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Monitoring uranium mine pollution on Native American lands: Insights from tree bark particulate matter on the Spokane Reservation, Washington, USA

Lonnie Flett[a], Claire L. McLeod[a,*], Jessica L. McCarty[b], Barry J. Shaulis[c], Justin J. Fain[b], Mark P.S. Krekeler[d,a]

[a] Department of Geology and Environmental Earth Science, Shideler Hall, Miami University, Oxford, OH, 45056, USA
[b] Department of Geography, Shideler Hall, Miami University, Oxford, OH, 45056, USA
[c] Trace Element and Radiogenic Isotope Laboratory (TRAIL), University of Arkansas, Fayetteville, AR, 72701, USA
[d] Department of Mathematical and Physical Sciences, Miami University Regionals, Hamilton, OH, 45011, USA

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ABSTRACT

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 and typically ignore contributions from airborne particulate matter. The Midnite Mine is a 350-acre inactive open pit uranium mine located on the Spokane Indian Reservation in eastern Washington that operated from 1954 to 1981. Approximately 2.4 million tons of ore and 33 million tons of waste rock were left behind in stockpiles and have also been utilized as gravel on access and haul roads. Although the Midnite Mine is now a Superfund Site, and governmental investigations of water and soil contamination have been done, no investigations of airborne particulate matter pollution have been conducted. This study applies tree bark from 31 *Pinus ponderosa* trees as a biomonitor of this airborne particulate matter. Bulk trace elemental analyses via inductively coupled plasma – mass spectrometry (ICP-MS) of tree bark show that U is the most abundant trace element of interest present up to 232 ppb. Other metals that are of potential human health concern include Th, Pb, and As which are present at 20 ppb, 104 ppb, and 20 ppb respectively. Calculated geoaccumulation indices determine these metals to be at high (U), moderate (Th), and low (Pb and As) levels of contamination. Detailed scanning electron microscopy (SEM) investigations of particulate matter from the surface of tree bark confirm that U and Th-bearing particulate matter exist in the $<PM_{10}$ size fraction while geospatial analyses indicate that uranium, thorium, and arsenic contamination are centralized along the Midnite Mine access road and at the nearby Dawn Mill where ore was further processed. Combined, these findings indicate that the nature and distribution of historic airborne particulate matter from the Midnite Mine and Dawn Mill provide context for potentially understanding past and current illness on the reservation. In addition, much needed context for future health and environmental studies for both local and national Native American populations is provided.

1. Introduction

Mine waste and its resulting pollution are of significant environmental concern both globally (e.g., Hancock and Turley, 2006; Meck et al., 2006; Bian et al., 2009; Bian et al., 2012; Cymes et al., 2017; Srafi et al., 2019) and in many regions of the United States (e.g., Brown 2005; Krekeler et al., 2008; Krekeler et al., 2010; Geise et al., 2011; Schellenbach and Krekeler, 2012). Pollution studies associated with uranium mines are commonly carried out within the context of watersheds (e.g., Fernandes and Franklin, 2001; Winde and Sandham, 2004; Winde, 2010; Committee on Uranium Mining in Virginia, 2011) or soils (Pehoiu et al., 2019; Committee on Uranium Mining in Virginia, 2011). While general air pollution studies (Basha et al., 2014) associated with uranium mines have been carried out, specific air dispersion investigations of U pollution from uranium mines are less common (e.g., Jeran et al., 1995). Clear concerns regarding atmospheric dispersal of uranium (U) particulate matter from mines are warranted (e.g., Jeran et al., 1995; Committee on Uranium Mining in Virginia, 2011) and detailed studies

* Corresponding author.
E-mail address: mcleodcl@miamioh.edu (C.L. McLeod).

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on the bulk distribution of U and the mineralogical controls are needed.

The negative impacts from mine waste on socio-economically disadvantaged communities worldwide continue to be documented in the peer-reviewed literature via documentation of groundwater and drinking water contamination, and environmental quality analyses (Dambacher et al., 2007; Garvin et al., 2009; Jiang et al., 2015; Aires et al., 2018; Babayan et al., 2019; Pal and Mandal, 2019). Within the context of the United States, this is particularly true with respect to Native American communities (Moore-Nall, 2015; Lewis et al., 2017). Adding complexity to mine waste studies is that access to Native American Lands are variously restricted and numerous complexities normally exist in research on Native American Lands (e.g., U.S. Department of the Interoir, Bureau of Indian Affairs, 2020).

However, compared to other regions and communities throughout the U.S., detailed studies of mine waste and its potential environmental and/or health impacts are uncommon (e.g., Zota et al., 2009; Credo et al., 2019). The Spokane Indian Reservation in Washington state is only one example of a Native American community that has historically been significantly impacted by mining operations, specifically uranium mining at the Midnite Mine. To date, the nature and spatial relationship of pollution from these intensive mining operations on the short and long-term health of the local communities remains poorly constrained. Specifically, the nature of potential airborne contaminants across the Spokane Indian Reservation remains unassessed.

The Midnite Mine is a 350-acre inactive open pit uranium mine located on the Spokane Indian Reservation in eastern Washington (Fig. 1). The site is currently in remediation. 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 (U_3O_8).

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 (Fig. 1). As part of the current remediation efforts, ponds and seeps in the mined area are pumped to the largest open pit where a water treatment plant implements barium chloride and lime to facilitate the precipitation of radium (Ra), U, and other toxic metals. The resulting radioactive sludge is then hauled to the Dawn Mill site for processing and disposal. The Dawn Mill is the Dawn Mining Company's mill site located adjacent to the reservation border ~20 km east of the Midnite Mine (Fig. 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 U, Ra, manganese (Mn), arsenic (As), lead (Pb), vanadium (V), nickel (Ni), cobalt (Co),

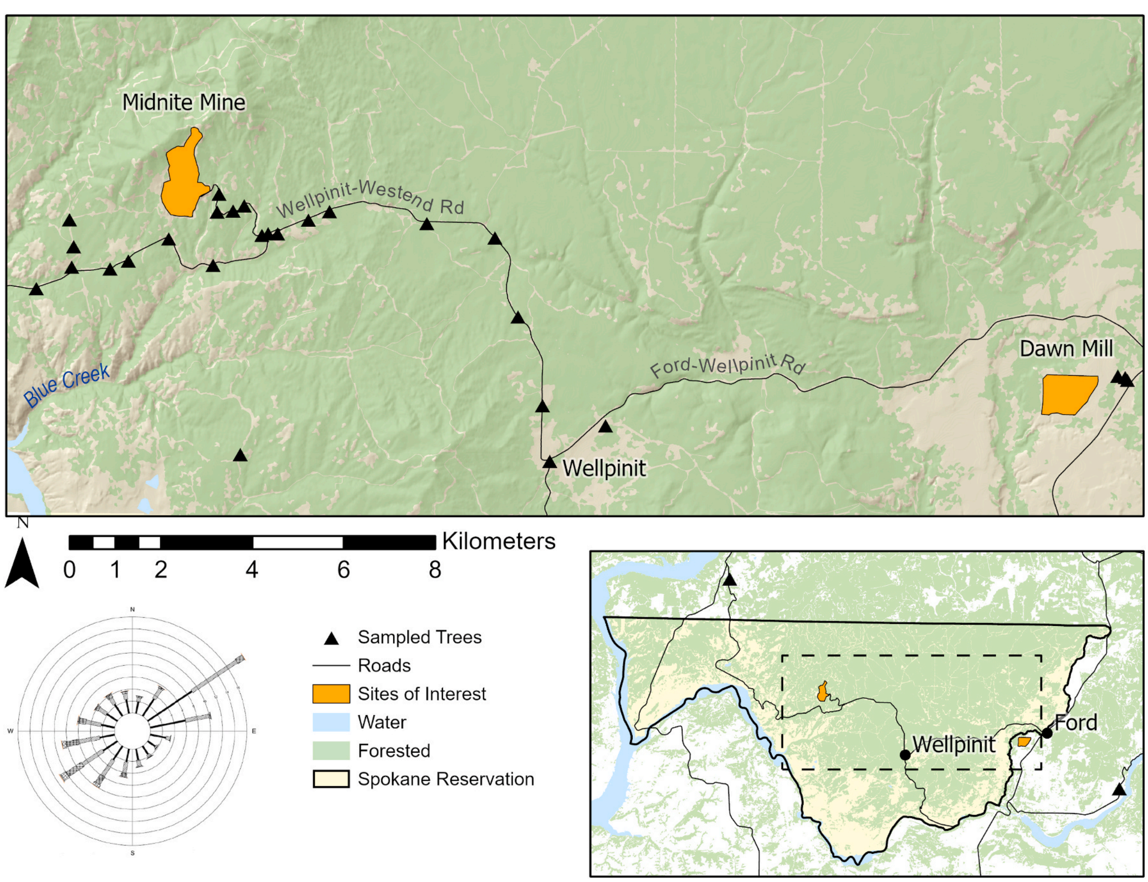

Fig. 1. Map of study area. Black triangles represent locations of sampled tree bark. The inset map shows the location of the study area within the Spokane Indian Reservation and the NW and SE background locations. The bottom left shows the dominant wind direction at the Midnite Mine is to the NE and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

chromium (Cr), and cadmium (Cd). From this work, 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.

The estimated population on the Spokane Indian Reservation is 2145 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 USEPA 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.

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 geologic 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). The processes associated with mining and milling work to increase the rate of weathering and transport of contaminants and pollutants 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; Schultze et al., 1996; Suzuki et al., 2002).

Across the United States an estimated 286,346 Native Americans live within <10 km of a uranium (or vanadium) mine site (Lewis et al., 2017). To date, a systematic study of the long-term impacts of pollution resulting from historic uranium mining on the health of the Spokane Indian Reservation remains lacking (Moore-Nall, 2015; McDermott, 2019). Historically, and potentially to a lesser degree, current inhalation of dust derived from the Midnite uranium mine across the reservation, particularly in proximity to the mine site, is of potential environmental health concern (Lewis et al., 2017; Hettiarachchi et al., 2018; Zychowski et al., 2018; Entwistle et al., 2019). Historic activities of the mine that contribute to dust dispersal include processes such as drilling, blasting, use of haul trucks, and wind action on ore and waste rock. Current processes that have the potential to release dust into the environment include continued wind action and the airborne transport of mine waste as stockpiles of material are used in resurfacing graveled roads. The extent to which historic dispersion of uranium mine waste has occurred throughout the reservation as a result of drilling and detonations, natural wind currents, and vehicular traffic remains unconstrained. To date, no study has systematically investigated the nature and dispersion of this airborne particulate matter. Although present day levels of airborne particulate matter are likely lower in its current remediation state compared to when the mine was active, historic levels were likely higher owing to the multiple active mining processes. This airborne particulate matter would have had the potential to be dispersed across the Spokane reservation away from the mine. From the 2011 EPA investigation radon gas was determined to be the most pertinent threat with respect to potential inhalation exposure. No COPCs were considered within inhalation contexts, either at the present day or historically.

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). To date, the nature of airborne particulate matter related to remediation activities also remains uncharacterized for its mineralogy and/or geochemistry.

Environmental media choices for investigating the nature and distribution of airborne particulate matter derived from the Midnite Mine are highly limited. There are no nearby lakes or ponds distributed such that they could spatially and temporally capture particulate matter in the fine-grained sediment on the lake floor (e.g., Korosi et al., 2018; Aliff et al., 2020). The surrounding area is however heavily forested with *Pinus ponderosa* (Ponderosa Pine) which occurs on hilly to mountainous terrain. The porous texture of the surface of the tree bark works to passively entrap particles from the air over extended periods of time, potentially throughout the life of the tree at that height (e.g., Martin and Coughtrey, 1982; Chrabaszcz and Mroz, 2017). This permits the 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 the Midwest of the United States (Bellis et al., 2000, 2001a; Conte et al., 2017). *Pinus* sp. in particular 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); Mondell pine (*Pinus eldarica Medw*.; Kord and Kord (2011); Scots pine (*Pinus sylvestris* L.; Laaksovirta et al., 1976; Dogan et al., 2010); 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; Schelle et al., 2007; Gueguen et al., 2011; Kousehlar and Widom, 2019, 2020). From a variety of previous environmental pollution-based studies, tree bark from the *Pinus ponderosa* in particular has also been established as a highly effective biomonitor of airborne particulate matter and as a time-integrated record of environmental pollution (Schaumloffel et al., 1998; Schulz et al., 1999; Padilla and Anderson, 2002; Saarela et al., 2005; Peckham et al., 2019).

The objective of this study is to therefore use *Pinus ponderosa* tree bark to: (1) characterize the historic nature of airborne particulate matter on the Spokane Indian Reservation with respect to the mineralogy and size of particulate matter and the associated concentration of elements of environmental concern; (2) assess the level of potential contamination that exists across the reservation via the establishment of geoaccumulation indices and; (3) determine if the 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 Pinus ponderosa on the Spokane reservation

Tree bark samples (n = 31) were collected across the study area in November 2017 where access was possible (Fig. 1). The tree species sampled was kept constant throughout the sample region. Accordingly, only *Pinus ponderosa* trees were sampled. The concentrations of metal contaminants in tree bark have been shown to vary significantly across the height of a tree with peak concentrations documented to occur between 1 and 2 m (Ward et al., 1974; Barnes et al., 1976). Therefore, a consistent sampling height of 1.5 m has been the long-running standard reported in the majority of tree bark studies (e.g., Hamp and Holl, 1974; Schulz et al., 1999; Gueguen et al., 2012; Birke et al., 2018). The ages of sampled trees varied from 70 to 139 years. This age range 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 processing site (n = 3) were taken in the direction facing the mill. Samples taken at background locations to the northwest and southeast of the reservation (n = 4) were sampled in the direction that faced away from any roads in order to minimize contamination from traffic-related particulate matter. The total number of background samples at n = 4 for this study is demonstrably comprehensive and was in part informed by prior work which also utilized biomonitors within the context of pollution (e.g., no background sample(s), Bellis et al., 2001; one background sample for 19 total samples, Conte et al., 2017; one background sample for 23 total samples, Kousehlar and Widom, 2020). A chisel was carefully used with gloved hands to undercut and remove a chunk of bark from the targeted tree, which was then stored in a heavy-duty Ziploc bag (sampled tree bark ranged from 7 g to 38 g with a median of 28 g). At each sampling location, GPS coordinates were taken using a Trimble Geo 7x handheld GNSS system.

2.2. Sample preparation

Sampled tree bark was dried at 100 °C for 24 h to remove 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 to 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 h). 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 utilizing the approach presented in Becker et al. (2000). 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 H_2O. 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% HNO_3. 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.

2.3. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Sampled tree bark ash, 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 (68 A and 71 B, 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.

2.4. Calculation of geoaccumulation indices (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.

2.5. 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).

2.6. Geospatial analysis

Geochemical and GPS point data were imported into ArcGIS Pro for spatial analyses of airborne U 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 the 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, the highest concentrations of Th, As, yttrium (Y), and heavy rare earth elements are recorded along the mine access road and at the mill.

When linear regressions are applied to the data (Fig. 2), U correlates positively with Y ($R^2 = 0.80$, $p < 0.001$), Nb ($R^2 = 0.76$, $p < 0.001$), and heavy rare earth elements such as ytterbium (Yb) ($R^2 = 0.89$, $p < 0.001$). U also positively correlates moderately well with Th ($R^2 = 0.59$, $p < 0.001$) and As ($R^2 = 0.56$, $p < 0.001$). Strong to moderate positive correlations also exist among all combinations of As, Co, Ni, and iron (Fe) (R^2 varying from 0.50 to 0.88 and all at $p < 0.001$) and all combinations of U, Th, As, Nb, Y, and Yb (R^2 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 Fig. 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 (1.14–1.69), while U is at moderate contamination levels in 8 samples (1.03–2.95), heavy contamination levels in 7 samples (3.17–4.93), and extreme contamination levels in 3 samples (5.26–5.73). 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 consideration in this study are U, Th, Pb, and As.

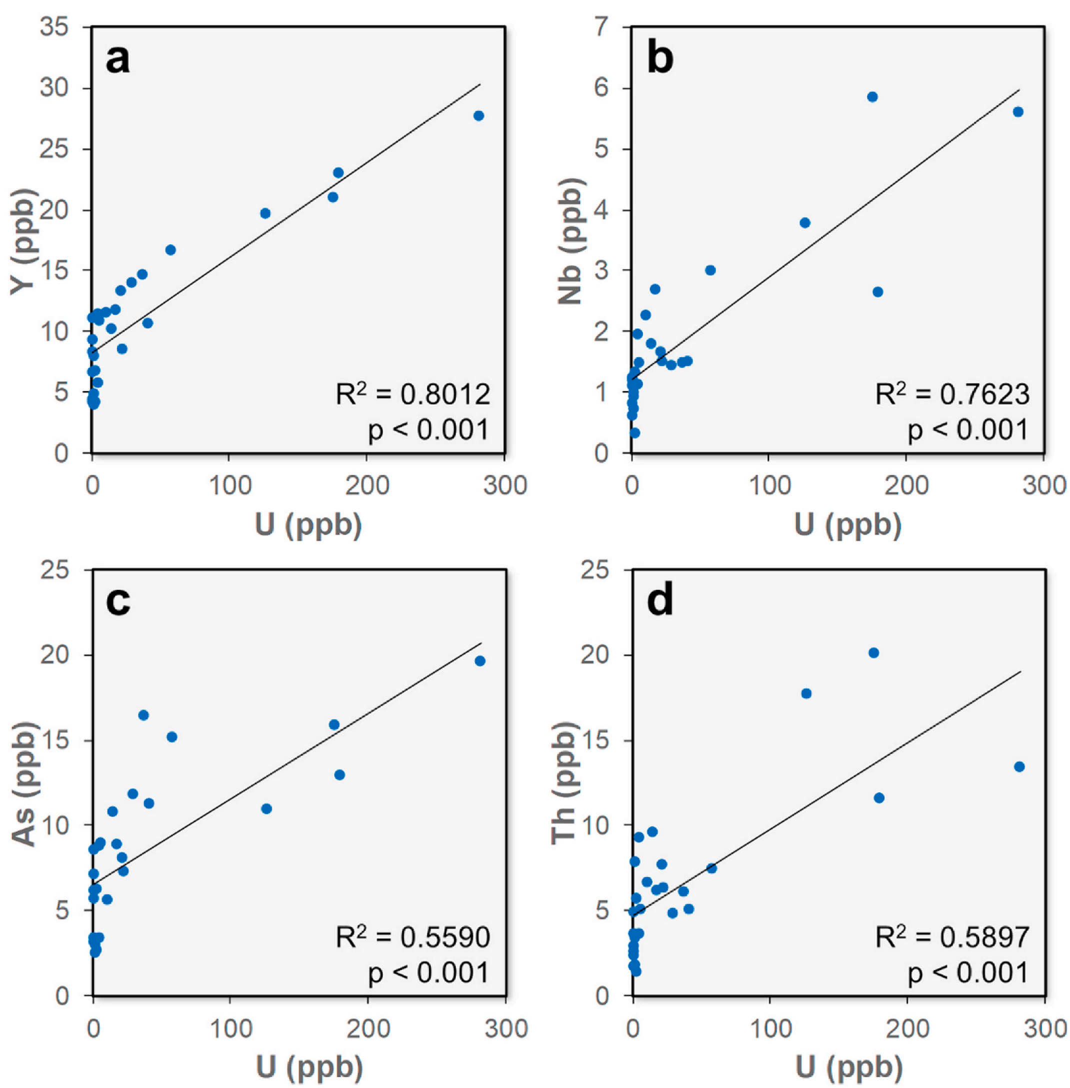

Fig. 2. Linear regressions of bulk geochemical data showing the correlations between elemental concentrations in tree bark ash among all samples (n = 31).

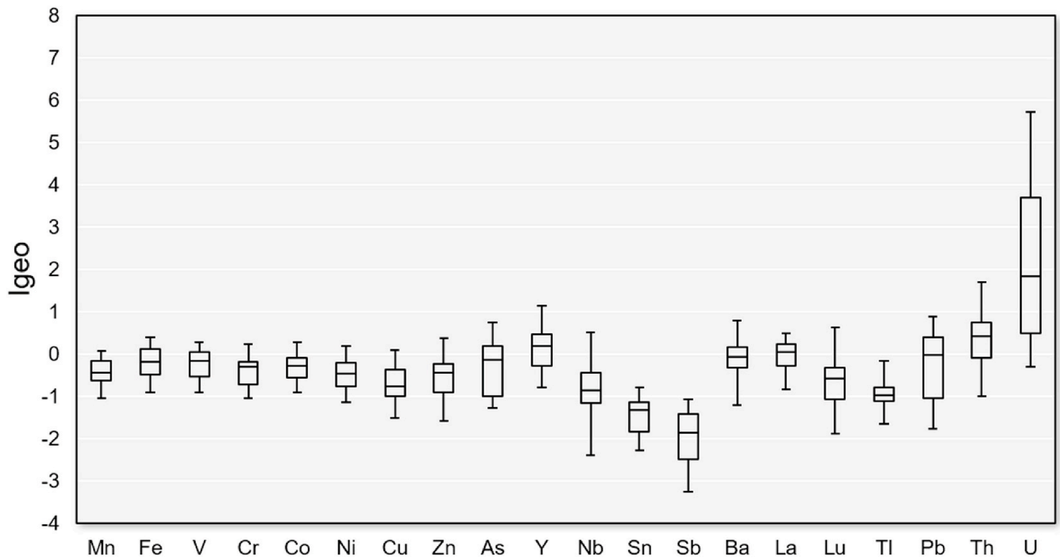

Fig. 3. The distribution of geoaccumulation (Igeo) indices of select elements in all non-background samples (n = 27). The boxes represent the 2nd and 3rd quartiles and the whiskers represent the 1st and 4th quartiles.

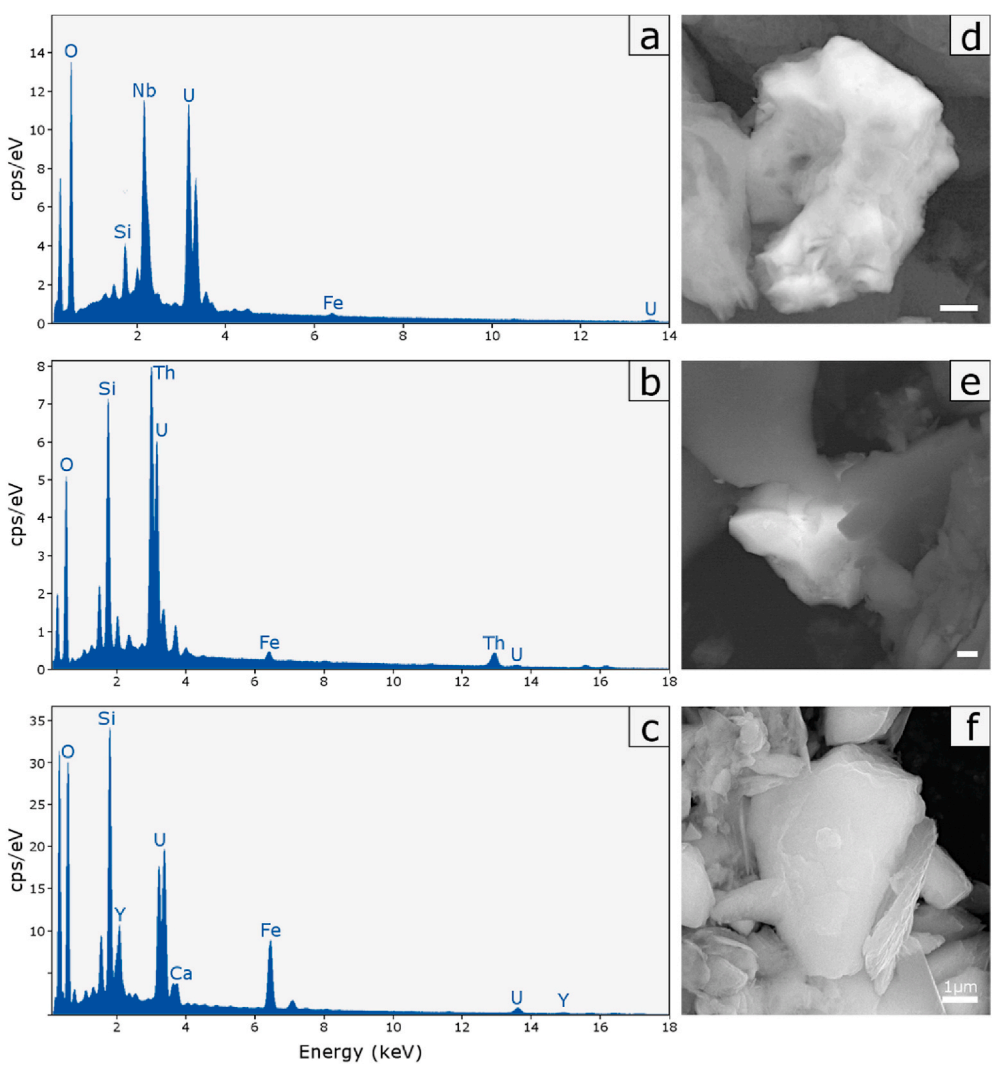

Fig. 4. EDS spectra (a–c) with paired micrographs of select U-rich particles (d–f). (**a**) Major peaks indicate U (3.164 and 13.612 keV), Nb (2.166 keV) and O (0.525 keV) are the major constituents. Si (1.739 keV), Fe (6.398 keV), and Al (1.486 keV) also present. (**b**) Prominent peaks indicate Th (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.

3.3. SEM

3.3.1. Uranium

In total, 6 U-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 U-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 Fig. 4.

3.3.2. Thorium

A total of 11 Th-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 Th-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 Fig. 5. Additionally, Th as a trace element in REE phosphates was ubiquitous throughout all sample types and locations.

3.4. 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 Fe-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.

3.5. Results of geospatial analysis

3.5.1. Concentration maps

In general, the highest U and As concentrations appear to concentrate along the mine access road and at the mill (Fig. 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.

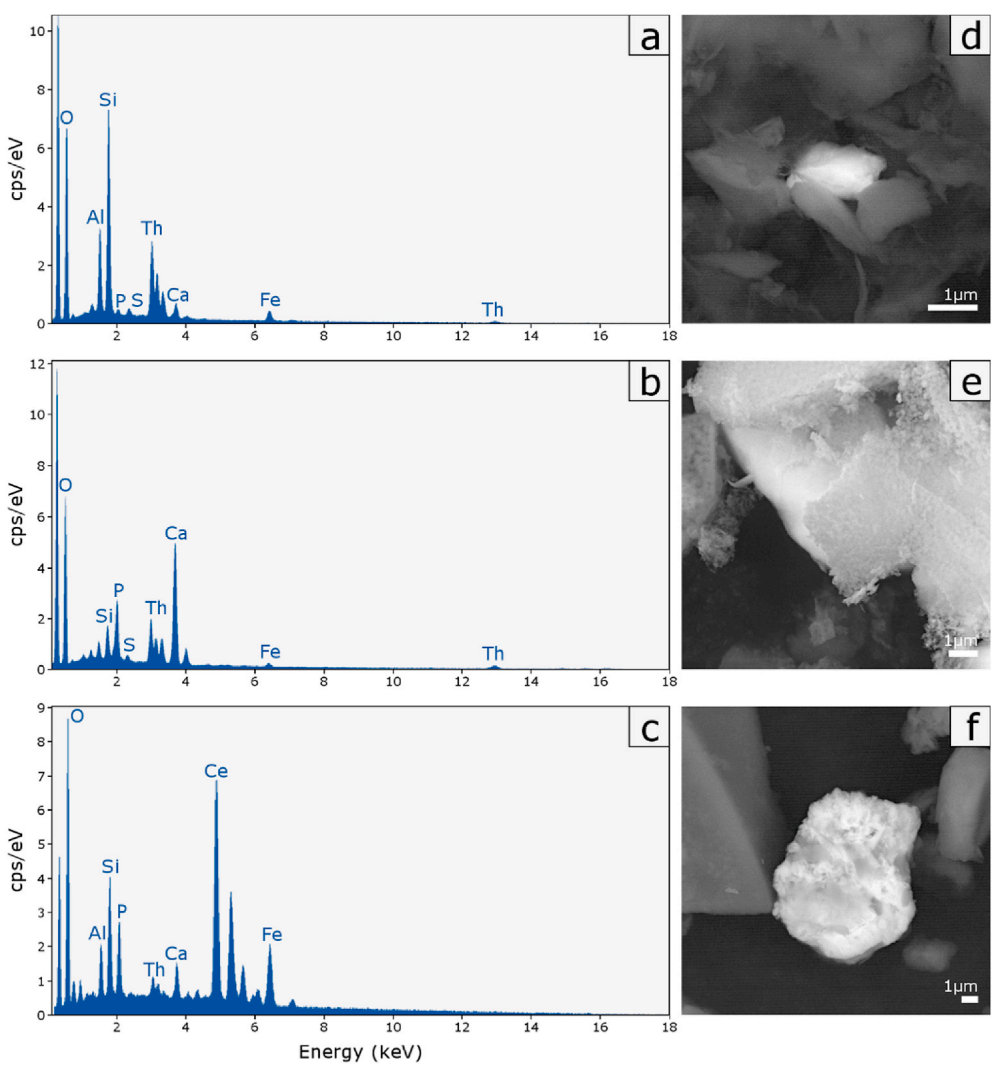

Fig. 5. EDS spectra (a–c) with paired micrographs of select Th-rich particles (d–f). (a) Major peaks indicate Th, Si, O, Al, Fe, Ca, P (2.103 keV), and S (2.307 keV) are present. (b) Peaks indicate Ca, P, O, Th, Si, S, and Fe are present. (c) Peaks indicate Ce, Th, O, Si, Al, P, Ca, and Fe are present. (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.

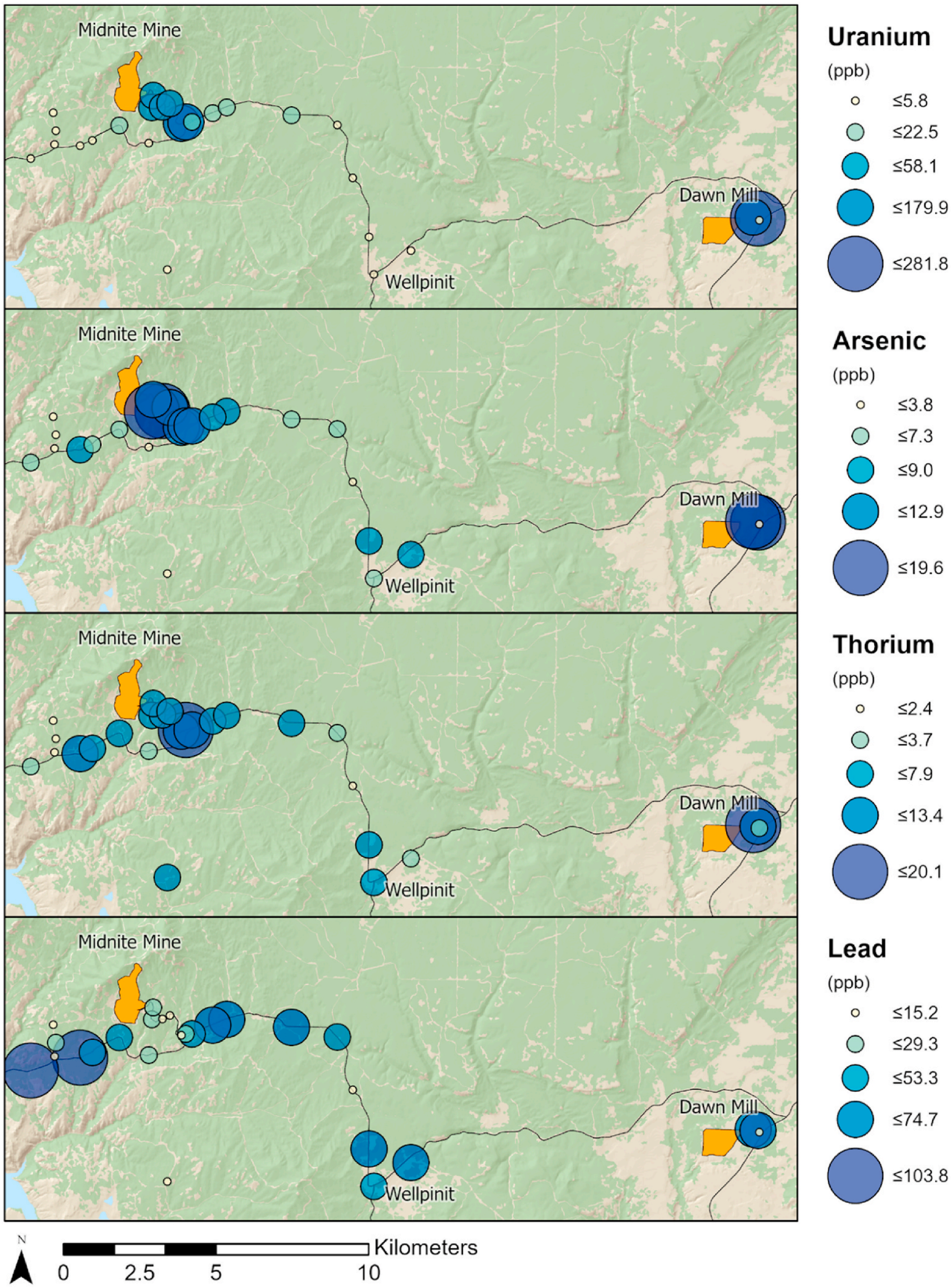

Fig. 6. Concentration maps of samples from U, As, Th, and Pb (concentrations of n = 27). Symbology classes based on Jenks natural breaks.

3.6. Igeo interpolation maps

The Igeo indices of the elements of U, Th, Pb, and As, are interpolated throughout the study area in Fig. 7. By these estimations, the level of uranium 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 as indicated by Igeo at <0 (Fig. 7). Levels of thorium 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 lead contamination are highest at four points along the main road to the east and west of the mine. Another area of relatively high estimated lead contamination occurs in Wellpinit. The mine access road is estimated to be uncontaminated by Pb, but there is the potential for low lead contamination levels near the mill. The level of arsenic 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

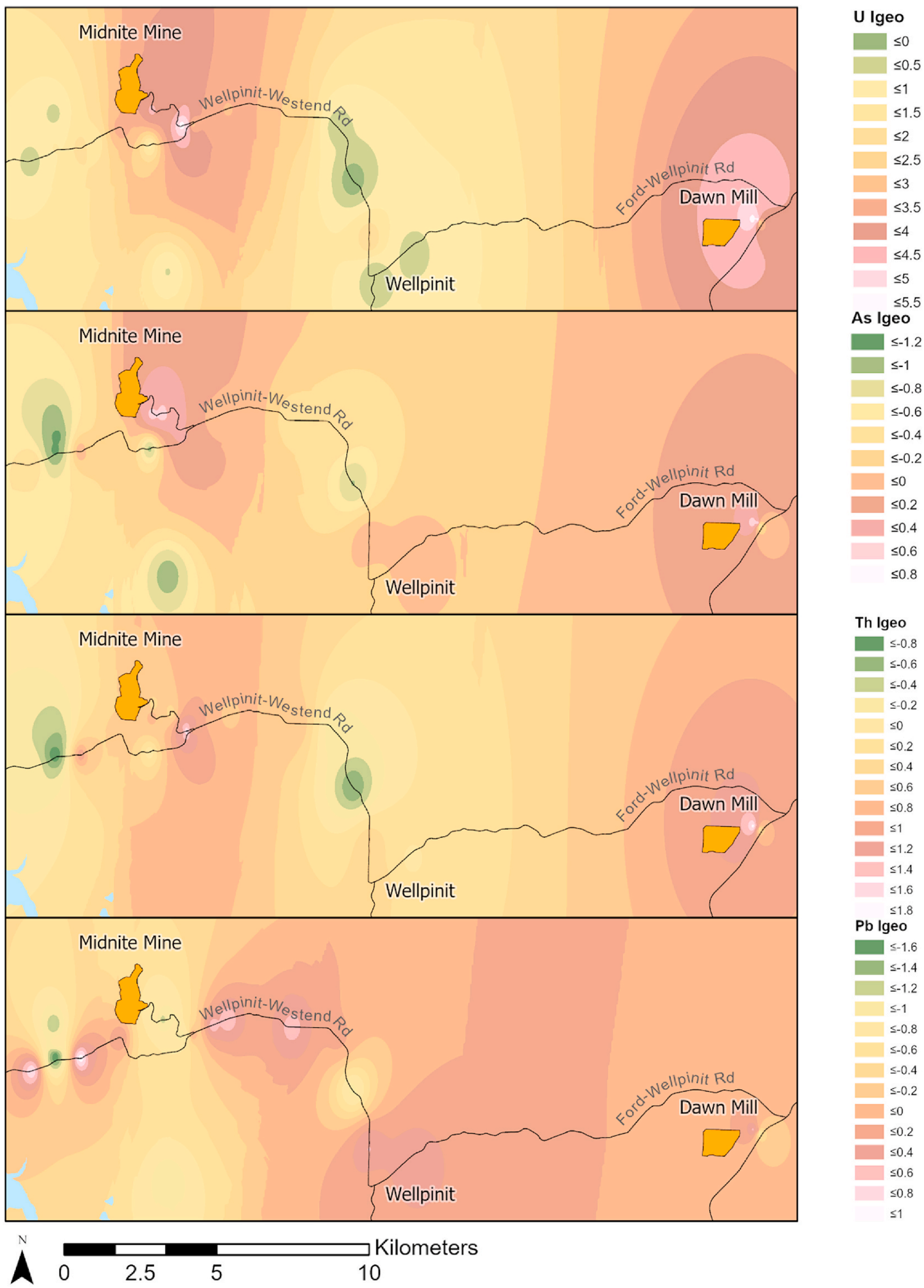

Fig. 7. Maps of select Igeo indices interpolated from Midnite Mine to Dawn Mill using inverse distance weighting (IDW) and all sample points (n = 31) of U, As, Th, and Pb.

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 (e.g., Valavanidis et al., 2008). In general, the smaller the diameter of airborne particulate matter, the greater the potential impact on human health as the smaller the particle, the higher the probability that particle has for penetrating the deep lung. The commonly used distinctions are PM_{10} (diameter less than 10 μm) and $PM_{2.5}$ (diameter less than 2.5 μm). PM_{10} is small enough to be inhaled, however $PM_{2.5}$ 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 PM_{10} (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 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

Although there is potential for U to be mobilized and taken up by trees, such as *Quercus velutina* (black oak), from water sources enriched in dissolved U (Edmands et al., 2011), U concentrations in bulk chemical analyses are interpreted to be from U particulate matter and not from dissolved U absorbed by tree bark. There is a reasonably strong correlation of niobium (Nb) and U in bulk chemical data and there is ample evidence of U-Nb-bearing particulate matter entrapped in the bark as indicated by SEM data. Literature exists on *Pinus ponderosa*, and related micronutrients (e.g., Walker et al., 2000; VanderSchaaf et al., 2004) but to date there has been no documentation 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 entirely associated with the particulate matter.

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 comprehensively 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 U 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; U.S. EPA 2005a; U.S. EPA 2005a, b; Church et al., 2007).

The U-rich particles observed in tree bark are considered small enough to be inhaled (aerodynamic diameter smaller than 10 μm) and in some cases can reach the deep lung (aerodynamic diameter smaller than 2.5 μm). Uranium-rich particles in the 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 all 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 and U share similar chemical properties and therefore can partition into the same minerals, 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 Th as a COPC in haul road soil (U.S. EPA, 2005a). The Th-rich particles observed in the tree bark and tree bark ash had diameters of 1.1 and 3.9 μm, indicating that there are $PM_{2.5}$ Th-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, As 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 As as an impurity (Majzlan et al., 2014). One of the most common U-bearing minerals at the Midnite Mine, coffinite, also commonly contains As (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 (U.S. EPA, 2005a; Church et al., 2007). Only one particle containing As was found using SEM, however it is possible that As 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 (<0.1 wt %; Kuisma-Kursula, 2000).

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 (U.S. EPA, 2005a; Church et al., 2007), 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 U, Th, and As. 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. Geospatial analysis of elemental abundances

Geospatial analysis shows that there is spatial variation associated with both absolute concentrations (Fig. 6) and Igeo indices interpolated from Midnite Mine to Dawn Mill using inverse distance weighting (IDW) for multivariate interpolation across this landscape (Fig. 7). These maps provide constraints for future extensive sampling for determination of concentration of metals as well as an interpolation to compare and test these distributions. Furthermore, these estimated distributions provide context for any future medical or environmental health surveys by providing a means to identify and prioritize areas related to various population activities (housing, work and subsistence activities, important transportation routes).

4.8. Disparities in health among native American populations

Uranium mining pollution on Indian reservations is common. During the uranium boom from the 1940s–1980s, mining and production of U heavily affected Native American lands, which tend to be rich in mineral deposits. The Navajo Nation alone had over 1000 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). An increase in inclusion of Native American communities in toxicological studies is greatly needed. Correspondingly, no detailed 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 (McDermott, 2019), future studies are needed and should focus specifically on the health of residents in relation to local uranium mining and milling activities. This investigation therefore provides much-needed environmental context for future investigations of disease where historic exposure to dust may be associated with negative health outcomes (Moore-Nall, 2015; McDermott, 2019).

5. Conclusions

The findings presented in this study demonstrate that airborne particulate matter pollution containing U, Th, Pb, and As has occurred on the Spokane Indian Reservation. Although challenging to detect, SEM investigations confirm that U- and Th-bearing particles on the surface of tree bark occur in size fractions that can be inhaled (the PM_{10} size fraction) and have the potential to reach the deep lung ($PM_{2.5}$). Bulk elemental analyses of sampled tree bark from *Pinus ponderosa* trees across the reservation reveal U and Pb concentrations up to 232 ppb and 104 ppb respectively, with Th and As at an order of magnitude lower concentration (maximum of 20 ppb). Geospatial modeling indicates that sources 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 is a 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.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Lonnie Flett is a member of the Spokane Tribe. She does not reside on the reservation. No compensation was offered or received for the preparation of this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2020.110619.

References

Aires, U.R.V., Santos, B.S.M., Coelho, C.D., da Silva, D.D., Calijuri, M.D., 2018. Changes in land use and land cover as a result of the failure of a mining tailings dam in Mariana, MG, Brazil. Land Use Pol. 70, 63–70.

Aliff, M.N., Reavie, E.D., Post, S.P., Zanko, L.M., 2020. Anthropocene geochemistry of metals in sediment cores from the Laurentian Great Lakes. PeerJ 8, e9034.

Ames, K.C., Matson, N.P., Suzuki, D.M., Sak, P.B., 1996. Inventory, Characterization, and Water Quality of Springs, Seeps, and Streams Near Midnite Mine. USGS Open-File Report, Stevens County, Washington, pp. 96–115.

ASTDR [Agency for Toxic Substances and Disease Registry], 2010. Public Health Assessment for Midnite Mine Site Wellpinit. Stevens County, Washington EPA Facility ID: WAD980978753.

Babayan, G., Sakoyan, A., Sahakyan, G., 2019. Drinking water quality and health risk analysis in the mining impact zone, Armenia. Sustainable Water Resources Management 5, 1877–1886.

Barbieri, M., 2016. The importance of enrichment factor (EF) and geoaccumulation index (Igeo) to evaluate the soil contamination. J. Geol. Geophys. 5, 1.

Barnes, D., Hamadah, M.A., Ottaway, J.M., 1976. The lead, copper and zinc content of tree rings and bark. Sci. Total Environ. 5, 63–67.

Barrington, J., Kerr, P.F., 1961. Uranium mineralization at the midnite mine. Spokane, Washington. Economic Geology 56, 241–258.

Basha, A.M., Yasovardhan, N., Satyanarayana, S.V., Reddy, G.V.S., Savitri, P.P., Prasad, K.V., Kumar, A.V., Tripathi, R.M., 2014. Seasonal variation of air quality and CAQI at tummalapalle uranium mining site and surrounding villages. Journal of Scientific Research and Reports 3, 700–710. https://doi.org/10.9734/JSRR/2014/5731.

Becker, J.S., Staton, B.S., McLeod, C.W., Dombovari, J., Becker, J.S., 2000. Determination of trace elements including platinum in tree bark by ICP mass spectrometry. Fresen. J. Anal. Chem. 368, 490–495.

Becraft, G.E., Weis, P.L., 1963. Geology and Mineral Deposits of the Turtle Lake Quadrangle, vol. 1131. USGS Bulletin, Washington. https://doi.org/10.3133/b1131.

Bellis, D., Ma, R., Bramall, N., McLeod, C.W., 2001a. Airborne emission of enriched uranium at Tokai-mura, Japan. Sci. Total Environ. 264, 283–286.

Bellis, D., Cox, A.J., Staton, I., McLeod, C.W., Satake, K., 2001b. Mapping airborne lead contamination near a metals smelter in Derbyshire, UK: spatial variation of Pb concentration and 'enrichment' factor for tree bark. J. Environ. Monit. 3, 512–514.

Bellis, D., Ma, R., Bramall, N., McLeod, C.W., Chapman, N., Satake, K., 2000. Airborne uranium contamination – as revealed through elemental and isotopic analysis of tree bark. Environ. Pollut. 114, 383–387.
Bian, Z.F., Dong, J.H., Lei, S.G., Leng, H.L., Mu, S.G., Wang, H., 2009. The impact of disposal and treatment of coal mining wastes on environment and farmland. Environ. Geol. 58, 625–634.
Bian, Z.F., Miao, X.X., Lei, S.G., Chen, S.E., Wang, W.F., Struthers, S., 2012. The challenges of reusing mining and mineral-processing wastes. Science 337, 702–703.
Birke, M., Rauch, U., Hofmann, F., 2018. Tree bark as a bioindicator of air pollution in the city of Stassfurt Saxony-Anhalt, Germany. J. Geochem. Explor. 167, 97–117.
Boltsov, V.E., Kaikova, T.M., 1964. Uranium and arsenic in the hydrothermal process. At. Energy. 18 (4), 473–479.
Boudette, E.L., Weis, P.L., 1956. Geology of the Midnite Mine Area, vol. 634. Spokane Indian Reservation, Stevens County, Washington. https://doi.org/10.3133/tei634. Trace Elements Investigations.
Brown, M.T., 2005. Landscape restoration following phosphate mining: 30 years of co-evolution of science industry and regulation. Ecol. Eng. 24, 309–329.
Campbell, I., Loofbourow, J.S., 1962. Geology of the Magnesite Belt of Stevens County Washington, vol. 1142. USGS Bulletin. https://doi.org/10.3133/b1142F.
Carvalho-Oliveira, R., Amato-Lourenco, L.F., Moreira, T.C.L., Rocha Silva, D.R., Vieira, B. D., Mauad, T., Mitiko, S., Nascimento Saldiva, P.H., 2017. Effectiveness of traffic-related elements in tree bark and pollen abortion rates for assessing air pollution exposure on respiratory mortality rates. Environ. Int. 99, 161–169.
Chrabaszcz, M., Mroz, L., 2017. Tree bark, a valuable source of information on air quality. Pol. J. Environ. Stud. 26 (2), 453–466.
Church, S.E., Kirschner, F.E., Choate, L.M., Lamothe, P.J., Budahn, J.R., Brown, Z.A., 2007. Determination of Premining Geochemical Background and Delinieation of Extent of Sediment Contamination in Blue Creek Downstream from Midnite Mine. USGS Scientific Investigations, Stevens County, Washington. Report 2007-5262.
Committee on Uranium Mining in Virginia, 2011 Dec 19. Uranium Mining in Virginia: Scientific, Technical, Environmental, Human Health and Safety, and Regulatory Aspects of Uranium Mining and Processing in Virginia. Committee on Uranium Mining in Virginia; Committee on Earth Resources, Washington (DC). National Academies Press (US), Washington (DC), 6, Potential Environmental Effects of Uranium Mining, Processing, and Reclamation. Available from: https://www.ncbi.nlm.nih.gov/books/NBK201052/.
Conte, E., Widom, E., Kuentz, D., 2017. Uranium isotopes in tree bark as a spatial tracer of environmental contamination near former uranium processing facilities in southwest Ohio. J. Environ. Radioact. 178–179, 265–278.
Coskun, M., 2006. Toxic metals in the Austrian Pine (Pinus nigra) bark in the Thrace region, Turkey. Environ. Monit. Assess. 121, 173–179.
Credo, J., Torkelson, J., Rock, T., Ingram, J., 2019. Quantification of elemental contaminants in unregulated water across Western Navajo Nation. Int. J. Environ. Res. Publ. Health 16, 2727.
Cymes, B.A., Krekeler, M.P.S., Nicholson, K.N., Grigsby, J.D., 2017. A transmission electron microscopy (TEM) study of silver nanoparticles associated with mine waste from New Caledonian nickel deposits: potential origins of silver toxicity in a World Heritage Site. Environmental Earth Sciences 76, 640.
Dambacher, J.M., Brewer, D.t., Dennis, D.M., Macintyre, M., Foale, S., 2007. Qualitative modelling of goldmine impacts on Lihir Island's socioeconomic system and reef edge community. Environ. Sci. Technol. 41, 555–562.
Dawn Mining Company, 2005. Final Completion Report for the Removal of Ore Debris along the Ford-Wellpinit Haul Road March 2005. Web. https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.scs&id=1001070&doc=Y&colid=30383&region=10&type=SC.
Dawn Mining Company, 2016. Dust Control and Air Quality Monitoring Plan for Remedial Action at Midnite Mine Superfund Site. Web, Stevens County, WA. https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.scs&id=1001070&doc=Y&colid=30383&region=10&type=SC.
DeLemos, J.L., Brugge, D., Cajero, M., Downs, M., Durant, J.L., George, C.M., Henio-Adeky, S., Nez, T., Manning, T., Rock, T., Seschillie, B., 2009. Development of risk maps to minimize uranium exposures in the Navajo Churchrock mining district. Environ. Health 8 (29). https://doi.org/10.1186/1476-069X-8-29.
Dogan, Y., Durkan, N., Baslar, S., 2007. Trace element pollution biomonitoring using the bark of Pinus brutia (Turkish red pin) in western Anatolian part of Turkey. Trace Elem. Electrolytes 17, 103–112.
Dogan, Y., Ugulu, I., Basalar, S., 2010. Turkish red pine as a biomonitor: a comparative study of the accumulation of trace elements in the needle and bark. Ekoloji 19, 88–96.
Duruibe, J.O., Ogwuegbu, M.O.C., Egwurugwu, J.N., 2007. Heavy metal pollution and human biotoxic effects. Int. J. Phys. Sci. 2 (5), 112–118.
Edmands, J.D., Brabander, D.j., Coleman, D.S., 2001. Uptake and mobility of uranium in black oaks: implications for biomonitoring depleted uranium-contaminated groundwater. Chemosphere 44, 789–795.
Entwistle, J.A., Hursthouse, A.S., Marinho Reis, P.A., Stweart, A.G., 2019. Metalliferous mine dust: human health impacts and the potential determinants of disease in mining communities. Current Pollution Reports 5, 67–83.
Fernandes, H.M., Franklin, M.R., 2001. Assessment of acid rock drainage pollutants release in the uranium mining site of Poços de Caldas – Brazil. J. Environ. Radioact. 54, 5–25.
Garvin, T., McGee, T.K., Smoyer-Tomic, K.E., Aubynn, E.A., 2009. Community-company relations in gold mining in Ghana. J. Environ. Manag. 90, 571–586.
Geise, G., LeGalley, E., Krekeler, M.P.S., 2011. Mineralogical and geochemical investigations of silicate-rich mine waste from a kyanite mine in central Virginia: implications for mine waste recycling. Environmental Earth Sciences 62, 185–196.
Gueguen, F., Stille, P., Geagea, M.L., Perrone, T., Chabaux, F., 2011. Atmospheric pollution in an urban environment by tree bark biomonitoring – part II: Sr, Nd and Pb isotopic tracing. Chemosphere 86, 641–647.
Hamp, R., Holl, W., 1974. Radial and axial distributions of lead concentration in bark and zylem of hardwoods. Arch. Environ. Contam. Toxicol. 2 (2), 143–151.
Hancock, G.R., Turley, E., 2006. Evaluation of proposed waste rock dump designs using the SIBERIA erosion model. Environ. Geol. 49, 765–779.
Harper, B.L., Flett, B., Harris, S., Abeyta, C., Kirschner, F., 2002. The Spokane Tribe's multipathway subsistence exposure scenario and screening level. RME. Risk Analysis 22, 513–526.
Hettiarachchi, E., Paul, S., Cadol, D., Frey, B., Rubasinhehe, G., 2019. Mineralogy controlled dissolution of uranium from airborne dust in simulated lung fluids (SLFs) and possible health implications. Environ. Sci. Technol. Lett. 6 (2), 62–67.
Hund, L., Bedrick, E.J., Miller, C., Huerta, G., Nez, T., Ramone, S., Shuey, C., Cajero, M., Lewis, J., 2015. A Bayesian framework for estimating disease risk due to exposure to uranium mine and mill waste on the Navajo Nation. J. Roy. Stat. Soc. 178 (4), 1069–1091.
Jeran, Z., Byrne, A.R., Batič, F., 1995. Transplanted epiphytic lichens as biomonitors of air-contamination by natural radionuclides around the Žirovski VRH uranium mine, Slovenia. Lichenologist 27, 375.
Jiang, X., Lu, W.X., Zhao, H.Q., Yang, Q.C., Chen, M., 2015. Quantitative evaluation of mining geo-environmental quality in Northeast China: comprehensive index method and support vector machine models. Environmental Earth Sciences 73, 7945–7955.
Kord, B., Kord, B., 2011. Heavy metal levels in pine (Pinus eldarica Medw.) tree barks as indicators of atmospheric pollution. BioResources 62, 927–935.
Korosi, J.B., Griffiths, K., Smol, J.P., Blais, J.M., 2018. Trends in historical mercury deposition inferred from lake sediment cores across a climate gradient in the Canadian High Arctic. Environ. Pollut. 241, 459–467.
Kousehlar, M., Widom, E., 2019. Sources of metals in atmospheric particulate matter in Tehran, Iran: tree bark biomonitoring. Appl. Geochem. 104, 71–82.
Kousehlar, M., Widom, E., 2020. Identifying the sources of air pollution in an urban-industrial setting by lichen biomonitoring – a multi-tracer approach. Appl. Geochem. 121, 104695.
Krekeler, M.P.S., Morton, J., Lepp, J., Tselepis, C.M., Samsonov, M., Kearns, L.E., 2008. Mineralogical and geochemical investigations of clay-rich mine tailings from a closed phosphate mine, Bartow, Florida, USA. Environ. Geol. 55 (1), 123–147.
Krekeler, M.P.S., Allen, C.S., Kearns, L.E., Maynard, J.B., 2010. An investigation of aspects of mine waste from a kyanite mine, Central Virginia, USA. Environmental Earth Sciences 61, 93–106.
Kuang, Y.W., Zhou, G.Y., Liu, S.Z., 2007. Heavy metals in bark of Pinus massoniana (Lamb.) as an indicator of atmospheric deposition near a smeltery at Qujiang, China. Environ. Sci. Pollut. Control Ser. 14, 270–275.
Kuisma-Kursula, P., 2000. Accuracy, precision and detection limits of SEM-WDS, SEM-EDS and PIXE in the multi-element analysis of medieval glass. X Ray Spectrom. 29, 111–118.
Laaksovirta, K., Olkonen, H., Alakuijala, P., 1976. Observation on the lead content of lichen and bark adjacent to a highway in southern Finland. Environ. Pollut. 11, 247–255.
Lewis, J., Hoover, J., MacKenzie, D., 2017. Mining and environmental health disparities in Native American communities. Current Environmental Health Reports 4, 130–141.
Ludwig, K.R., Nash, J.T., Naeser, C.W., 1981. U-Pb isotope systematics and are of uranium mineralization. Midnite Mine, Washington. Economic Geology 76, 89–110.
Majzlan, J., Drahota, P., Filippi, M., 2014. Paragenesis and crystal chemistry of arsenic minerals. Rev. Mineral. Geochem. 79, 17–184.
Marcy, A.D., Scheibner, B.J., Toews, K.L., Boldt, C.M.K., 1994. Hydrogeology and Hydrochemistry of the Midnite Mine. US Bureau of Mines, northeastern Washington. Report of Investigations 9484.
Marron, D.C., 1989. Trends in arsenic concentration and grain-size distribution of metal-contaminated overbank sediments along the Belle Fourche River downstream from Whitewood Creek, South Dakota. USGS Water-Resources Investigations Report 88–4420, 211–216.
Martin, M.H., Coughtrey, P.J., 1982. Biological Monitoring of Heavy Metal Pollution: Land and Air. Print. Applied Science Publishers, London and New York.
McDermott, T., 2019. Deb Abrahamson Blames Mining Pollution for Her Cancer, Keeps Fighting Toxic Legacy on Spokane Reservation. The Spokesman-Review, 09.29.20 and available online: https://www.spokesman.com/stories/2019/dec/01/deb-abrahamson-blames-mining-pollution-for-her-can/.
Meck, M., Love, D., Mapani, B., 2006. Zimbabwean mine dumps and their impacts on river water quality—a reconnaissance study. Phys. Chem. Earth 31, 797–803.
Moore-Nall, A., 2015. The legacy of uranium development on or near Indian reservations and health implications rekindling public awareness. Geosciences 5, 15–29.
Nash, J.T., Lehrman, N.J., 1975. Geology of the Midnite uranium mine, Stevens County, Washington – a preliminary report. USGS Open-File Report 75–402. https://doi.org/10.3133/ofr75402.
Nel, A., 2005. Air pollution-related illness: effects of particles. Atmosphere 308, 804–806.
Oliva, S. Rossini, Mingorance, M.D., 2006. Assessment of airborne heavy metal pollution by above- ground plant parts. Chemosphere 65, 177–182.
Ong, J., Erdei, E., Rubin, R.L., Miller, C., Ducheneaux, C., O'Leary, M., Pacheco, B., Mahler, M., Nez Henderson, P., Pollar, K.M., Lewis, J.L., 2014. Mercury, autoimmunity, and environmental factors on Cheyenne River Sioux tribal lands. Autoimmune Dis. 2014.
Padilla, K.L., Anderson, K.A., 2002. Trace element concentration in tree-rings biomonitoring centuries of environmental change. Chemosphere 49, 575–585.

Pal, S., Mandal, I., 2019. Impact of aggregate quarrying and crushing on socio-ecological components of Chottanagpur plateuar fringe area of India. Environmental Earth Sciences 78, 661.

Peckham, M.A., Gustin, M.S., Weisberg, P.J., 2019. Assessment of the suitability of tree rings as archives of global and regional atmospheric mercury pollution. Environ. Sci. Technol. Lett. 53, 3663–3671.

Pehoiu, G., Radulescu, C., Murarescu, O., Dulama, I.D., Bucurica, I.A., Teodorescu, S., Stirbescu, R.M., 2019. Health risk assessment associated with abandoned copper and uranium mine tailings. Bull. Environ. Contam. Toxicol. 102, 504–510. https://doi.org/10.1007/s00128-019-02570-9.

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. J. Air Waste Manag. Assoc. 56, 709–742.

Saarela, K.E., Harju, L., Rajander, J., Lill, J.O., Heselius, S.J., Lindroos, A., Mattsson, K., 2005. Elemental analyses of pine bark and wood in an environmental study. Sci. Total Environ. 343, 231–241.

Schelle, E., Rawlins, B.G., Lark, R.M., Webster, R., Staton, I., McLeod, C.W., 2007. Mapping aerial metal deposition in metropolitan areas from tree bark: a case study in Sheffield, England. Environ. Pollut. 155, 164–173.

Schellenbach, W.L., Krekeler, M.P.S., 2012. Mineralogical and geochemical investigations of pyrite-rich mine waste from a kyanite Mine in central Virginia with comments on recycling. Environmental Earth Sciences 66, 1295–1307.

Schultze, L.E., Nilsen, D.N., Isaacson, A.E., Lahoda, E.J., 1996. U.S. Bureau of Mines Final Report: Midnite Mine Water Treatment Studies. US Bureau of Mines. Report of Investigations 9605.

Schulz, H., Popp, P., Huhn, G., Stark, H.J., Schurmann, G., 1999. Biomonitoring of airborne inorganic and organic pollutants by means of pine tree barks, I. temporal and spatial variations. Sci. Total Environ. 232, 49–58.

Schaumloffel, J.C., Filby, R.H., Moore, B.C., 1998. Ponderosa pine tree rings as historical monitors of zinc and cadmium pollution. J. Environ. Qual. 27 (4), 851–859.

Seaton, A., MacNee, W., Donaldson, K., Godden, D., 1995. Particulate air pollution and acute health effects. Lancet 345, 176–178.

Setianto, A., Triandini, T., 2013. Comparison of kriging and inverse distance weighted (IDW) interpolation methods in lineament extraction and analysis. Journal of Applied Geology 5 (1). https://doi.org/10.22146/jag.7204.

Srafi, F., Rachdi, R., Rol, R., Gocke, M.I., Brahim, N., Slimshimi, N., 2019. Stream sediments geochemistry and the influence of flood phosphate mud in mining area, Metlaoui, Western south of Tunisia. Environmental Earth Sciences 78, 211.

Steiff, L.R., Stern, T.W., Sherwood, A.M., 1956. Coffinite, a uranous silicate with hydroxyl substitution: a new mineral. American Minerlogist 41, 675–688.

Stroud, W.P., Droullar, R.F., 1995. Midnite Mine Radiation Survey. US Bureau of Mines. Report of Investigation 9610.

Suzuki, Y., Kelly, S.D., Kemner, K.M., Banfield, J.F., 2002. Microbial populations stimulated for hexavalent uranium reduction in uranium mine sediment. Appl. Environ. Microbiol. 69 (3), 1337–1346.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K., Sutton, D.J., 2012. Heavy metal toxicity and the environment. In: Luch, A. (Ed.), Molecular, Clinical and Environmental Toxicology. Experientia Supplementum, vol. 101. Springer, Basel.

U.S. EPA [U.S. Environmental Protection Agency], 2005a. Midnite Mine Human Health Risk Assessment Report. Web. https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.scs&id=1001070&doc=Y&colid=30383&region=10&type=SC.

U.S. EPA [U.S. Environmental Protection Agency], 2005b. Midnite Mine Remedial Investigation Report. Web. https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.scs&id=1001070&doc=Y&colid=30383&region=10&type=SC.

U.S. EPA [U.S. Environmental Protection Agency], 2011. Spokane Tribe of Indians Airborne Radiological Surveys Spokane. Web, WA. https://cumulis.epa.gov/supercpad/SiteProfiles/index.cfm?fuseaction=second.scs&id=1001070&doc=Y&colid=30383&region=10&type=SC.

US Department of Commerce, 2017. United States Census Bureau. 2013-2017 American Community Survey 5-Year Estimates (Census.gov/tribal).

US Department of Commerce, 2019. United States Census Bureau. American Community Survey Briefs. Poverty: 2017 and 2018.

U.S, 2020. Department of the Interior. Bureau of Indian Affairs. https://www.bia.gov/about-us.

VanderSchaaf, C.L., Moore, J.A., Kingery, J.L., 2004. The effect of multi-nutrient fertilization on understory vegetation nutrient concentrations in inland Northwest conifer stands. For. Ecol. Manag. 190, 201–218.

Valavanidis, A., Fiotakis, K., Vlachogianni, T., 2008. Airborne particulate matter and human health: toxicological assessment and importance of size and composition of particles for oxidative damage and carcinogenic mechanisms. Journal of Environmental Science and Health Part C 26, 339–362.

Walker, R.F., Johnson, D.W., Geisinger, D.R., Ball, J.T., 2000. Growth, nutrition, and water relations of ponderosa pine in a field soil as influence by long term exposure to elevated atmospheric CO2. Forest Ecological Management 137, 1–11.

Ward, N.I., Brooks, R.R., Reeves, R.D., 1974. Effect of lead from motor-vehicle exhausts on trees along a major thoroughfare in Palmerston North, New Zealand. Environ. Pollut. 6, 149–158.

Winde, F., 2010. Uranium pollution of the Wonderfonteinspruit, 1997-2008 Part 1: uranium toxicity, regional background and mining-related sources of uranium pollution. SA Journal of Radiology 36, 239–256.

Winde, F., Sandham, L.A., 2004. Uranium pollution of South African streams – an overview of the situation in gold mining areas of the Witwatersrand. Geojournal 61, 131–149.

Zota, A.R., Willis, R., Jim, R., Norris, G.A., Shine, J.P., Duvall, R.M., Schaider, L.A., Spengler, J.D., 2009. Impact of mine waste on airborne respirable particulates in northeastern Oklahoma, United States. J. Air Waste Manag. Assoc. 59, 1347–1357.

Zyvhowski, K.E., Kodali, V., Harmon, M., Tyler, C.R., Sanchez, B., Suarez, Y.O., Herbet, G., Wheeler, A., Avasarala, S., Cerrato, J.M., Kunda, N.K., Muttil, P., Shuey, C., Brearley, A., Ali, A.-M., Lin, Y., Shoeb, M., Erdely, A., Campen, M.J., 2018. Respirable uranyl-vanadate-containing particulate matter derived from a legacy uranium mine site exhibits potentiated cardiopulmonary toxicity. Toxicol. Sci. 162 (1), 101–114.