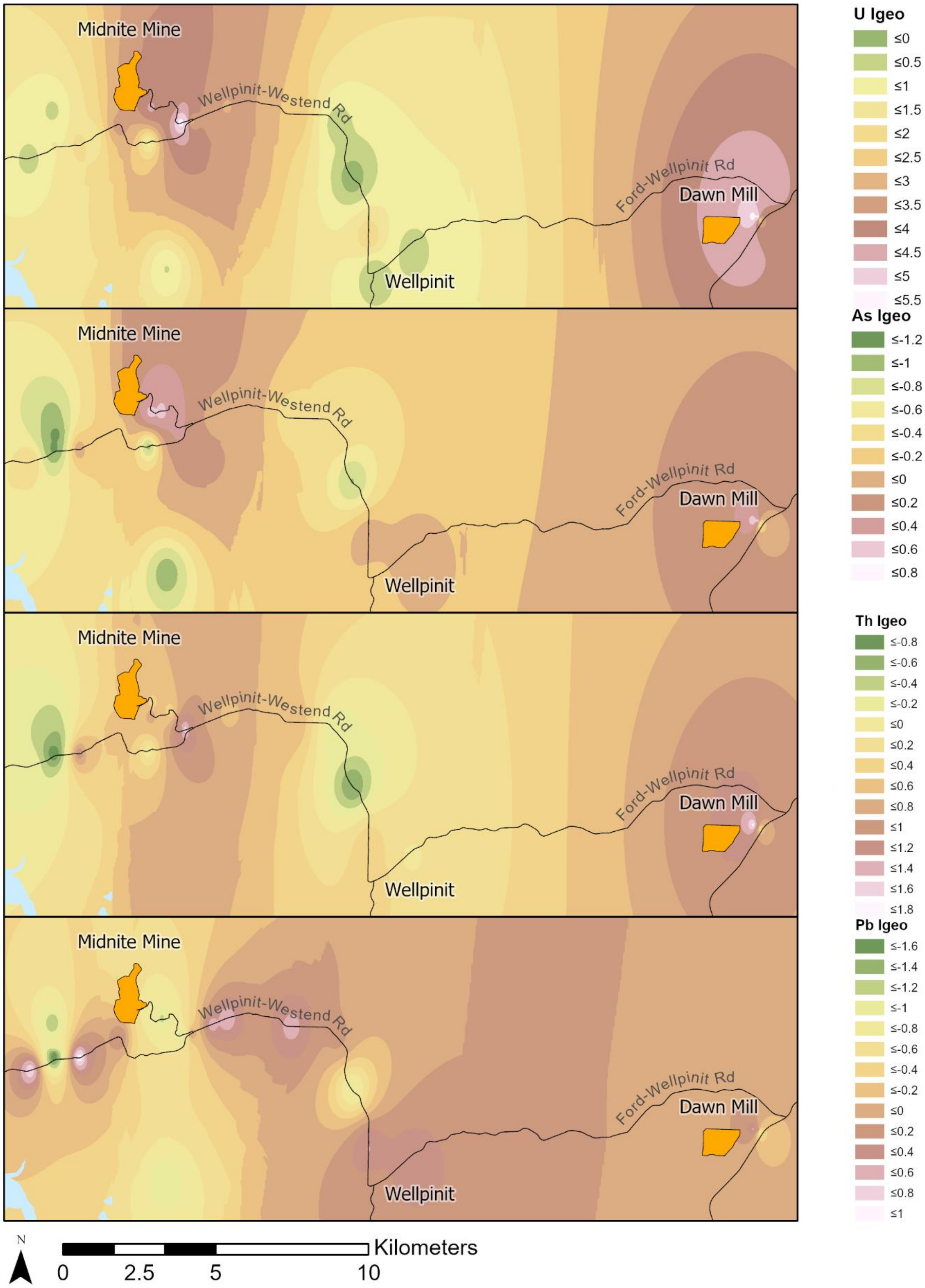

Figure 7. Maps of select Igeo indices interpolated from Midnite Mine to Dawn Mill using inverse distance weighting (IDW) and all sample points (n=31) of U, As, Th, and Pb.