Arsenic concentrations, distributions and bioaccessibilities at a UNESCO World Heritage Site (Devon Great Consols, Cornwall and West Devon Mining Landscape)

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Abstract

Devon Great Consols (DGC) is a region in southwest England where extensive mining for Cu, Sn and As took place in the nineteenth century. Because of its historical and geological significance, DGC has protected status and is part of the Cornwall and West Devon Mining Landscape UNESCO World Heritage Site. Recently, the region was opened up to the public with the construction or redevelopment of various trails, tracks and facilities for walking, cycling and field visits. We used portable x-ray fluorescence spectrometry to measure, in situ, the concentrations of As in soils and dusts in areas that are accessible to the public. Concentrations ranged from about 140 to 75,000 $\mu g\ g^{-1}$ ($n = 98$), and in all but one case exceeded a Category 4 Screening Level for park-type soil of 179 $\mu g\ g^{-1}$. Samples returned to the laboratory and fractionated to < 63 μm were subjected to an in vitro assessment of both oral and inhalable bioaccessibility, with concentrations ranging from < 10 to 25,500 $\mu g\ g^{-1}$ and dependent on the precise nature and origin of the sample and the physiological fluid applied. Concentrations of As in PM_{10} collected along various transects of the region averaged over 30 ng m^{-3} compared with a typical concentration in UK air of < 1 ng m^{-3}. Calculations using default EPA and CLEA estimates and that factor in for bioaccessibility suggest a six-hour visit to the region results in exposure to As well in excess of that of minimum risk. The overall risk is exacerbated for frequent visitors to the region and for workers employed at the site. Based on our observations, we recommend that the remodelling or repurposing of historical mine sites require more stringent management and mitigation measures.

Keywords: contaminated land; mining; arsenic; soils; exposure; bioaccessibility

Capsule: High levels of total and bioaccessible arsenic remain on an old mine site now opened up to the public.

1. Introduction

Legacy pollution is a widespread problem created by centuries of industrialisation and has resulted in large areas of contaminated land that require careful remediation or management (Rosenbaum et al., 2003; Hartley et al., 2009). Sites of historical extraction and processing of mineral ores are a source of contamination of soils and aquatic systems by toxic metals and metalloids that may pose significant environmental and public health risks (Thornton, 1996; Mighanetara et al., 2009, Nikolaidis et al., 2013).

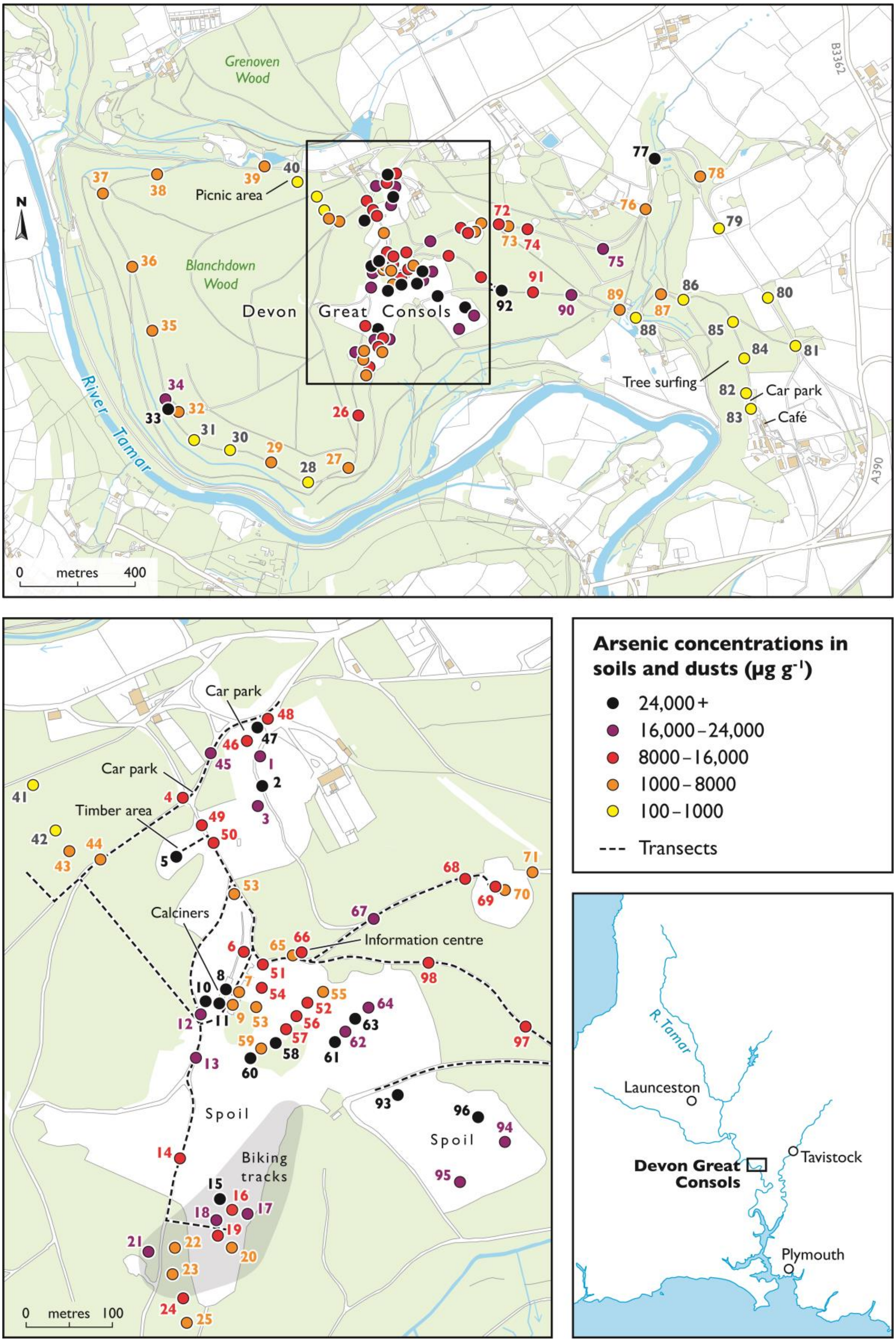
Large areas of Cornwall and west Devon in south west England are highly mineralised and many metals exhibit natural elevation in soils. However, extensive historical mining for metals, and mainly Cu, Sn and As, have resulted in significant, but heterogeneous, contamination of terrestrial, aquatic and indoor environments (Rieuwerts et al., 2006; Anagboso et al., 2013). Contemporary contamination and health risks may also be exacerbated by exposure pathways resulting from activities that involve disturbing or engineering legacy soils or tailings for clearance, access, construction or recreation (Middleton et al., 2017).

One particular region of both historical and contemporary significance is Devon Great Consols (DGC), a mine complex in the Tamar Valley (Hamilton-Jenkin, 1974; Figure 1). At DGC, five mines were constructed in the mid-18th century over an area of 67 ha in order to extract copper ore and the region soon became the largest producer of the metal in Europe. As competition for Cu began to intensify, attention was shifted to arsenic and by the 1870s the area that included DGC was responsible for one half of the world’s production of the metalloid. Here, As pyrites were crushed before being roasted in a series of calciners, with evaporated As drawn up flues and crystallised on brick labyrinths where they were subsequently scraped off and purified thermally (Hamilton, 2000). With a decline in the price of As the mines ceased production in 1901 and, despite, operations resuming on a smaller scale 14 years later, mining had completely ceased by 1930.

Much of the complex is now privately owned and occupied by coniferous plantations that are partly used for timber production but over the past three decades the site has been the focus of various conservation projects. Currently, the region falls within the Tamar Valley Area of Outstanding Natural Beauty (AONB), is a Site of Special Scientific Interest due to its unique geology and, because of its contribution to the Industrial Revolution and the development of modern industrial society, is part of the broader Cornwall and West Devon Mining Landscape UNESCO World Heritage Site (Tamar Valley AONB, 2010). In 2013, a 25 km network of trails for outdoor activities and supplemental facilities (for example, carparks and a café) was completed in an area of the Tamar Valley that included the DGC complex and many other locations that had not been previously accessible to the public. Permissive routes are leased from private owners and are managed by the local council and the Tamar Valley AONB. They are used by individuals, families and organised groups for walking, dog-walking, running, cycling, horse riding and picnicking. Other areas, including the western spoil heaps, are available for more specialist activities, such as mountain-biking, with permission from the landowners (Carey et al., 2015). The region is also popular for field visits of environmental science, geology and conservation and management students (Stokes et al., 2012) and is the workplace for forestry staff.

Studies undertaken at DGC before the construction of the trails indicated high concentrations of total (1280 to 205,000 $\mu g\ g^{-1}$) and orally bioaccessible (12 to 13,300 $\mu g\ g^{-1}$) As in soils and tailings around the complex (Klinck et al., 2005; Palumbo-Roe and Klinck, 2007) and at least one incidence of As poisoning associated with motorcycling around the site (Hamilton, 2000). Since no remediation of the region has been documented, high concentrations of As could now be encountered in areas open to the public, including the trails, and pose a health hazard to visitors on foot, cycling or horse-riding, and at sites where woodland management takes place. To this end, the present study examines contemporary concentrations and bioaccessibilities of As along the trails and in areas now accessible to the public (i.e. not fenced off, and permissible or otherwise). The soils and dusts of the region were firstly monitored for As by portable x-ray fluorescence (XRF) spectrometry before more strategic samples were returned to the laboratory for an in vitro assessment of oral and inhalable bioaccessibility of the metalloid. Concentrations of PM_{10} were monitored on site under different weather conditions and selected airborne dust samples analysed for total As content. The results provide information on As exposure and risk at the DGC site and have more general implications for the engineering or remodelling of areas in the vicinity of abandoned mines.

Figure 1: Location and layout of the Devon Great Consols region. Sample sites for XRF analysis are numbered and coloured according to As concentration. The routes of transects for the collection of airborne dusts are shown as dashed lines.


Grenoven Wood
Blanchdown Wood
Devon Great Consols
River Tamar
Picnic area
Tree surfing
Car park
Café
B3362
A390
N
0 metres 400
0 metres 100
Car park
Car park
Timber area
Calciners
Information centre
Spoil
Spoil
Biking tracks
Arsenic concentrations in soils and dusts (μg g⁻¹)
● 24,000+
● 16,000–24,000
● 8000–16,000
● 1000–8000
● 100–1000
--- Transects
R. Tamar
Launceston
Tavistock
Devon Great Consols
Plymouth

2. Materials and methods

2.1. Site visits and sampling

The DGC region was visited on foot on seven occasions. Thus, firstly, soils and dusts from various trails, cycle tracks and public facilities (e.g. car parks, information centre, picnic area), as well as the calciners, acidic and unvegetated spoil heaps, timber yards and a lakeside, were screened in situ for As and a suite of other contaminant elements. This visit coincided with a lengthy spell of warm and dry weather in July 2017 and measurements were performed using a portable, battery-operated, energy-dispersive x-ray fluorescence (XRF) spectrometer (Niton model XL3t 950 He GOLDD+). Based on the As distributions and concentrations established in situ, the region was revisited on two occasions in June 2019 in order to retrieve a range of publically accessible material types for further As characterisation and, in particular, accessibility of the metalloid to various physiologically-based extractants. In June and July 2018, the region was revisited on four occasions under contrasting meteorological conditions (but with no precipitation) in order to monitor particulate dusts and collect airborne samples for As determination.

2.2. In situ measurements of As in soils and dusts

At the 98 locations shown in Figure 1, and after any stones and other debris (e.g. large fragments of vegetation) had been discarded, soil or dust from an area of a few cm^2 was gathered into a mound a few mm deep using a plastic spatula. The 8-mm diameter detector window of the XRF spectrometer was then positioned centrally and vertically-downward over the sample, a process aided by imagery generated from an integrated CCD camera. Readings were taken for one minute in a mining mode, comprising successive counting periods of 20 s each in a main (50 kV/40 μA), low (20 kV/100 μA) and high (50 kV/40 μA) energy range. Quintuplicate As measurements of the same sample were reproducible to within 10%, while measurements of separate mounds created from different areas across a transect of approximately 2 m in length on a footpath returned relative standard deviations of up to 25%.

Samples in shady locations that were visibly damp (*n* = 9) were returned to the laboratory for repeated measurements in order to evaluate the impacts of water content and soil heterogeneity on measurements conducted in situ. Oven-drying was performed on ~ 20 g sample aliquots in a series of crucibles for 2 h at 70°C with moisture content established from weights before and after drying. Milling of ~ 10 g subsample aliquots was subsequently accomplished in a series of 80 mL agate bowls, each containing five 20 mm agate milling balls, using a Fritsch planetary mill (model Pulverisette 5) at 300 rpm for 3 min. Milled and unmilled subsamples were analysed by XRF with the instrument configured nose-up in a laboratory accessory stand and samples mounded to a depth of at least 10 mm on 3.6 μm SpectraCertified Mylar polyester film placed centrally over the detector window. As a performance check, a reference sediment (BCR-320R; certified As = 21.7±2.0 μg g^{-1}) and a reference loam (MSH 101; certified As = 1090±16.7 μg g^{-1}) were analysed in quintuplicate, and returned concentrations of 21.3±3.5 μg g^{-1} and 1230±8.0 μg g^{-1}, respectively.

Arsenic concentrations measured in the laboratory versus As concentrations measured in situ and corrected for the mass of water present (up to 25%) were significantly correlated (r = 0.978; $p < 0.01$) with a slope of 1.13 derived from linear regression analysis and forced through the origin. This suggests that there was a relatively small impact on As concentrations measured in situ due to the absorption of primary and secondary x-rays from water. A comparison of As concentrations returned for milled and unmilled subsamples resulted in a significant correlation (r = 0.968; $p < 0.01$) with a slope of 1.31 derived from linear regression analysis. Neglecting the sample returning the highest As concentrations (108,000 μg g^{-1} when milled and 75,000 μg g^{-1} when unmilled) reduced the slope to near unit value (0.99). This suggests that heterogeneity amongst the present samples has an impact on results only at the highest As concentrations, presumably because of the presence and dispersion of As-rich grains within the sample.

2.3. Samples for acid digestion and extraction in physiological solutions

At 30 of the locations shown in Figure 1 that exhibited a range of As concentrations, samples of about 100 g each were collected using a plastic spatula and sieved through a 2 mm Nylon mesh on site and into a series of paper bags to remove coarse organic and inorganic debris. In the laboratory, samples were oven dried at 70°C before being ground with a porcelain pestle and mortar and sieved through a 63 μm Nylon mesh. This size fraction was selected as an intermediary between readily ingestible (< 250 μm) and readily inhalable (< 10 μm) particles.

2.4. Aqua regia digestion

Quasi-total digestion of material was accomplished using boiling *aqua regia* (AR). Thus, in triplicate, about 0.5 g of each sample was weighed into a series of acid-cleaned 50 ml Pyrex beakers to which 12 ml aliquots of AR (3 parts HCl to 1 part HNO_3, both Fisher TraceMetal Grade) were added. The contents were covered with a watch glass and allowed to stand at room temperature for 1 h before being heated on a hot plate and simmered for a further hour. After being allowed to cool overnight, digests were filtered through Whatman 1005-125 qualitative filter papers (pore size = 2.5 μm) into individual volumetric flasks that were filled to mark with Millipore Milli-Q water (MQW). For quality assurance purposes a contaminated soil certified for concentrations of As and other elements (SCP Science SS-2) was digested in triplicate and controls were performed in triplicate but in the absence of solids.

2.5. Physiological extractions

Analytical reagent grade reagents purchased from Fisher Scientific, Merck and Sigma Aldrich were used for the physiological extractions. In order to evaluate the oral bioaccessibility of As in the soil and dust samples, a physiologically-based extraction test (PBET) was employed that simulates the chemical conditions of the paediatric gastro-intestinal tract and that is described in detail elsewhere (Turner and Price, 2008). Briefly, a gastric solution was prepared by dissolving 1.25 g of pepsin, 0.5 g of sodium citrate, 0.5 g of sodium malate, 420 μL of lactic acid and 500 μL of acetic acid in 1 L of MQW and adjusting the contents to pH 2.5 by dropwise addition of 7 M HCl.

In triplicate, samples of 0.4 g were weighed into individual 50 mL polyethylene bottles and 40 mL of gastric solution added to each. The capped contents were incubated at 37°C in a temperature-controlled water bath and under constant, lateral agitation. After 1 h, subsamples of 5 mL were pipetted into a series of 15 mL centrifuge tubes and the contents centrifuged at 3000 rpm for 10 min, with supernatants (the “stomach phase” or PBET-s) transferred to individual Sterilin tubes and stored frozen. Meanwhile, 5 ml of gastric solution, 70 mg of bile salts and 20 mg of pancreatin were added to each tube and the pH of the contents adjusted to 7.0 with sodium bicarbonate. Incubation continued as above, with subsamples being centrifuged after a period of 4 h and supernatants (“intestinal phase” or PBET-i) stored frozen. Controls were performed in triplicate likewise, but in the absence of solids.

To simulate exposure to inhalable particles in the extracellular environment of the deep lung, a standard simulated lung fluid (SLF; Gamble’s solution) was used (Moss, 1979). The solution was prepared by adding the following (and, to avoid precipitation of salts, in the order shown) to 1 L of MQW: 0.204 g $MgCl_2.6H_2O$, 6.022 g NaCl, 0.299 g KCl, 0.127 g

Na_2HPO_4, 0.063 g Na_2SO_4, 0.367 g $CaCl_2.2H_2O$, 0.575 g $C_2H_3O_2Na$, 2.604 g $NaHCO_3$ and 0.098 g $C_6H_8O_7Na_3.2H_2O$; and the pH was adjusted to 7.4 using 7 M HCl. In triplicate, samples of 0.4 g were weighed into individual 50 mL polyethylene centrifuge tubes to which 40 mL aliquots of SLF were added. The contents were incubated at 37°C for 24 h before 5 mL subsamples were processed above but stored under refrigeration.

A more acidic, artificial lysosomal fluid (ALF) was used to simulate the intracellular conditions with which inhaled particles would be exposed to after phagocytosis by alveolar and interstitial macrophages within the lung (Colombo et al., 2008). The solution was prepared by adding the following (and in the order shown) to 1 L of MQW: 0.051 g $MgCl_2.6H_2O$, 3.207 g NaCl, 0.299 g KCl, 0.072 g Na_2HPO_4, 0.039 g Na_2SO_4, 0.128 g $CaCl_2.2H_2O$, 0.078 g $C_6H_8O_7Na_3.2H_2O$, 6.00 g NaOH, 20.80 g H_2NCH_2COOH, 0.090 g $C_4H_4O_6Na_2$ and 0.077 g $C_3H_4O_3$; and the pH was adjusted to 4.4 using 7 M HCl. The protocols for incubation and subsample processing and storage were identical to those described for the SLF exposures above.

2.6. ICP analysis of digests and extracts

Aqua regia digests and extracts from the physiological extractions were analysed for As and a suite of other elements by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermoscientific iCAP 7400. The instrument was calibrated using four mixed standards and a blank prepared by serial dilution of CPI International standards in 2% HNO_3, and settings in both UV and visible light were as follows: exposure time = 2 s; RF power = 1150 W; nebuliser, coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min^{-1}, respectively; viewing height = 12 mm; uptake time = 50 s; wash time = 15 s.

Mass to volume concentrations derived from the ICP were converted to μg g^{-1} on a dry weight basis. The mean concentration returned for As in the reference soil (3.5 μg g^{-1}) was close to the reported consensus value (3.9 μg g^{-1}), with the range of measured concentrations within the reported tolerance interval (1.8 to 4.9 μg g^{-1}). Precisions for As determined in the triplicated *aqua regia* digestions and physiological extractions are shown in Table 1. Median values were always below 25% but values above 50% were returned for the PBET solutions arising from one sample whose extractable As concentrations were among the lowest measured.

Table 1: Precisions (as percentage relative standard deviation) for As determined in the 30 *aqua regia* (AR) digests and PBET and lung fluid extractions (n = 3 in all cases). PBET-s: stomach phase; PBET-i: intestinal phase; SLF: standard simulated lung fluid; ALF: artificial lysosomal fluid.

	AR	PBET-s	PBET-i	SLF	ALF
median	4.36	22.7	19.1	5.71	7.21
min	0.12	1.8	2.31	0.29	1.63
max	35.6	87.1	61.1	14.7	31.2

2.7. Collection and analysis of airborne dusts

A Haz-Dust EPAM-5000 particulate monitor (Environmental Devices Corporation) with 10 μm particle size impactor was used to measure and collect airborne dusts (PM_{10}) during nine transects along the trail routes indicated in Figure 1 and where public or worker activities are focussed. Specifically, on four occasions, routes of between about 100 and 800 m were walked with the monitor in a wheelbarrow for a timed period of 10 to 20 min with the air inlet of the monitor set at 4 L min^{-1} and fixed at 1 m above ground level. On two occasions, pre-dried 47 mm diameter Whatman quantitative 41 circles filters were used to collect PM_{10}

from various combined transects. Once sufficient material had accumulated, filters were retrieved and stored sealed in individually labelled petri dishes.

Filters arising from sampling of PM_{10} ($n = 5$), along with three blank filters and 250 mg of the certified reference soil, were digested in 6 mL of boiling *aqua regia* as above before being transferred and diluted in a series of volumetric flasks. Digests were analysed for As by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermoscientific X Series II with a concentric glass nebuliser and conical spray chamber that was calibrated with four standards and a blank and operated under conditions described elsewhere (Turner and Holmes, 2015). The mean concentration of As returned for the reference soil was 3.4 μg g^{-1} and within 15% of the reported consensus value. Arsenic concentrations in the PM_{10} samples are given in ng m^{-3} and have been derived from blank-corrected concentrations in digests and the volumes of air passing through the particulate monitor.

3. Results

3.1. In situ analyses

Figure 1 shows the distribution of As concentrations arising from the in situ analysis of soils and dusts by XRF (and, as necessary, corrected for moisture content determined in the laboratory). Table 2 summarises the concentrations of other elements that were mined in the region (Sn, Pb, Cu), are important indicators of metallic mine pollution (Fe), or are in the same group of the periodic table as the metalloid (Sb, Bi). Note that the measurement detection limits are indicative and based on three counting errors arising from the lowest signals returned by the instrument throughout the measurement campaign, and the number of samples detected (n) has been used to determine the summary statistics shown. Also given in Table 2 are representative concentrations of the elements in soils from the entire Tamar river catchment. These are defined as 50th percentile values determined in top-soils fractionated to < 2 mm by energy- or wavelength-dispersive XRF and reported by Rawlins et al. (2003).

Among the trace elements (i.e. with the exception of Fe), As was detected in the most cases and displayed the highest mean, median and maximum concentrations. This reflects the ubiquitous, but heterogeneous, As contamination of the site by the practice and legacy of historical mining activities. Enrichment of As based on the median concentration relative to the catchment soil concentration is about 600 and relative to a normal background As concentration for mineralised soils (290 μg g^{-1}; Middleton et al., 2017), enrichment is about 45.

Table 2: Measurement limit of detection (LOD), number of detects and summary statistics for As and other elements determined by XRF in 98 samples from the DGC region. Catchment soil concentrations are 50th percentile values reported by Rawlins et al. (2003).

	As	Sb	Sn	Bi	Pb	Cu	Fe
LOD, μg g^{-1}	4.7	25.2	21.6	8.9	8.5	16.7	62.7
n	98	15	89	76	94	96	98
mean, μg g^{-1}	13,000	1900	1550	280	147	1090	94,200
st dev, μg g^{-1}	12,300	6910	2350	1170	254	989	53,000
median, μg g^{-1}	12,700	112	900	106	98.4	910	81,100
min, μg g^{-1}	136	25.5	42.2	11.7	11.9	34.9	12,500
max, μg g^{-1}	74,500	26,800	18,900	10,300	2350	5510	231,000
catchment soil, μg g^{-1}	22	1.80	3.1	0.55	35.0	28.7	42,900

Figure 2 shows the frequency distribution of As concentrations in soils and dusts from the DGC region. The highest concentration of As of about 75,000 μg g^{-1} was found in soil adjacent to the remains of a calciner (site 11); significantly, this is the only location in the region where the public are warned about hazardous concentrations of As and advised to remain on the footpath. Concentrations above 24,000 μg g^{-1} were encountered on or close to spoil heaps that included part of a biking track (site 15), an area which had been shaped into a visitor car park (site 2) and a yard used to store and process timber (site 5). Arsenic concentrations above 16,000 μg g^{-1} were observed more frequently on trails and cycle tracks near to abandoned mines and spoil heaps. Anecdotally (personal communication with locals, 2017), a mining spoil heap in the north of the area shown inset in Figure 1 was removed and material distributed along the paths to create the car parking area and access to the spoil heaps for car rallies. Visible inspection (e.g. colour and grain size) and elemental ratios (e.g. Fe:As) of the materials on such access paths provide some support for this assertion. Concentrations above 8,000 μg g^{-1} were found on public routes more frequently and at greater distances from obvious sources of As, including the dusts within the remains of the office buildings now used to display visitor information (site 66). Concentrations below 1000 μg g^{-1} (but > 100 μg g^{-1}) were encountered at locations farthest from the spoil heaps and towards the periphery of the region, and included soils from a café carpark (sites 82 and 83), a small play and picnic area (site 40) and a trail route into a tree surfing facility (site 84).

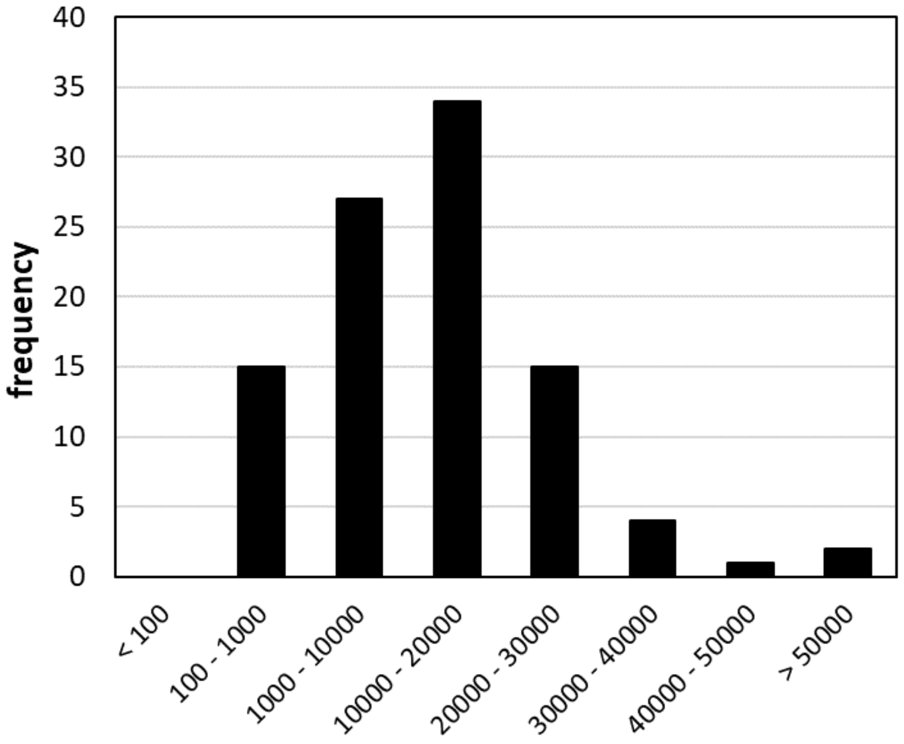


Figure 2: Frequency distribution of As concentrations (μg g^{-1}) in soils and dusts of the DGC region and as determined in situ by XRF.

3.2. Quasi-total and bioaccessible arsenic

Table 3 shows a summary of As concentrations digested in the 30 soils and dusts that had been collected during the second, more targeted sampling campaign and fractionated to < 63 μm. Despite differences between the precise samples analysed (including their grain size distribution) and AR representing a quasi-total means of sample digestion, the magnitude and distribution of As concentrations are similar to those returned in situ by XRF and reported above. Also shown in Table 3 is a summary of the concentrations of As available to each of the simulated physiological extractants along with corresponding measures of bioaccessibility (defined as the percentage of As extracted relative to the AR-digestible concentration and representing the fraction of As that is available for absorption into the systemic circulation). In Figure 3 concentrations available to each extractant are shown relative to AR-digestible concentrations for all samples analysed.

Concentrations of As extracted by the PBET stomach solution range from about 10 to 3700 μg g^{-1}, with bioaccessibilities ranging from < 1 to 23.9%, and concentrations extracted by the PBET intestinal solution range from about 13 to 1130 μg g^{-1}, with bioaccessibilities ranging from < 1 to 35.3%. In 21 cases As concentrations were higher in the intestinal phase compared with the preceding stomach phase while in 9 cases concentrations were lower in the intestinal phase. Arsenic extracted by the SLF exhibited a similar range and distribution of concentrations and accessibilities as the PBET phases. However, concentrations extracted by the ALF were significantly greater, often approaching and sometimes exceeding corresponding concentrations digested in AR and resulting in bioaccessibilities that averaged around 100% (and data that were close to unit slope in Figure 3).

Table 3: Concentrations of As in the 30 soil and dust samples (fractionated to < 63 μm) as determined by ICP following *aqua regia* (AR) digestion or physiological extraction (PBET-s: stomach phase; PBET-i: intestinal phase; SLF: standard simulated lung fluid; ALF: artificial lysosomal fluid). Bioaccessibilities were calculated from extractable relative to AR-digestible concentrations.

	AR, μg g^{-1}	PBET-s, μg g^{-1}	PBET-s/AR, %	PBET-i, μg g^{-1}	PBET-i/AR, %	SLF, μg g^{-1}	SLF/AR, %	ALF, μg g^{-1}	ALF/AR, %
mean, μg g^{-1}	10300	418	5.31	394	6.33	442	5.89	1000	105
st dev, μg g^{-1}	8260	697	5.09	279	7.13	365	3.53	6540	26.1
median, μg g^{-1}	9340	221	3.53	401	4.13	414	4.76	10,100	107
min, μg g^{-1}	141	9.72	0.77	13.4	0.82	18.3	0.72	114	39.8
max, μg g^{-1}	37500	3700	23.9	1130	35.3	1840	15.0	25,500	154

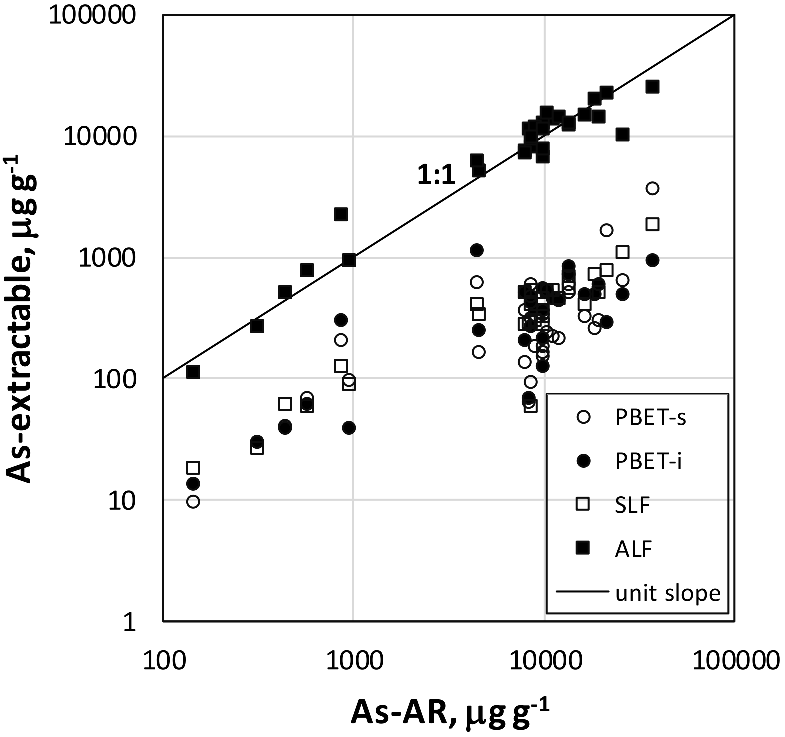


Figure 3: Concentrations of As available to the four physiological extractants versus quasi-total As concentrations digestible in AR for the 30 soil and dust samples (fractionated to < 63 µm) (PBET-s: stomach phase; PBET-i: intestinal phase; SLF: standard simulated lung fluid; ALF: artificial lysosomal fluid).

3.3. Airborne dusts

Table 4 shows the concentrations of PM_{10} determined along nine transects and on four occasions whose meteorological conditions are summarised. Concentrations are given as the median resulting from each sampling and the overall maximum value observed for each occasion. There was no systematic difference in values between the sites sampled on different occasions and no clear relationship between median values and weather conditions. However, the lowest (south westerly) wind speed returned the lowest overall maximum PM_{10} concentrations and was often associated with the lowest median PM_{10} values.

Table 4: Median concentrations of PM_{10} recorded along each of nine transects and on four occasions whose meteorological conditions are summarised. Note that the maximum concentration arising from each measurement date is also shown along with its location (in parentheses).

date	max T	max wind speed	ave direction	ave humidity	1	2	3	4	5	6	7	8	9	max
	°C	(km h^{-1})		(%)					(μg m^{-3})					
01/06/2018	19.2	11	SW	92	13	2	13	2	2	4	7			31 (3)
12/06/2018	21.6	13	WNW	77	22	2	2	4	3	2	8	6	2	653 (1)
29/06/2018	28.4	19	ENE	57	10	31	27	12	28	27	8	62		233 (2)
03/07/2018	13.3	21	E	69	14	3	2	23	2	6	21	24	15	293 (1)

The concentrations of As in airborne dusts (PM_{10}) are shown in Table 5. Concentrations ranged from about 15 to 80 ng m^{-3} and, overall, average 32 ng m^{-3}. By comparison, a report by Maggs (2000) indicated annual mean concentrations of arsenic in UK rural and urban air range from 1 - 4 ng m^{-3} and 5 - 7 ng m^{-3}, respectively; a more recent report, however, suggests that typical particulate concentrations in UK air are below 1 ng m^{-3} (Department for Environment, Food and Rural Affairs, 2017).

Table 5: Concentrations of As in airborne PM_{10} collected on filters deployed over different transects and for different periods of time. The mean and standard deviation arising from triplicate analyses of the same sample digest is shown in each case.

date	transects	duration (s)	As (ng m^{-3})
29/06/2018	3,2,5,8,4,1	5391	80.5 ± 0.3
29/06/2018	6,7	1861	19.0 ± 0.1
03/07/2018	2,3,6,7,9	5385	14.2 ± 0.1
03/07/2018	8	1067	30.4 ± 0.2
03/07/2018	1,4,5	2509	14.9 ± 0.2

4. Discussion

The results presented here in terms of both the concentration and oral bioaccessibility of As are broadly similar to those reported by Kavanagh et al. (1997), Klick et al. (2005) and Palumbo-Roe and Klinck (2007) for soils and tailings sampled from the region prior to the construction of the trail network and opening of the facilities to the public. These authors reported a median oral bioaccessibility of 15%, with spatial variability reflecting variations in mineralogy; specifically, As associated with sulphides was less bioaccessible than As associated with Fe oxyhydroxides, with the degree of crystallinity of the latter also believed to have an impact on the precise bioaccessibility. We observed significant relationships ($p < 0.05$) between PBET-s bioaccessibilities of As and Fe ($r = 0.593$) and PBET-i bioaccessibilities of As and Fe ($r = 0.827$) suggesting that the oral bioaccessibility of As is at least partly accounted for by the concentration of Fe oxyhydroxides. Measurements in the DGC region have also shown that scorodite, a hydrated iron arsentate, may act as a passivation layer around arsenopyrite grains (Rieuwerts et al., 2014). The dissolution of this mineral increases with pH in the range 3 to 6 (Harvey et al., 2006) which may, therefore, account for the higher extraction of As by the ALF compared with the acidified stomach PBET.

Health-based soil guideline values for As developed by the Environment Agency (2009a) are 39 μg g^{-1} for home gardens, 43 μg g^{-1} for allotments and 640 μg g^{-1} for commercial land. The present data generated by XRF indicate exceedances of garden and allotment soil guidelines in all cases and exceedance of commercial soil guidelines in 85 of 98 samples. A more appropriate guideline for the land use in the present context, however, is the Category 4 Screening Level (C4SL) for park-type soil of 179 μg g^{-1}; here, land is considered to be recreational but at a sufficient distance from housing that there is negligible tracking back of material (Department for Environment, Food and Rural Affairs, 2014). On this basis, As concentrations in the DGC region measured by XRF exceed the C4SL in all but one sample. Screening levels are, however, predicated on 100% bioavailability and assume that As uptake from soil is equal to intake (Middleton et al., 2017). Significantly, therefore, bioaccessible concentrations of As exceed the C4SL in between 19 (PBET-s) and 30 (ALF) of the 30 soil and dust samples tested.

Regarding air samples, all particulate As concentrations returned over the transects monitored exceed the current EU Directive annual average target value of 6 ng m^{-3} (Department for Environment, Rural Affairs and Agriculture, 2017), and in one case exceedance is by more than an order of magnitude. Based on percentage bioaccessibilities through inhalation of fugitive particles, target values could be exceeded by bioaccessible concentrations in some (SLF) or all (ALF) cases (assuming that As bioaccessibilities evaluated on soils and deposited dusts of < 63 μm in diameter are representative of As accessibilities in PM_{10} captured by the impactor).

Overall exposure to As in the DGC region depends on the practices undertaken (e.g., walking, running, horse-riding, cycling, picnicking), the weather conditions, and the length and frequency of visits. For staff, exposure could be a daily occurrence, depending on the location of the work carried out, with the highest risk adjacent to spoil heaps and within the timber storage area. Exposure through ingestion may be most significant if food is consumed on site without hands being washed thoroughly, while exposure through inhalation may be more acute during dry and windy weather or when dusts are disturbed by cyclists on contaminated tracks and vehicles moving in the car parking areas. The ready generation of airborne material is exemplified by reports describing a 100 m high cloud of dust resulting from a four-wheel drive car rally that took place on the site (Hamilton, 2000) and by observations of dust plumes above tailing heaps made by the authors and by other visiting scientists under turbulent conditions (Stokes et al., 2012). Dry weather also appears to promote the formation of efflorescent As salts on the tailing heap surfaces which is then readily transported by wind (Hamilton, 2000). More sustained, indirect exposure may also arise through tracking dust and soil from shoes, clothing and pets into vehicles and homes, a process that is generally more important during wet conditions and winter months (Hunt et al., 2006).

Clearly, concentrations of As in the DGC region are sufficiently high to be of public health concern, with one of the main considerations in this respect being the increased risk of cancer of the skin, lung, liver and urinary tract (Nikolaidis et al., 2013). No safe concentrations or intakes of As can be recommended but UK guidance estimates that a daily intake of 1 μg of As averaged over a lifetime would increase the risk of cancer between about 1:4000 and 1:17,000 (Department for Environment, Food and Rural Affairs, 2002). Accordingly, an Index Dose of minimal risk from the combined ingestion and inhalation of As is 0.302 μg kg^{-1} bw day^{-1} (Hartley et al., 2009).

Studies reviewed by the Environmental Protection Agency have resulted in best estimates for daily soil and dust ingestion (including inhalation and subsequent swallowing) of 100 mg for children (between 1 and 21 years old) and 50 mg for adults (U.S. EPA, 2011). These values have also been adopted in the Contaminated Land Exposure Assessment (CLEA) model for different land uses and form the basis of soil guideline values (Environment Agency, 2009b). Thus, an adult visiting DGC for a period of six hours and ingesting 12.5 mg of material containing 13,000 μg g^{-1} As (the median concentration determined by XRF) is exposed to 163 μg of the metalloid; this is equivalent to 2.3 μg kg^{-1} bw day^{-1} for a body weight of 70 kg, or well in excess of the Index dose of minimal risk. For children of 9.8 kg and 19.7 kg, representing average female body weights for age ranges of 1-2 years and 5-6 years, respectively, and employed as default values in the CLEA model, ingestion of 25 mg of material results in a total As exposure of 325 μg which is equivalent to 33 μg kg^{-1} bw day^{-1} and 16 μg kg^{-1} bw day^{-1}, respectively, and more than an order of magnitude greater than the dose of minimal risk. Factoring in for median oral or inhalation bioaccessibilities would reduce exposure estimates but would still result in significant exceedances of this risk, especially for young children.

There is more uncertainty regarding the risk arising from dermal exposure to As from soils and other geosolids, largely because current models assume that uptake is equal to intake, or that all of the contaminant is available to traverse the skin into the systemic circulation (Environment Agency, 2009b; U.S. EPA, 2011). The factors determining uptake according to CLEA are the total concentration of contaminant in soil, the exposed area of skin, the sediment to skin adherence factor and a chemical-specific dermal absorption factor (= 0.03 for As). For an As concentration of 13,000 μg g^{-1} and an exposure period of six hours, data reported by the U.S. EPA for an adult 70 kg adult (a passive outdoor adherence factor of 0.1 mg cm^{-2} and exposed area of skin consisting of the face, hands, forearms and lower legs of 0.53 m^2) yields an intake of 103 μg g^{-1}, or about 1.5 μg kg^{-1} bw d^{-1}. For a child of six years old (a passive outdoor adherence factor of 0.1 mg cm^{-2} and exposed area of skin of 0.21 m^2), a daily intake of 41 μg g^{-1}, or about 2 μg kg^{-1} bw d^{-1}, is predicted. Clearly, the importance of the dermal route of exposure relative to the ingestive pathway depends on the ability of As to mobilise from soil to the skin surface. Nevertheless, it could represent a significant risk if a child or pet were to play in or become covered by wet, contaminated soil, or for a mountain-biker who takes a fall on the spoil heaps.

Within the DGC region there is a warning about high As concentrations in the vicinity of the calciners, and the World Heritage nomination documentation (International Council on

Monuments and Sites, 2006) and trails management code of conduct (Tamar Valley AONB, 2010) mention the potential toxicity of the spoil heaps, with the former document also calling for contamination control to be implemented. That said, significant As contamination is observed more widely, presumably because of the extensive disturbance of the site and the mobility of As-rich waste material, and extends to areas used for car parking, walking and cycling. Clearly, therefore, there is a general risk of As exposure to members of the public on the trails around DGC which is greatest for frequent visitors (as well as maintenance volunteers and workers in the timber industry) and during windy conditions, and for occupants of vehicles and households where contaminated material is regularly tracked in.

Hamilton (2000) reports an incident whereby a motorcyclist contracted As poisoning after riding across the site in rain and attributes the effect to the dissolution of arsenical sulphates in rain water and their subsequent ingestion. The author also reports a case of skin cancer in a male occupant of a house close to the DGC site, although the disease was officially attributed to exposure to sunlight. Hamilton (2000) also suggests that other cases arising from exposure to As in the vicinity of DGC may have been overlooked because the early symptoms of As poisoning are generic and not easily recognised. A recommendation is that local residents and workers on the site are monitored for As exposure and poisoning (Hwang et al., 2002).

Any risk to health arising directly from recreational or occupational access to DGC may also exacerbate the long-term exposure of As to residents within the wider region of the Devon/Cornwall mining area. For example, Middleton et al. (2017) reported 69% of soils at residential properties in Cornwall (n = 127) exceeded the relevant 37 μg g^{-1} As C4SL, and highlighted the potential vulnerability of infants and small children. In addition, a survey of 512 private water supplies (out of an estimated 3500) in Cornwall found that nearly 6%

exceeded the prescribed concentration or value (PCV) of 10 µg L^{-1} As (range 11-233 µg L^{-1}; BGS, 2014), initiating a study of biological samples from affected householders.

In the county of Cornwall, over 1% (120 km^2) of land is predicted to be highly contaminated by As based on soil measurements (Abrahams and Thornton, 1987) and the findings reported here should serve to highlight the importance of site monitoring and assessment before land impacted by historical mining is repurposed or opened to the public. We note that another facility in the Cornwall and West Devon Mining Landscape UNESCO World Heritage Site (a series of interconnecting mineral tramways 70 km to the west of DGC) that was opened to the public was subject to retrospective remediation measures, including restricting access to certain areas, removal of waste and covering tailings with top soil. This followed reports of As concentrations and bioaccessibilities in soils, tailings and overburden at targeted sites along the converted trails that were elevated (but whose median values were an order of magnitude lower than those reported here; 1770 µg g^{-1}, $n = 38$) (Bowell et al., 2013).

5. Conclusions

An historic mining site in southwest England that has protected status and that has recently opened up for public access has levels of As in soils and dusts that greatly exceed soil guideline values. Factoring in for oral and inhalable bioaccessibility of As, concentrations still exceed these guidelines in many cases and calculations performed using default parameter values and a median As concentration of 13,000 µg g^{-1} reveal exposures that are significantly greater than a dose of minimal risk. Overall, the risk is greatest for frequent visitors to the region, and in particular those that disturb soils and dusts like mountain-bikers, and for employees at the site. Future areas impacted by historical mining activities that are considered for repurposing should be subject to more careful monitoring, assessment and mitigation.

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