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Terrestrial ecological risk analysis via dietary exposure at uranium mine sites in the Grand Canyon watershed (Arizona, USA)

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HIGHLIGHTS

- First terrestrial ecological risk analysis at uranium mines near Grand Canyon.
- Uranium was not the driver of ecological risk.
- Arsenic, cadmium, copper, and zinc are of concern for biota consuming invertebrates.
- No observed adverse effect levels were not exceeded for herbivores or carnivores.
- Relative risks were generally low for all biological receptor models.

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ABSTRACT

The U.S. Department of the Interior recently included uranium (U) on a list of mineral commodities that are considered critical to economic and national security. The uses of U for commercial and residential energy production, defense applications, medical device technologies, and energy generation for space vehicles and satellites are known, but the environmental impacts of uranium extraction are not always well quantified. We conducted a screening-level ecological risk analysis based on exposure to mining-related elements via diets and incidental soil ingestion for terrestrial biota to provide context to chemical characterization and exposures at breccia pipe U mines in northern Arizona. Relative risks, calculated as hazard quotients (HQs), were generally low for all biological receptor models. Our models screened for risk to omnivores and insectivores (HQs>1) but not herbivores and carnivores. Uranium was not the driver of ecological risk; arsenic, cadmium, copper, and zinc were of concern for biota consuming ground-dwelling invertebrates. Invertebrate species composition should be considered when applying these models to other mining locations or future sampling at the breccia pipe mine sites. Dietary concentration thresholds (DCTs) were also calculated to understand food concentrations that may lead to ecological risk. The DCTs indicated that critical concentrations were not approached in our model scenarios, as evident in the very low HQs for most models. The DCTs may be used by natural resource and land managers as well as mine operators to screen or monitor for potential risk to terrestrial receptors as mine sites are developed and remediated in the future.

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1. Introduction

The United States was a leading producer of uranium (U) from the mid-to late 20th century, with U primarily used for nuclear power production (OECD 2006). When U price declined in the late 1970s, the lower grade deposits of U ore present in the United States could not compete with higher-grade deposits in Australia and Canada. Uranium production in the United States consequently dropped significantly (USEIA 2019). However, energy independence and energy dominance of domestic mineral resources has been emphasized within the United States in recent years. In 2018, the U.S. Department of the Interior published a list of mineral commodities that are considered critical to economic and national security (Federal Register 2018). Uranium was included on the list of minerals being identified as critical for commercial and residential energy production, U.S. defense applications, medical

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device technologies, and energy generation for space vehicles and satellites (Fortier et al., 2018). Evaluating the potential impacts associated with alternative energy sources and their extraction may be useful to estimate life cycle costs (both financial and environmental) for various types of power generation. The environmental impacts of uranium extraction are not always well quantified and may vary among ecological settings.

The Grand Canyon in northern Arizona was established as one of the first national parks in 1919 and added as a World Heritage Site in 1979. The unique geologic formations that contributed to these designations also contain naturally occurring radioactive material. Some areas have unique features called breccia pipes; the breccia pipes contain some of the highest-grade U ore in the United States (>0.5% U_3O_8; Alpine 2010). As a result, U extraction from breccia pipe deposits has occurred for decades within the Grand Canyon watershed (Alpine 2010). The proximity of these mines to the Grand Canyon has increased the scrutiny of mining operations, and outcomes from ecological risk analysis are of interest to a broad group of stakeholders (Fig. 1). Breccia pipe mines located on Federal lands require natural resource managers to balance the protection of public and natural resources with sustainable production of fuel minerals. With uranium prices remaining relatively low for these past several years, industry stakeholders may use the analysis for planning environmental mitigation and/or remediation strategies. Despite the relatively small footprints of these breccia pipe uranium mining operations (generally <20 acres; Alpine 2010), the environmental consequences of U extraction have been a concern because the Grand Canyon and surrounding areas host cultural and economic resources that are important to tribes, ranchers, and recreational users. Tribal nations and environmental groups have expressed concern over potential mining impacts to cultural properties/resources and natural resources. Private citizens, such as landowners and recreational users, may have questions related to their property protection or activity safety. The mere concept of U mining can elicit perceptions of risk associated with radioactivity that may not be supported by empirical data. Such perceptions ignore the complex nature of these mining sites, including the presence of natural sources of radioactivity, chemical as well as radiological risks, contaminants of concern list that needs to extend beyond U, and the potential bioaccumulation of elements and radionuclides into the local food web (Hinck et al., 2017; Bern et al., 2019; Cleveland et al. 2019, 2021; Van Gosen et al., 2020).

Several ecological exposure pathways, including direct contact, inhalation, ingestion, and dietary uptake, have been identified at breccia pipe mines (Hinck et al., 2014). These mines often have small footprints (<20 acres), limited production life spans (5–7 years), restricted site access (i.e., fencing), and no on-site milling (only ore storage; Alpine 2010). These characteristics generally reduce ecological exposure potentials and thus risk scenarios (Hinck et al. 2014, 2017; Cleveland et al., 2021). However, other factors need to be considered. For example, the complex groundwater hydrology in this region contributes to uncertainty about how mining activities affect local aquifer systems and consequently the biota using seeps and springs as water sources (Jones et al., 2018; Tobin et al., 2018). Mining-related elements (e.g., U, thallium (Tl), lead (Pb), nickel (Ni), copper (Cu), arsenic (As)) can be transported off-site via aeolian deposition, resulting in exposure and risk to biota inhabiting or foraging in areas near mining operations (Hinck et al., 2017; Walton-Day et al., 2019). Chemical and radiological exposure of wildlife have been documented in various U mining stages within the region (Cleveland et al. 2019, 2021; Hinck et al., 2017; Minter et al., 2019). While radiation risks to rodents were determined to be minimal (Minter et al., 2019), chemical risks from mining-related elements have not been quantified.

Cleveland et al. (2019; 2021) were the first to report that active production of U ore resulted in elevated elemental concentrations in some local biota at breccia pipe mines in northern Arizona compared to non-mineralized reference or pre-mining sites, indicating chemical uptake and exposure from the local environment. Cleveland et al. (2021) went on to note that their data would be useful for site-specific ecological risk analysis that could contribute to future decisions regarding mineral extraction in the region. Our objective was to conduct a screening level ecological risk analysis based on exposure to mining-related elements via diets and incidental soil ingestion to provide context to the chemical characterization and exposures at breccia pipe mines reported by Cleveland et al. (2019; 2021). Although these breccia pipe deposits are known for their U ore, U was not expected to drive wildlife risk based on existing ecotoxicological literature. Most organisms that have been studied (e.g., birds, small mammals) have less sensitivity to the chemical toxicity of uranium (Alpine 2010); other co-occurring elements like As and Cu likely drive ecological risk based on receptor sensitivity and mode of toxicity. Moreover, most of the elemental constituents present in breccia pipe deposits generally do not

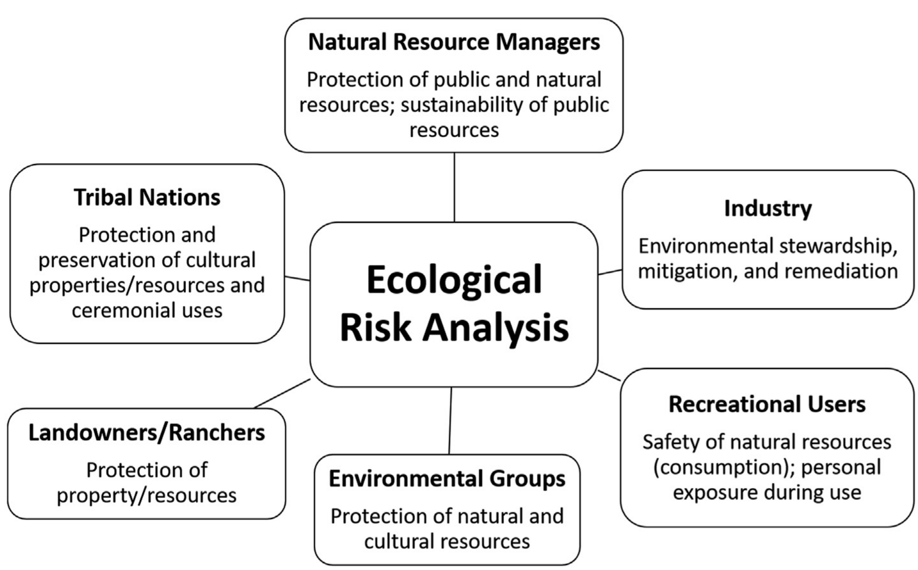

Fig. 1. Examples of stakeholders and their potential interests in ecological risk analysis results at mining sites.

bioaccumulate or biomagnify. Therefore, we hypothesized that U would not be the main risk driver at breccia pipe mines and that the greatest risk would be for biota at lower trophic levels (herbivores and omnivores).

2. Methods and materials

2.1. Study areas

Five sites were located in the Grand Canyon watershed in northern Arizona (Fig. 2) and represented the pre-production, active production, and post-production phases of the breccia pipe uranium mining lifecycle as well as a non-mineralize reference area. This arid area generally has sparse vegetation and is dominated by sagebrush and grasslands (Mann and Duniway 2020); areas around all study sites are open to grazing and managed by the U.S. Bureau of Land Management or U.S. Forest Service. The Pinenut Mine (36°30′18.04″ N, 112°43′52.42″ W; elevation 1659 m), located 52 km southwest of Fredonia, was an active production site with ore extraction occurring during sampling (in 2015). The Arizona 1 Mine (36°30′32.38″ N, 112°48′15.99″ W; elevation 1665 m), located 6.7 km west of Pinenut Mine, was in a post-production phase, during which all surface operations (buildings, ore pad, shaft overburden) were still intact and small amounts of ore remained on site. Production and shipment of ore from Arizona 1 Mine was discontinued in 2014, but the mine remains on standby for future ore extraction. All ore was shipped to a mill in Utah for processing; no processing was performed at Pinenut or Arizona 1 mines. Little Robinson Tank (36°30′2.97″ N, 112°50′35.7″ W; elevation 1634 m), located 3.3 km west/southwest of Arizona 1 Mine, was a non-mineralized area (i.e., no breccia pipe) considered to be a non-mining reference site. The Pinenut Mine, Arizona 1 Mine, and Little Robinson Tank study sites, located north of Grand Canyon National Park, are in a semi-desert shrub ecoregion. Canyon Mine, (35°52′57.50″ N, 112°05′44.52″ W; elevation 1982 m) located approximately 10 km south of Tusayan, AZ, was considered a pre-production site. Compared to the other sites, Canyon Mine is at a higher elevation and supports a ponderosa pine community with a sagebrush understory. Surface infrastructure at Canyon Mine was complete at the time of sampling (2013), but ore had not yet been brought to the surface. Additional information about the study sites is available in Cleveland et al. (2019; 2021), Hinck et al. (2017), and Mann and Duniway (2020).

2.2. Sample collection and elemental analysis

Soil and biological (vegetation, invertebrate, and deer mouse) sample collection, processing, and chemical analyses from the mine sites and reference site (2012–2015) have been described in detail elsewhere (Cleveland et al., 2021; Hinck et al., 2017; Naftz and Walton-Day 2016; Walton-Day et al., 2019). Biota were collected in the summer months of 2013 (Canyon Mine) and 2015 (Pinenut Mine, Arizona 1 Mine, Kanab North Mine, and Little Robinson Tank); soil samples were collected in June 2014 (Arizona 1 Mine), October 2014 (Pinenut Mine), November 2015 (Little Robinson Tank), and Kanab North (June 2016). Soil samples were collected using incremental sampling methodologies, which established decision units (DUs) around the perimeter of each mine site (Naftz and Walton-Day 2016; Walton-Day et al., 2019). The number of DUs varied from 15 to 18 among mine sites and 9 for the reference site, and DU areas ranged from 4880 to 44,800 m^2. The number of individual incremental samples collected and composited in triplicate from the DUs ranged from 30 to 75. Surface soil (top 5 cm; field-sieved to <2 mm) was collected in triplicate for each DU (Naftz and Walton-Day 2016; Walton-Day et al., 2019). Above-ground plant tissue (e.g., blades, stems/stalks, leaves) was collected using a random sampling approach within the soil DU, identified to species, and composited by functional group (i.e., forb, grass, and shrub) regardless of species (Mann and Duniway 2020). Ground-dwelling terrestrial insects and spiders were collected using unbaited pitfall traps, which were placed around Western harvester ant (*Pogonomyrmex occidentalis*) mounds to obtain sufficient mass for chemical analyses. Deer mice (*Peromyscus maniculatus*) were collected using live traps (Sherman Traps, Tallahassee, Florida).

In the laboratory, biological samples were lyophilized,

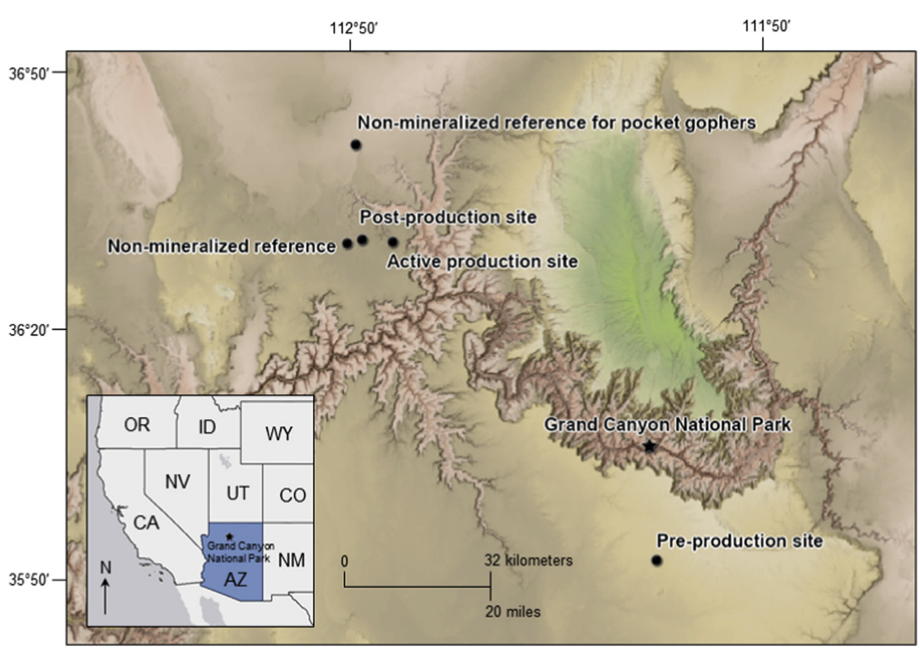

Fig. 2. Location of the study sites in relation to Grand Canyon National Park (GCNP) in northern Arizona, USA. The non-mineralized reference, active, and post-production sites were located north of GCNP; and the pre-production site was located near the south rim of GCNP. (Note: intended for color production on the web and black-and-white in print).

homogenized, and acid-digested for total recoverable elemental analyses by inductively coupled plasma-mass spectrometry. All biological samples were processed as collected in the field (i.e., not washed) to represent dietary, dermal, grooming, and inhalation pathways to animals. Invertebrate composite samples were primarily ants, beetles, and spiders (Hinck et al., 2017; Cleveland et al., 2019). Deer mouse whole body samples consisted of everything but livers, kidneys, and lungs, which were used for other analyses; animals were not depurated. Soil samples (<2-mm) were further ground in the laboratory to <105-μm, homogenized, composited and analyzed for total elements, as described in Naftz and Walton-Day (2016) and Walton-Day et al. (2019). Elements considered in this study were As, cadmium (Cd), Cu, Pb, molybdenum (Mo), Ni, Tl, uranium (U), and zinc (Zn); concentrations were reported on a dry weight basis (mg kg-1 dw) and are summarized in Table 1. Soil and tissue concentrations of other elements at breccia pipe U mines, as well as concentrations from other U mine and mill sites are available to compare to those at breccia pipe U mines (Supplemental Table 1; Cleveland et al., 2019, Cleveland et al., 2021, Hinck et al., 2017, Walton-Day et al., 2019).

2.3. Screening level risk analysis

This study can be considered the risk characterization phase within the screening level ecological risk assessment framework (Norton et al., 1992). Problem formulation (Hinck et al., 2014) and exposure and effects assessments (Cleveland et al., 2021) have been described elsewhere. Risk to wildlife was evaluated with models based on adult dietary exposure. Model species considered in the risk analysis represented multiple trophic levels, including herbivores of varying sizes (elk, *Cervus elaphus canadensis*; mule deer, *Odocoileus hemionus*; black-tailed jackrabbit, *Lepus californicus*; 100% vegetation diet), an omnivore (deer mouse; 50% vegetation:50% ground-dwelling invertebrate diet), insectivores (Western Bluebird, *Sialia mexicana*; Merriam's shrew, *Sorex merriami*; 100% ground-dwelling invertebrate diet), and a carnivore (coyote, *Canis latrans*; 100% mammal diet). These species are known to occur in the study area and represent components of the local food web. Risks to herbivores and omnivores were assessed on a vegetation-type basis (grasses, shrubs, forbs) based on data available from Cleveland et al. (2021) and Hinck et al. (2017).

Dietary elemental exposure doses (E; mg kg-1 day-1) were calculated according to the following equation:

$$E = \left(FIR{*}C_{food}\right) + \left(FIR{*}C_{food}{*}P_{soil}\right)$$

where FIR represents the food ingestion rate (kg kg-1 day-1; dry weight), C represents elemental concentration (mg kg-1; dry weight), and P_{soil} represents incidental soil ingestion (proportion of FIR). We assumed 100% bioavailability of elements and 100% site use to be conservative. Biota samples were not washed prior to analysis; tissue results may include some metals from adhering soil and dust. While incidental soil ingestion is intended to capture this portion of direct exposure to contaminants in soil, it also includes soil ingested while grooming or burrowing, in addition to ingestion of food. The degree to which using unwashed tissue samples will increase overall exposure estimates is uncertain, but previous studies have shown washing can decrease surficial concentrations (e.g., Bennet et al., 2007; Hawkins and Ragnarsdóttir 2009; Hinck et al., 2017; Pushon et al., 2004). The digestion method used in the chemical analysis of the biota is considered a total extraction and may result in higher concentrations than would be bioavailable to biota under natural conditions. With these considerations, the resulting estimates of exposure are considered conservative and suitable for screening for potential risks. Parameters for FIR (based on the allometric equation [x(kg body mass)^y]/kg body mass) can be found in Supplemental Table 2. The minimum, mean, and maximum dry-weight concentration in food items and soils from each site were used to provide bounding risk ranges for each element.

Dietary-based toxicity reference values (TRVs) based on no observed adverse effect levels (NOAELs) from the scientific

Table 1
Range of elemental concentrations (mg kg-1 dry weight) in biotic and abiotic samples (Hinck et al., 2017; Walton-Day and Naftz, 2019; Cleveland et al., 2021).

Site	n	Arsenic	Cadmium	Copper	Molybdenum	Nickel	Lead	Thallium	Uranium	Zinc
Reference										
Soil	27	11.9–56	0.1–0.3	9.7–33.4	0.62–2.38	6.8–19.8	10.6–20.5	0.3–0.5	1.2–2.1	28–61
Invertebrates	1	3.47	0.32	22.1	0.59	2.06	1.53	<0.05	0.1	193
Forbs	24	0.25–1.03	<0.1–0.13	5.48–10.4	0.36–1.33	0.30–1.30	0.14–0.53	<0.03	<0.03	10.8–27.6
Grasses	24	0.12–0.81	<0.1	3.01–4.78	0.64–1.21	0.43–0.78	0.05–0.34	<0.01	<0.03	14.4–23.3
Shrubs	24	0.14–0.56	<0.1–0.13	6.36–12.8	0.31–0.66	0.78–1.89	0.17–0.57	<0.02	<0.02–0.03	15.3–25.9
Deer mouse	10	0.22–1.13	<0.06–0.10	7.08–10.9	0.47–1.13	1.28–2.12	0.20–1.35	<0.01	<0.05–0.07	122–476
Pre-production										
Soil	54	7.1–18	0.3–0.8	14.5–89.4	0.75–2.38	12.5–24.8	14.1–25	0.4–0.8	1.4–6.2	40–76
Invertebrates	12	1.15–4.01	0.14–7.85	13.7–96.2	0.45–1.71	1.68–4.87	0.77–2.61	0.03–0.10	0.04–0.16	85–543
Forbs	3	2.27–6.47	0.29–0.40	7.17–11.3	0.74–1.44	4.71–10	2.62–5.88	0.12–0.25	0.18–0.35	25.9–41.3
Grasses	24	0.09–2.3	0.04–0.15	3.37–7.27	0.82–2.89	0.84–5.47	0.44–3.18	0.01–0.12	0.02–0.18	14–41.4
Shrubs	24	0.62–1.43	0.022–0.60	4.14–13.7	0.29–2.11	0.98–4.25	0.25–2.73	<0.01–0.11	0.008–0.14	10.6–52.8
Deer mouse	10	<1.2	0.02–0.26	7.97–15.6	0.46–0.87	<0.36–1.26	0.16–1.19	<0.05–0.02	<0.01–0.08	84.9–241
Active Production										
Soil	45	6.3–33.6	0.1–0.3	19.3–55	0.92–4.42	12–34.2	11.1–37.7	0.2–0.5	2–15.2	34–136
Invertebrates	5	4.26–7.94	0.10–0.25	22.1–57.8	0.86–3.30	0.93–4.02	0.40–1.88	<0.05	1.62–13.1	100–192
Forbs	33	0.40–4.58	<0.04–0.18	7.01–38.6	1.30–8.19	1.02–3.22	0.30–6.33	<0.02–0.03	0.18–12.3	12.9–39.5
Grasses	33	0.35–3.52	<0.05–0.61	3.5–33.5	1.02–11	0.65–3.34	0.28–1.67	<0.02–0.05	0.28–19.3	8.2–28.4
Shrubs	33	0.34–5.93	<0.1	11.2–65.9	0.64–3.44	1.09–5.29	0.30–2.32	<0.02–0.05	0.75–34.9	13.3–25.6
Deer mouse	13	<0.45–0.99	<0.02–0.11	6.58–17.1	<0.05–0.98	1.39–2.51	0.19–2.60	<0.03	<0.03–2.34	79.9–296
Post-production										
Soil	45	3.7–15.8	0.1–0.3	10.8–39	0.5–2.69	12.1–20.4	11.1–19.1	0.3–0.5	1.5–22.4	37–64
Invertebrates	7	0.45–12.6	<0.05–0.40	10.7–36.1	0.04–2.23	0.53–5.97	0.10–3.24	<0.05	0.12–7.52	84.6–191
Forbs	30	0.27–2.16	<0.1–0.19	9.33–13.9	1.14–10.7	0.94–2.61	0.31–1.89	<0.01–0.05	0.10–5.82	13.0–29.8
Grasses	30	0.23–1.72	<0.03–0.19	3.06–6.89	0.90–10.8	0.64–1.98	0.16–1.99	<0.02–0.06	0.13–8.38	8.54–23.4
Shrubs	30	0.29–4.36	<0.1–0.19	10.0–25.4	0.80–3.29	1.35–5.00	0.46–4.33	<0.02–0.09	0.31–19.0	15.6–33.7
Deer mouse	7	<1.08–1.88	<0.06–0.08	8.11–13.5	0.61–1.75	1.75–2.80	0.12–4.16	<0.01–0.18	<0.02–3.21	90.7–156

literature were used for most elements (Table 2). Consensus-based TRVs developed for the USEPA ecological soil screening levels were used for As, Cd, Cu, Pb, Ni, and Zn (USEPA 2005a; 2005b; 2005c; 2005d; 2007a; 2007b; 2007c). These TRVs were derived through a multi-stakeholder workgroup and were designed to be protective of ecological receptors that commonly come into contact with soil or that ingest biota that live in or on soil. Literature-based TRVs were used for Mo, Tl (mammal only), and U (Downs et al., 1960; Haseltine and Sileo 1983; Murray et al., 2014; Stafford et al., 2016). Hazard quotients (HQs) were calculated according to the following equation:

$$HQ = \frac{E}{TRV}$$

Given the conservative exposure assumptions and the use of NOAEL TRVs, an HQ < 1 indicates the absence of risk. Dietary concentration thresholds (DCTs) that would result in an HQ = 1 were then calculated according to the following equation:

$$\text{If } E = TRV, \text{ then } HQ = 1$$
$$\text{therefore}$$
$$\frac{TRV}{FIR} = C_{food}$$

The maximum soil concentration from each mine site was used for P_{soil} in these calculations (Table 1). Food concentrations represent food plus incidental soil ingestion because samples were not washed prior to chemical analysis. All DCTs are reported as dry weight (dw).

3. Results

3.1. Dietary exposure dose models

Hazard quotients were generally low for all model types; models indicated no risk at the non-mineralized reference site except for Cu in the Western Bluebird model (Table 3; Supplemental Table 3). Hazard quotients were <1 for all elemental constituents and sites in the carnivore model (coyote; HQs<0.19; Table 3; Supplemental Table 3). Herbivore models of jackrabbit (HQs<0.54), mule deer (HQs<0.20), and elk (HQs<0.05) had similar patterns. These results indicate minimal to no risk for carnivores and herbivores at all breccia pipe mine sites. Hazard quotients were >1 for Cu in the omnivore (deer mouse) model at the pre-production and active production sites for all vegetation functional groups, based on the maximum concentration in dietary items and incidental soil ingestion. Hazard quotients were also >1 for As in the omnivore (deer mouse) model at the active production (shrub only) and post-production sites (all 3 vegetation functional groups) based on maximum concentrations.

The NOAEL exceedances were more prevalent for insectivore models compared to the other models (Table 3; Supplemental Table 3). Hazard quotients for Cu were generally >1 at all breccia pipe mine sites in the Western Bluebird model; this varied among minimum, mean, and maximum concentrations in dietary items and incidental soil ingestion (Supplemental Table 3). Cadmium and Zn at the pre-production site and As at the post-production site also exceeded the NOAEL in the Western Bluebird model. Hazard quotients were >1 for Cu at all breccia pipe mine sites in the shrew model, primarily based on mean and maximum concentrations in dietary items and incidental soil ingestion. Cadmium and Zn at the pre-production site and As at the active and post-production sites also exceeded the NOAEL in the Merriam's shrew model.

3.2. Dietary concentration thresholds (DCTs)

Most concentrations did not exceed DCTs and are considered unlikely to pose adverse effects to the ecological receptors. The DCTs were only exceeded for As, Cd, Cu, and Zn (Table 4; Fig. 3); more analysis is needed to determine the potential for and magnitude of adverse effects of DCT exceedances. The DCTs for As were 5.7 mg kg-1 for shrews, 7.4 mg kg-1 for mice, and 10 mg kg-1 for birds. Four of 25 ground-dwelling invertebrate samples from the active (n = 2) and post-production (n = 2) sites exceeded 5.7 mg kg-1 As (range 5.74–12.6 mg kg-1); none of the 312 vegetation samples exceeded 7.4 mg kg-1 As. The DCTs for Cd were 4.2 mg kg-1 for shrews, 5.5 mg kg-1 for mice, and 6.7 mg kg-1 for birds. Two of 25 ground-dwelling invertebrate samples from the pre-production site exceeded 4.2 mg kg-1 Cd (range 5.45–7.85 mg kg-1). The DCTs for Cu were 18 mg kg-1 for birds, 30 mg kg-1 for shrews, and 40 mg kg-1 for mice. Twenty-three of 25 ground-dwelling invertebrate samples from all site types exceeded 18 mg kg-1 Cu (range 19.4–96.2 mg kg-1). Ten of 312 vegetation samples from the active production site exceeded 40 mg kg-1 Cu (range 40.6–65.9 mg kg-1). The DCTs for Zn were 300 mg kg-1 for bird and 410 mg kg-1 for shrews. Two of 25 ground-dwelling invertebrate samples from the pre-production site exceeded 300 mg kg-1 Zn (range 413–542 mg kg-1).

4. Discussion

Uptake of and exposure to elemental constituents associated with breccia pipe mines has been documented in local biota (e.g., As, Cu, Mo, U; Cleveland et al., 2021; Hinck et al., 2017). Ecological

Table 2
Toxicity Reference Values (TRV) for avian and mammal receptors.

Element	Avian		Mammal	
	TRV (mg kg-1 day-1)	Source	TRV (mg kg-1 day-1)	Source
Arsenic	2.24[a]	USEPA (2005b)	1.04[c]	USEPA (2005b)
Cadmium	1.47[b]	USEPA (2005c)	0.77[c]	USEPA (2005c)
Copper	4.05[c]	USEPA (2007a)	5.6[c]	USEPA (2007a)
Lead	1.63[c]	USEPA (2005d)	4.7[c]	USEPA (2005d)
Molybdenum	13.4	Stafford et al. (2016)	40	Murray et al. (2014)
Nickel	6.71[b]	USEPA (2007b)	1.7[c]	USEPA (2007b)
Thallium	–[d]		0.62	Downs et al. (1960)
Uranium	16	Haseltine and Sileo (1983)	28.8	Maynard and Hodge (1949)
Zinc	66.1[b]	USEPA (2007c)	75.4[b]	USEPA (2007c)

[a] Lowest no-observed-adverse-effect level (NOAEL) for reproduction, growth, and survival.
[b] Geometric mean NOAEL for reproduction and growth.
[c] Highest bound NOAEL for reproduction, growth, and survival.
[d] –, no TRVs found in literature.

Table 3
Exposure dose models that resulted in a hazard quotient (HQ) > 1.0 based on minimum (a), mean (m), and maximum (z) concentration in dietary items and incidental soil ingestion. The – notation indicates HQ < 1.0.

Model Type (Diet)	Reference	Pre-production	Active Production	Post-production
Herbivore (100% vegetation)				
Elk - Forb	–	–	–	–
Elk - Grass	–	–	–	–
Elk -Shrub	–	–	–	–
Deer - Forb	–	–	–	–
Deer - Grass	–	–	–	–
Deer - Shrub	–	–	–	–
Rabbit - Forb	–	–	–	–
Rabbit - Grass	–	–	–	–
Rabbit - Shrub	–	–	–	–
Omnivore (50% vegetation, 50% ground-dwelling invertebrates)				
Mouse - Forb	–	Cu (z)	Cu (z)	As (z)
Mouse - Grass	–	Cu (z)	Cu (z)	As (z)
Mouse - Shrub	–	Cu (z)	As (z), Cu (z)	As (z)
Insectivore (100% ground-dwelling invertebrates)				
Bluebird	Cu (amz)	Cd (z), Cu (mz), Zn (z)	Cu (amz)	As (z), Cu (mz)
Shrew	–	Cd (z), Cu (mz), Zn (z)	As (mz), Cu (mz)	As (z), Cu (z)
Carnivore (100% mammal)				
Coyote	–	–	–	–

Table 4
Dietary concentrations (mg kg-1 dry weight) that result in a hazard quotient (HQ) > 1, and the ranges of HQ for reference and mine samples from this study.

Model and Diet	Arsenic	Cadmium	Copper	Lead	Molybdenum	Nickel	Thallium	Uranium	Zinc
Herbivore – Rabbit									
Diet	23	17	125	105	892	38	14	642	1681
HQ range	0.01–0.30	<0.01–0.04	0.03–0.54	<0.01–0.07	<0.01–0.02	0.01–0.28	<0.01–0.02	>0.01–0.06	0.01–0.03
Herbivore – Deer									
Diet	62	46	333	280	2379	101	37	1713	4484
HQ range	<0.01–0.11	<0.01–0.01	0.01–0.20	<0.01–0.07	<0.01	<0.01–0.10	<0.01–0.01	<0.01–0.02	<0.01–0.01
Herbivore – Elk									
Diet	135	100	726	609	5185	220	80	3733	9773
HQ range	<0.01–0.05	<0.01–0.01	<0.01–0.01	<0.01–0.01	<0.01	<0.01–0.01	<0.01	<0.01–0.01	<0.01–0.01
Omnivore - Deer Mouse									
Diet	7.4	5.5	40	33	284	12	4.4	204	535
HQ range[a]	0.06–1.19	<0.01–0.78	0.18–1.59	0.01–0.15	<0.01–0.03	0.10–0.66	<0.01–0.04	<0.01–0.12	0.09–0.56
Insectivore – Bluebird									
Diet	10	6.7	18	7.4	61	34	nd	73	300
HQ range	0.05–1.27	<0.01–1.18	0.59–5.34	0.04–0.49	<0.01–0.06	0.02–0.19	nd	<0.01–0.18	0.28–1.82
Insectivore – Shrew									
Diet	5.7	4.2	30	26	218	9.3	3.4	157	410
HQ range	0.09–2.28	0.01–1.88	0.36–3.22	0.01–0.14	<0.01–0.02	0.08–0.69	0.01–0.03	<0.01–0.09	0.21–1.33
Carnivore – Coyote									
Diet	35	26	190	159	1354	58	21	975	2553
HQ range	0.01–0.08	<0.01–0.01	0.04–0.10	<0.01–0.03	<0.01	0.01–0.06	<0.01–0.01	<0.01	0.03–0.19

nd, not determined because lack of toxicity reference value.
Calculations to determine HQ > 1.
Dietary elemental exposure dose = (Food Ingestion Rate * Concentration $_{food}$) + (Food Ingestion Rate * Concentration $_{soil}$ * Incidental soil ingestion).
If dietary elemental exposure dose = Toxicity Reference Value, then HQ = 1.
[a] HQs based on diet of 50% vegetation and 50% insectivore.

risk analyses at breccia pipes in northern Arizona have been absent or very limited, primarily because of the lack of empirical data available for these types of mines (Liz Schuppert/US Forest Service and Rody Cox/US Bureau of Land Management, written communications August 11, 2018). Species-specific soil screening thresholds for elemental constituents were developed for the Arizona chisel-toothed kangaroo rat (*Dipodomys microps leucotis*), a species of conservation concern that is endemic to the Grand Canyon region (Hinck et al., 2013). Hinck et al. (2013) concluded that elemental constituents in soils within and near reclaimed breccia pipe mines generally posed minimal risk to kangaroo rats; most exceedances were for As and Tl and were associated with weathered mine wastes.

Breccia pipe features are unique in terms of their formation and location compared to other types of U mines (e.g., conventional open pit, *in situ* leaching). Nevertheless, their geochemical footprint throughout the mining life cycle has been reported to be similar to other U mine and mill sites (Van Gosen 2016). The elemental concentrations in soil, vegetation, invertebrates, and rodents at the breccia pipe uranium mines included in our study were generally comparable to those at other U mine and milling sites (Supplemental Table 1). Similarities in concentrations among mine sites exist despite variation in ore grade, tonnage, and processing among the sites; however, our analysis was a gross comparison of means and ranges rather than a rigorous statistical comparison. Taxa differences in terms of elemental uptake were not evaluated. Concentrations of Cu (vegetation), Pb (vegetation), Ni (vegetation, invertebrates), and U (soil, vegetation, invertebrates, rodents) were greater at breccia pipe mines (including the pre-production site) compared to a nearby reference site (Cleveland et al., 2021),

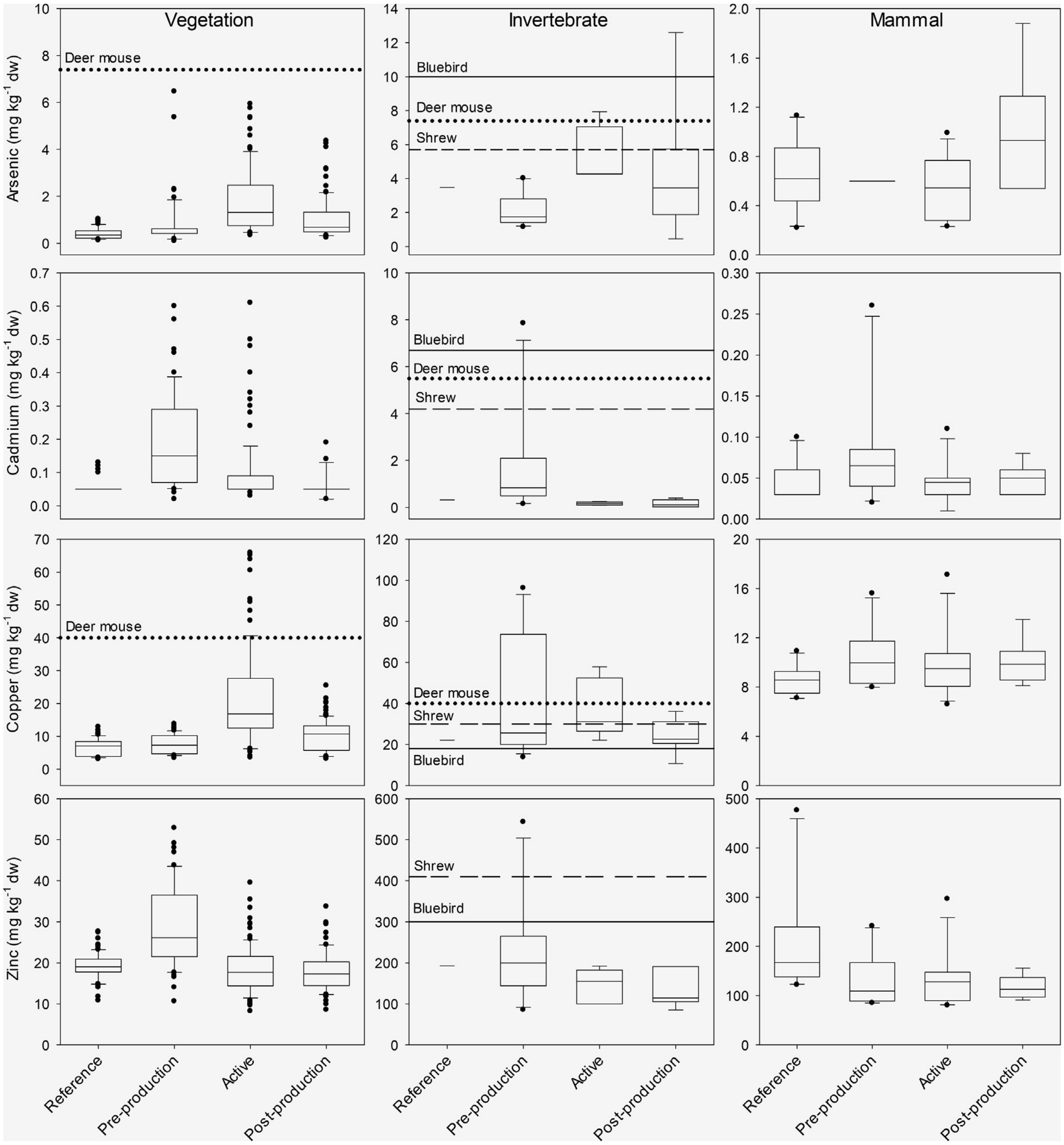

Fig. 3. Concentration data in vegetation, invertebrates, and mammals from each study site modified from Cleveland et al. (2021). Dietary concentration thresholds (DCTs) exceedances for arsenic, cadmium, copper, and zinc are shown as horizontal lines for deer mouse (omnivore), bluebird (insectivore), and shrew (insectivore). Shown for each box plot are the median (black horizontal line), interquartile range (box), and the 10th and 90th percentiles (whiskers), with outliers depicted as single points.

indicating that these elements may be associated with the mineralization of the pipe itself, rather than directly with mining. The co-occurrence of these elements at breccia pipe mines is consistent with findings from previous geochemical studies in breccia pipe areas (Van Gosen 2016; Van Gosen and Wenrich 1991; Van Gosen et al., 2020; Wenrich 1985). Breccia pipes are known to have higher copper concentrations (Van Gosen and Wenrich 1991; Wenrich 1985); and in fact, copper is expected to be mined from the Canyon Mine (pre-production site; Mathisen et al., 2017). Soil and invertebrate concentrations of Cu at the reference site were generally less than or similar to those from the mine sites, perhaps indicating overall Cu enrichment in the region. Copper concentrations at the reference site (a surficial sinkhole depression) are likely associated with sulfates from gypsum solutioning within the Kaibab Limestone. As such, it may not be surprising that Cu concentrations were greater than the avian TRV at the reference site.

How ecological risk changes throughout the breccia pipe mining life cycle is unknown. Understanding whether specific periods within the mining life cycle pose greater risk to ecological receptors may help resource managers and mine operators to devise strategies that mitigate potential transport, uptake, exposure, and thus risk from mining-related elements to the local environment. Our limited study sought to evaluate if risk to terrestrial receptors changes throughout the mining life cycle. Risk to biota was anticipated to be low during pre-production but was hypothesized to increase during active production and post-production because U ore is stored on-site during these phases. Weathering, aging, and leaching of mined material may influence chemical speciation and thus affect environmental mobility, bioavailability, and toxicity of mining-related elements. However, our results did not support this hypothesis. The relatively high concentrations of certain elements at the pre-production site may indicate that breccia pipe geochemistry can vary among pipes; alternately, or in addition, the collection and analysis of different species among sites and differences in elemental uptake may have also influenced our results (Hinck et al., 2017; Mann and Duniway 2020). Regional variation in soil geochemistry may also be a factor because the greatest concentrations of As in soil were measured at our reference site. However, it is also important to consider that the total elemental concentrations in the soils, as measured, may not be reflective of bioavailable concentrations. Ideally, future risk analysis will be performed throughout the mining life cycle at a single location (e.g., Canyon Mine).

The mere mention of U mining can elicit strong reaction on the perception of ecological risk, primarily due to radiation concerns. Results from this study are for elemental risks via dietary exposure in the terrestrial food web only. Radiation risks for these breccia pipe mines sites were evaluated separately (Minter et al., 2019); radiation exposures at breccia pipe mines did not exceed dose limits (1 mGy d^{-1}) in rodents, but radium-226 bioaccumulated in rodents, likely from ^{226}Ra in the soil or food. Our analysis focused on screening for ecological risk through dietary (ingestion) exposure; other routes of exposure include inhalation and absorption. These exposure routes likely contribute to less exposure than ingestion (including incidental soil ingestion) of elements present at breccia pipe mines (Lowers 2018; Suter et al., 2000). Specific life history traits such as grooming is accounted for by incidental soil ingestion in our models.

The availability of aquatic habitat near breccia pipe uranium mines is limited. Mine ponds have been more consistent sources of water compared to ephemeral streams and earthen stock tanks, with emergent aquatic vegetation present (Supplemental Fig. 1). As such, mine ponds may become attractive nuisances to biota in arid regions if elemental concentrations in pond water and sediments exceed toxicity thresholds (Hinck et al., 2017). Ecological risks via dietary exposure for the aquatic food chain were not included in this study; access to the mine ponds was not permitted during our 2015 collections. Mine ponds may be a source of mining-related constituents to biota utilizing the water resource as reported in Hinck et al. (2017) for a pre-production breccia pipe mine, but aquatic biota elemental concentration data for active and post-production sites have not been adequately characterized (Cleveland et al., 2021). Additional risk analyses for aquatic biota at uranium mine sites are warranted.

As hypothesized, U was not the driver of ecological risk. In general, most of the elemental constituents present in breccia pipe deposits do not bioaccumulate nor biomagnify. Therefore, risk from elemental exposure was anticipated to be greatest in lower levels of the food web (herbivores and omnivores). We found no risk from elemental exposure to herbivores or carnivores at breccia pipe U mines in northern Arizona based on dietary exposure to As, Cd, Cu, Pb, Mo, Ni, Tl, U, and Zn. Our study indicated no risk to rabbit, deer, or elk models, even using a conservative assumption of 100% site usage. For animals like elk with large home ranges, actual risk from dietary exposure is likely less than reported here. Our models do not consider or account for any potential human health risks that may be associated with consumption of organs for traditional or ceremonial uses (e.g., Ratelle et al., 2018; Rock et al., 2019).

Our models did screen for risk to omnivores and insectivores (HQs>1); elemental concentrations, specifically As, Cd, Cu, and Zn, in ground-dwelling invertebrates appear to be driving the risk. Studies have shown that invertebrates are important in element transfer from soil into the food web (e.g., Bengtsson and Rundgren 1984; Del Toro et al., 2010; Hunter and Thompson, 1987). Our models do have uncertainty including relatively small sample sizes, variation in species composition among sites, and assumption of 100% bioavailability of all elements. Another factor that may be driving the risk is that our samples, which were collected using unbaited pitfall traps, were not washed or depurated to remove dust and soil prior to chemical analysis to best simulate exposures to wildlife. However, sites with the greatest concentrations of elements in invertebrate tissues did not consistently have the greatest corresponding elemental concentrations in soil. Therefore, invertebrate concentrations are not just a function of soil concentrations, indicating that bioavailability (and potentially elemental speciation) may differ between sites. Invertebrate species composition may be a more important factor in the risk model outcomes (see Cleveland et al., 2021). For example, the greatest As concentration was measured in a Lepidoptera (caterpillar) sample, a sample type only collected at the post-production site (Cleveland et al., 2021). Nevertheless, Araneae (spider) and Coleoptera (beetle) samples still exceeded an HQ > 1 at this site when the Lepidoptera sample was excluded from the analysis. Although these samples were collected in pitfall traps, soil exposure would typically be minimal because of feeding behaviors (i.e. plants for caterpillars, prey for spiders). Given these results, we need a better understanding of how these invertebrate exposure pathways move elements through the local food web. Invertebrate species composition should be considered when applying these models to other mining locations or future sampling at the breccia pipe mine sites. In addition, Hinck et al. (2014) documented insectivorous avian ground foragers in the vicinity of Canyon Mine. Studies monitoring or targeting the avian species may be warranted if mining progresses at this breccia pipe mine site.

Understanding food and soil concentrations that can lead to ecological risk is important for natural resource and land managers as well as mine operators. The food and incidental soil DCTs that were developed in this study are based on published TRVs and FIRs; therefore, they could be used in a variety of environmental settings, not just breccia pipe mines in Grand Canyon watershed. Our DCTs indicate that critical concentrations were not approached in our model scenarios for breccia pipe mine sites, as evident in the very low HQs for most models. The DCTs from this study could be used as a guide to screen or monitor for risk to terrestrial receptors. For example, As concentrations that exceed 100 mg kg-1 in vegetation may be of concern for rabbit and deer but not elk (Table 4). As noted previously, U tends to be the focus of concern at U mining sites. However, food concentrations of U that would pose a risk through ingestion are relatively high, with bluebirds being the most sensitive at 73 mg kg-1 U in food (ground-dwelling invertebrates). These DCTs for other animals considered in the risk analysis are orders of magnitude (range 157–3733 mg kg-1) greater than what was measured at breccia pipe mine sites for invertebrates (max 13.1 mg kg-1).

5. Conclusions

Results from this study help define the ecological risks of U, which is an important consideration as an identified critical element for energy production. Overall, we found that the risk to the terrestrial food chain from mining-related metals at breccia pipe U mines in the Grand Canyon watershed was low based on our limited data and conservative ingestion models. As hypothesized, U was not the driver of ecological risk. Arsenic, Cd, Cu, and Zn were of concern for biota consuming ground-dwelling invertebrates. Models did not exceed NOAELs for herbivores or carnivores. The DCTs for metals developed for this study can be used by natural resource and land managers as well as mine operators to screen for risk at these sites as breccia pipe mines are developed in the future. In our models, specific species of ground-dwelling invertebrates appear to be driving the risk. Therefore, managers may want to consider invertebrate species composition when applying these models to other mining locations or future sampling at the breccia pipe mine sites. Studies monitoring or targeting the insectivorous avian species may be warranted as mining progresses at breccia pipe mine sites. Finally, our results do not address potential risks for aquatic biota at U mine sites nor human health risks.

Author contribution

Jo Ellen Hinck: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Validation, Writing – original draft, Writing – review & editing; Danielle Cleveland: Methodology, Formal analysis, Data curation, Writing – review & editing; Bradley E. Sample: Methodology, Resources, Validation, Writing – review & editing

Data availability

Supplemental information for this manuscript is available on the https://doi.org/10.1016/j.chemosphere.2020.129049. Metadata and digital datasets are also available, per USGS Data Management Policy, at https://doi.org/10.5066/P94OVQO9 (active and post-production; non-mining reference) and https://doi.org/10.5066/F7QF8R16 (pre-mining).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in 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.chemosphere.2020.129049.

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