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

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23 **Abstract**

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

44

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

46

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

49 **1. Introduction**

50 Legacy pollution is a widespread problem created by centuries of industrialisation and has
51 resulted in large areas of contaminated land that require careful remediation or management
52 (Rosenbaum et al., 2003; Hartley et al., 2009). Sites of historical extraction and processing
53 of mineral ores are a source of contamination of soils and aquatic systems by toxic metals
54 and metalloids that may pose significant environmental and public health risks (Thornton,
55 1996; Mighanetara et al., 2009, Nikolaidis et al., 2013).

56

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

65

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

75 price of As the mines ceased production in 1901 and, despite, operations resuming on a
76 smaller scale 14 years later, mining had completely ceased by 1930.

77

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

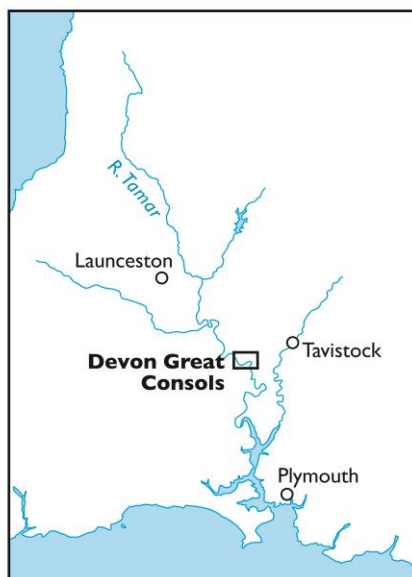
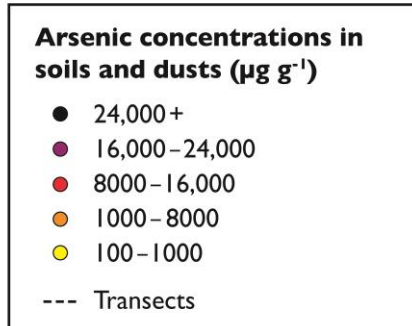
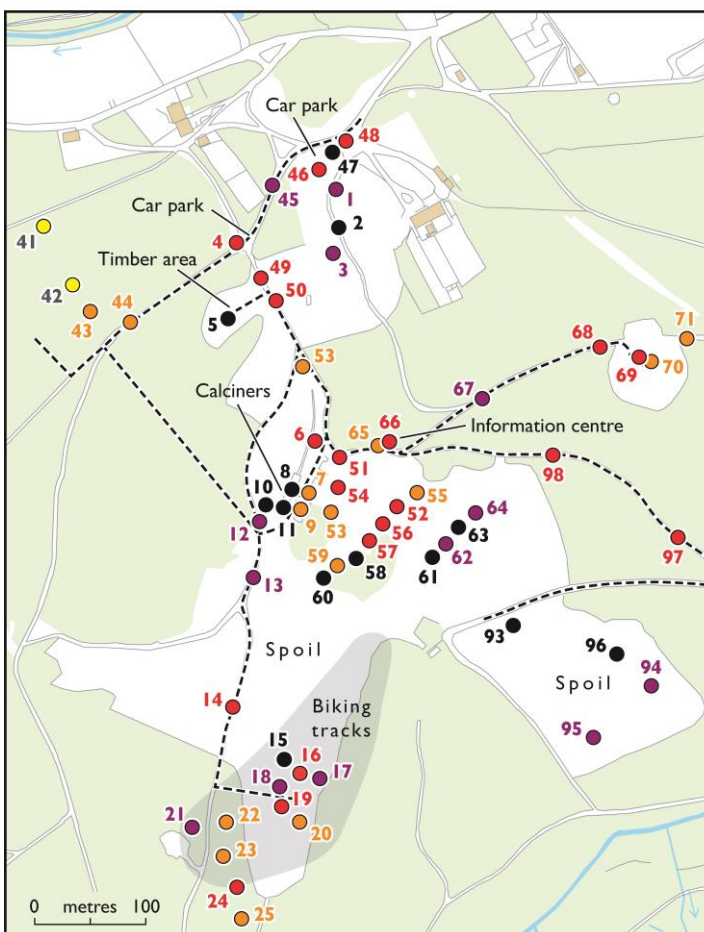
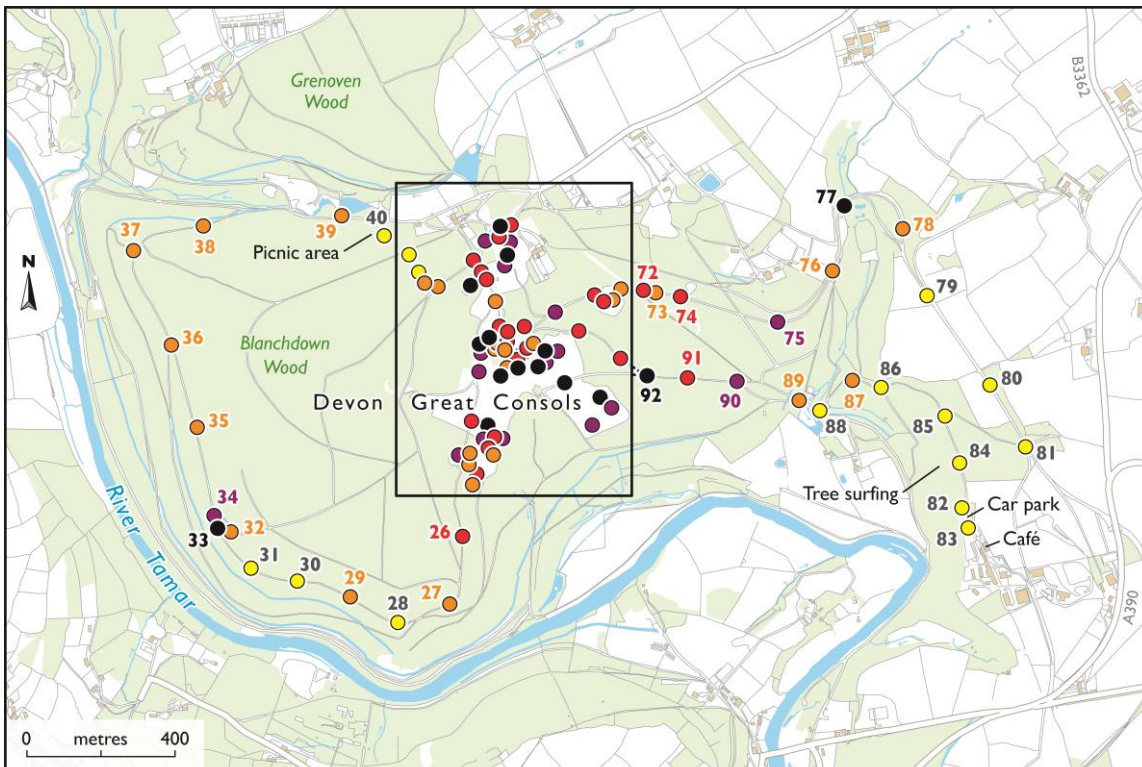
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96 Studies undertaken at DGC before the construction of the trails indicated high concentrations
97 of total (1280 to 205,000 $\mu\text{g g}^{-1}$) and orally bioaccessible (12 to 13,300 $\mu\text{g g}^{-1}$) As in soils
98 and tailings around the complex (Klinck et al., 2005; Palumbo-Roe and Klinck, 2007) and at
99 least one incidence of As poisoning associated with motorcycling around the site (Hamilton,
100 2000). Since no remediation of the region has been documented, high concentrations of As

101 could now be encountered in areas open to the public, including the trails, and pose a health
102 hazard to visitors on foot, cycling or horse-riding, and at sites where woodland management
103 takes place. To this end, the present study examines contemporary concentrations and
104 bioaccessibilities of As along the trails and in areas now accessible to the public (i.e. not
105 fenced off, and permissible or otherwise). The soils and dusts of the region were firstly
106 monitored for As by portable x-ray fluorescence (XRF) spectrometry before more strategic
107 samples were returned to the laboratory for an in vitro assessment of oral and inhalable
108 bioaccessibility of the metalloid. Concentrations of PM₁₀ were monitored on site under
109 different weather conditions and selected airborne dust samples analysed for total As
110 content. The results provide information on As exposure and risk at the DGC site and have
111 more general implications for the engineering or remodelling of areas in the vicinity of
112 abandoned mines.

113

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



117

118

119 **2. Materials and methods**

120 *2.1. Site visits and sampling*

121 The DGC region was visited on foot on seven occasions. Thus, firstly, soils and dusts from
122 various trails, cycle tracks and public facilities (e.g. car parks, information centre, picnic
123 area), as well as the calciners, acidic and unvegetated spoil heaps, timber yards and a
124 lakeside, were screened in situ for As and a suite of other contaminant elements. This visit
125 coincided with a lengthy spell of warm and dry weather in July 2017 and measurements
126 were performed using a portable, battery-operated, energy-dispersive x-ray fluorescence
127 (XRF) spectrometer (Niton model XL3t 950 He GOLDD+). Based on the As distributions
128 and concentrations established in situ, the region was revisited on two occasions in June
129 2019 in order to retrieve a range of publically accessible material types for further As
130 characterisation and, in particular, accessibility of the metalloid to various physiologically-
131 based extractants. In June and July 2018, the region was revisited on four occasions under
132 contrasting meteorological conditions (but with no precipitation) in order to monitor
133 particulate dusts and collect airborne samples for As determination.

134

135 *2.2. In situ measurements of As in soils and dusts*

136 At the 98 locations shown in Figure 1, and after any stones and other debris (e.g. large
137 fragments of vegetation) had been discarded, soil or dust from an area of a few cm² was
138 gathered into a mound a few mm deep using a plastic spatula. The 8-mm diameter detector
139 window of the XRF spectrometer was then positioned centrally and vertically-downward
140 over the sample, a process aided by imagery generated from an integrated CCD camera.
141 Readings were taken for one minute in a mining mode, comprising successive counting
142 periods of 20 s each in a main (50 kV/40 μA), low (20 kV/100 μA) and high (50 kV/40 μA)
143 energy range. Quintuplicate As measurements of the same sample were reproducible to
144 within 10%, while measurements of separate mounds created from different areas across a

145 transect of approximately 2 m in length on a footpath returned relative standard deviations of
146 up to 25%.

147

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

161

162 Arsenic concentrations measured in the laboratory versus As concentrations measured in situ
163 and corrected for the mass of water present (up to 25%) were significantly correlated ($r =$
164 0.978 ; $p < 0.01$) with a slope of 1.13 derived from linear regression analysis and forced
165 through the origin. This suggests that there was a relatively small impact on As
166 concentrations measured in situ due to the absorption of primary and secondary x-rays from
167 water. A comparison of As concentrations returned for milled and unmilled subsamples
168 resulted in a significant correlation ($r = 0.968$; $p < 0.01$) with a slope of 1.31 derived from
169 linear regression analysis. Neglecting the sample returning the highest As concentrations
170 ($108,000 \mu\text{g g}^{-1}$ when milled and $75,000 \mu\text{g g}^{-1}$ when unmilled) reduced the slope to near

171 unit value (0.99). This suggests that heterogeneity amongst the present samples has an
172 impact on results only at the highest As concentrations, presumably because of the presence
173 and dispersion of As-rich grains within the sample.

174

175 *2.3. Samples for acid digestion and extraction in physiological solutions*

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

183

184 *2.4. Aqua regia digestion*

185 Quasi-total digestion of material was accomplished using boiling *aqua regia* (AR). Thus, in
186 triplicate, about 0.5 g of each sample was weighed into a series of acid-cleaned 50 ml Pyrex
187 beakers to which 12 ml aliquots of AR (3 parts HCl to 1 part HNO₃, both Fisher TraceMetal
188 Grade) were added. The contents were covered with a watch glass and allowed to stand at
189 room temperature for 1 h before being heated on a hot plate and simmered for a further hour.
190 After being allowed to cool overnight, digests were filtered through Whatman 1005-125
191 qualitative filter papers (pore size = 2.5 µm) into individual volumetric flasks that were filled
192 to mark with Millipore Milli-Q water (MQW). For quality assurance purposes a
193 contaminated soil certified for concentrations of As and other elements (SCP Science SS-2)
194 was digested in triplicate and controls were performed in triplicate but in the absence of
195 solids.

196

197 *2.5. Physiological extractions*

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

206

207 In triplicate, samples of 0.4 g were weighed into individual 50 mL polyethylene bottles and
208 40 mL of gastric solution added to each. The capped contents were incubated at 37°C in a
209 temperature-controlled water bath and under constant, lateral agitation. After 1 h,
210 subsamples of 5 mL were pipetted into a series of 15 mL centrifuge tubes and the contents
211 centrifuged at 3000 rpm for 10 min, with supernatants (the “stomach phase” or PBET-s)
212 transferred to individual Sterilin tubes and stored frozen. Meanwhile, 5 ml of gastric
213 solution, 70 mg of bile salts and 20 mg of pancreatin were added to each tube and the pH of
214 the contents adjusted to 7.0 with sodium bicarbonate. Incubation continued as above, with
215 subsamples being centrifuged after a period of 4 h and supernatants (“intestinal phase” or
216 PBET-i) stored frozen. Controls were performed in triplicate likewise, but in the absence of
217 solids.

218

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

223 Na₂HPO₄, 0.063 g Na₂SO₄, 0.367 g CaCl₂·2H₂O, 0.575 g C₂H₃O₂Na, 2.604 g NaHCO₃ and
224 0.098 g C₆H₈O₇Na₃·2H₂O; and the pH was adjusted to 7.4 using 7 M HCl. In triplicate,
225 samples of 0.4 g were weighed into individual 50 mL polyethylene centrifuge tubes to which
226 40 mL aliquots of SLF were added. The contents were incubated at 37°C for 24 h before 5
227 mL subsamples were processed above but stored under refrigeration.

228

229 A more acidic, artificial lysosomal fluid (ALF) was used to simulate the intracellular
230 conditions with which inhaled particles would be exposed to after phagocytosis by alveolar
231 and interstitial macrophages within the lung (Colombo et al., 2008). The solution was
232 prepared by adding the following (and in the order shown) to 1 L of MQW: 0.051 g
233 MgCl₂·6H₂O, 3.207 g NaCl, 0.299 g KCl, 0.072 g Na₂HPO₄, 0.039 g Na₂SO₄, 0.128 g
234 CaCl₂·2H₂O, 0.078 g C₆H₈O₇Na₃·2H₂O, 6.00 g NaOH, 20.80 g H₂NCH₂COOH, 0.090 g
235 C₄H₄O₆Na₂ and 0.077 g C₃H₄O₃; and the pH was adjusted to 4.4 using 7 M HCl. The
236 protocols for incubation and subsample processing and storage were identical to those
237 described for the SLF exposures above.

238

239 *2.6. ICP analysis of digests and extracts*

240 *Aqua regia* digests and extracts from the physiological extractions were analysed for As and
241 a suite of other elements by inductively coupled plasma-optical emission spectrometry (ICP-
242 OES) using a Thermoscientific iCAP 7400. The instrument was calibrated using four mixed
243 standards and a blank prepared by serial dilution of CPI International standards in 2% HNO₃,
244 and settings in both UV and visible light were as follows: exposure time = 2 s; RF power =
245 1150 W; nebuliser, coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min⁻¹, respectively;
246 viewing height = 12 mm; uptake time = 50 s; wash time = 15 s.

247

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

256

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

261

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

265

266 2.7. Collection and analysis of airborne dusts

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

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

276

277 Filters arising from sampling of PM₁₀ ($n = 5$), along with three blank filters and 250 mg of
278 the certified reference soil, were digested in 6 mL of boiling *aqua regia* as above before
279 being transferred and diluted in a series of volumetric flasks. Digests were analysed for As
280 by inductively coupled plasma-mass spectrometry (ICP-MS) using a Thermoscientific X
281 Series II with a concentric glass nebuliser and conical spray chamber that was calibrated
282 with four standards and a blank and operated under conditions described elsewhere (Turner
283 and Holmes, 2015). The mean concentration of As returned for the reference soil was 3.4 μg
284 g^{-1} and within 15% of the reported consensus value. Arsenic concentrations in the PM₁₀
285 samples are given in ng m^{-3} and have been derived from blank-corrected concentrations in
286 digests and the volumes of air passing through the particulate monitor.

287

288 **3. Results**

289 *3.1. In situ analyses*

290 Figure 1 shows the distribution of As concentrations arising from the in situ analysis of soils
291 and dusts by XRF (and, as necessary, corrected for moisture content determined in the
292 laboratory). Table 2 summarises the concentrations of other elements that were mined in the
293 region (Sn, Pb, Cu), are important indicators of metallic mine pollution (Fe), or are in the
294 same group of the periodic table as the metalloid (Sb, Bi). Note that the measurement
295 detection limits are indicative and based on three counting errors arising from the lowest
296 signals returned by the instrument throughout the measurement campaign, and the number of
297 samples detected (n) has been used to determine the summary statistics shown. Also given in
298 Table 2 are representative concentrations of the elements in soils from the entire Tamar river

299 catchment. These are defined as 50th percentile values determined in top-soils fractionated to
 300 < 2 mm by energy- or wavelength-dispersive XRF and reported by Rawlins et al. (2003).

301
 302 Among the trace elements (i.e. with the exception of Fe), As was detected in the most cases
 303 and displayed the highest mean, median and maximum concentrations. This reflects the
 304 ubiquitous, but heterogeneous, As contamination of the site by the practice and legacy of
 305 historical mining activities. Enrichment of As based on the median concentration relative to
 306 the catchment soil concentration is about 600 and relative to a normal background As
 307 concentration for mineralised soils (290 µg g⁻¹; Middleton et al., 2017), enrichment is about
 308 45.

309
 310 Table 2: Measurement limit of detection (LOD), number of detects and summary statistics
 311 for As and other elements determined by XRF in 98 samples from the DGC region.
 312 Catchment soil concentrations are 50th percentile values reported by Rawlins et al. (2003).

313
 314

	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
<i>n</i>	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

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 319

320 Figure 2 shows the frequency distribution of As concentrations in soils and dusts from the
321 DGC region. The highest concentration of As of about 75,000 $\mu\text{g g}^{-1}$ was found in soil
322 adjacent to the remains of a calciner (site 11); significantly, this is the only location in the
323 region where the public are warned about hazardous concentrations of As and advised to
324 remain on the footpath. Concentrations above 24,000 $\mu\text{g g}^{-1}$ were encountered on or close to
325 spoil heaps that included part of a biking track (site 15), an area which had been shaped into
326 a visitor car park (site 2) and a yard used to store and process timber (site 5). Arsenic
327 concentrations above 16,000 $\mu\text{g g}^{-1}$ were observed more frequently on trails and cycle tracks
328 near to abandoned mines and spoil heaps. Anecdotally (personal communication with locals,
329 2017), a mining spoil heap in the north of the area shown inset in Figure 1 was removed and
330 material distributed along the paths to create the car parking area and access to the spoil
331 heaps for car rallies. Visible inspection (e.g. colour and grain size) and elemental ratios (e.g.
332 Fe:As) of the materials on such access paths provide some support for this assertion.
333 Concentrations above 8,000 $\mu\text{g g}^{-1}$ were found on public routes more frequently and at
334 greater distances from obvious sources of As, including the dusts within the remains of the
335 office buildings now used to display visitor information (site 66). Concentrations below
336 1000 $\mu\text{g g}^{-1}$ (but $> 100 \mu\text{g g}^{-1}$) were encountered at locations farthest from the spoil heaps
337 and towards the periphery of the region, and included soils from a café carpark (sites 82 and
338 83), a small play and picnic area (site 40) and a trail route into a tree surfing facility (site 84).
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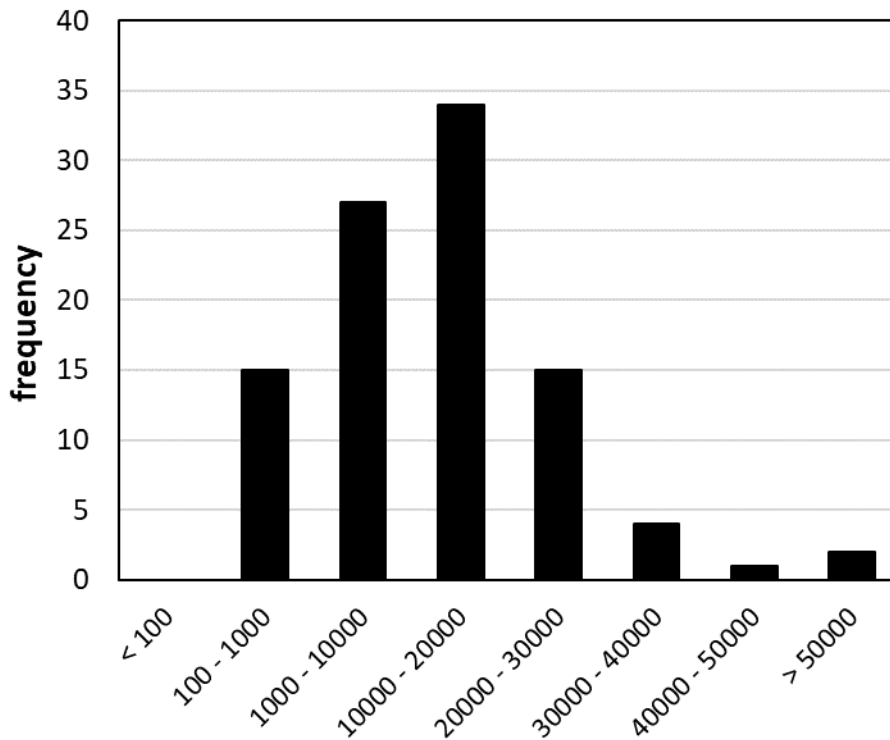


Figure 2: Frequency distribution of As concentrations ($\mu\text{g g}^{-1}$) in soils and dusts of the DGC region and as determined in situ by XRF.

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 $< 63 \mu\text{m}$. 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.

372

373 Concentrations of As extracted by the PBET stomach solution range from about 10 to 3700
 374 $\mu\text{g g}^{-1}$, with bioaccessibilities ranging from < 1 to 23.9%, and concentrations extracted by the
 375 PBET intestinal solution range from about 13 to 1130 $\mu\text{g g}^{-1}$, with bioaccessibilities ranging
 376 from < 1 to 35.3%. In 21 cases As concentrations were higher in the intestinal phase
 377 compared with the preceding stomach phase while in 9 cases concentrations were lower in
 378 the intestinal phase. Arsenic extracted by the SLF exhibited a similar range and distribution
 379 of concentrations and accessibilities as the PBET phases. However, concentrations extracted
 380 by the ALF were significantly greater, often approaching and sometimes exceeding
 381 corresponding concentrations digested in AR and resulting in bioaccessibilities that averaged
 382 around 100% (and data that were close to unit slope in Figure 3).

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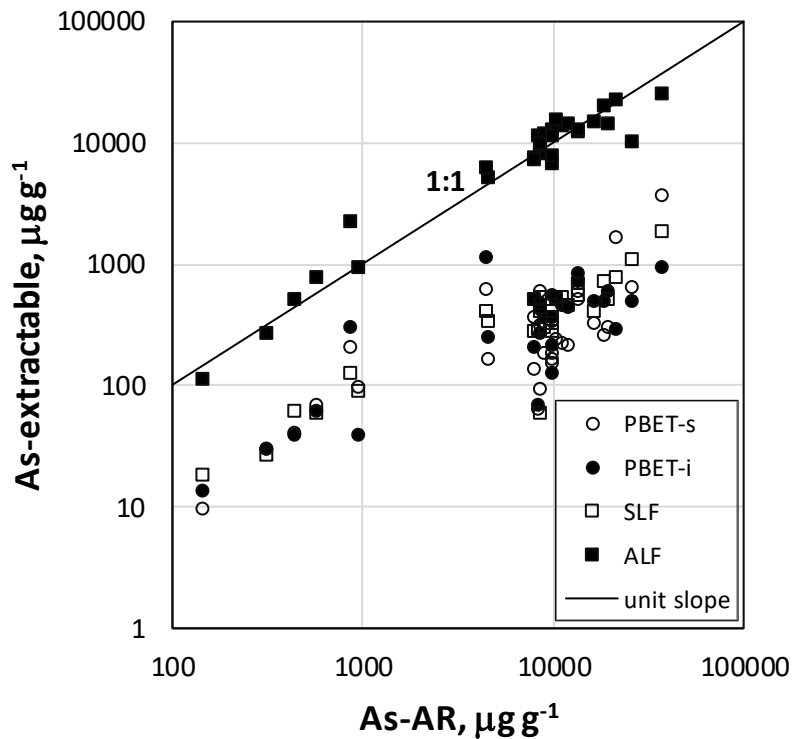
384 Table 3: Concentrations of As in the 30 soil and dust samples (fractionated to < 63 μm) as
 385 determined by ICP following *aqua regia* (AR) digestion or physiological extraction (PBET-
 386 s: stomach phase; PBET-i: intestinal phase; SLF: standard simulated lung fluid; ALF:
 387 artificial lysosomal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

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390

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

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397 Figure 3: Concentrations of As available to the four physiological extractants versus quasi-
 398 total As concentrations digestible in AR for the 30 soil and dust samples (fractionated to <
 399 63 μm) (PBET-s: stomach phase; PBET-i: intestinal phase; SLF: standard simulated lung
 400 fluid; ALF: artificial lysosomal fluid).

401

402 3.3. Airborne dusts

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

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Table 4: Median concentrations of PM₁₀ 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 (PM₁₀) 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 PM₁₀ 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

433 **4. Discussion**

434 The results presented here in terms of both the concentration and oral bioaccessibility of As
435 are broadly similar to those reported by Kavanagh et al. (1997), Klick et al. (2005) and
436 Palumbo-Roe and Klinck (2007) for soils and tailings sampled from the region prior to the
437 construction of the trail network and opening of the facilities to the public. These authors
438 reported a median oral bioaccessibility of 15%, with spatial variability reflecting variations
439 in mineralogy; specifically, As associated with sulphides was less bioaccessible than As
440 associated with Fe oxyhydroxides, with the degree of crystallinity of the latter also believed
441 to have an impact on the precise bioaccessibility. We observed significant relationships ($p <$
442 0.05) between PBET-s bioaccessibilities of As and Fe ($r = 0.593$) and PBET-i
443 bioaccessibilities of As and Fe ($r = 0.827$) suggesting that the oral bioaccessibility of As is at
444 least partly accounted for by the concentration of Fe oxyhydroxides. Measurements in the
445 DGC region have also shown that scorodite, a hydrated iron arsenate, may act as a
446 passivation layer around arsenopyrite grains (Rieuwerts et al., 2014). The dissolution of this
447 mineral increases with pH in the range 3 to 6 (Harvey et al., 2006) which may, therefore,
448 account for the higher extraction of As by the ALF compared with the acidified stomach
449 PBET.

450

451 Health-based soil guideline values for As developed by the Environment Agency (2009a) are
452 $39 \mu\text{g g}^{-1}$ for home gardens, $43 \mu\text{g g}^{-1}$ for allotments and $640 \mu\text{g g}^{-1}$ for commercial land. The
453 present data generated by XRF indicate exceedances of garden and allotment soil guidelines
454 in all cases and exceedance of commercial soil guidelines in 85 of 98 samples. A more
455 appropriate guideline for the land use in the present context, however, is the Category 4
456 Screening Level (C4SL) for park-type soil of $179 \mu\text{g g}^{-1}$; here, land is considered to be
457 recreational but at a sufficient distance from housing that there is negligible tracking back of
458 material (Department for Environment, Food and Rural Affairs, 2014). On this basis, As

459 concentrations in the DGC region measured by XRF exceed the C4SL in all but one sample.
460 Screening levels are, however, predicated on 100% bioavailability and assume that As
461 uptake from soil is equal to intake (Middleton et al., 2017). Significantly, therefore,
462 bioaccessible concentrations of As exceed the C4SL in between 19 (PBET-s) and 30 (ALF)
463 of the 30 soil and dust samples tested.

464

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

473

474 Overall exposure to As in the DGC region depends on the practices undertaken (e.g.,
475 walking, running, horse-riding, cycling, picnicking), the weather conditions, and the length
476 and frequency of visits. For staff, exposure could be a daily occurrence, depending on the
477 location of the work carried out, with the highest risk adjacent to spoil heaps and within the
478 timber storage area. Exposure through ingestion may be most significant if food is consumed
479 on site without hands being washed thoroughly, while exposure through inhalation may be
480 more acute during dry and windy weather or when dusts are disturbed by cyclists on
481 contaminated tracks and vehicles moving in the car parking areas. The ready generation of
482 airborne material is exemplified by reports describing a 100 m high cloud of dust resulting
483 from a four-wheel drive car rally that took place on the site (Hamilton, 2000) and by
484 observations of dust plumes above tailing heaps made by the authors and by other visiting

485 scientists under turbulent conditions (Stokes et al., 2012). Dry weather also appears to
486 promote the formation of efflorescent As salts on the tailing heap surfaces which is then
487 readily transported by wind (Hamilton, 2000). More sustained, indirect exposure may also
488 arise through tracking dust and soil from shoes, clothing and pets into vehicles and homes, a
489 process that is generally more important during wet conditions and winter months (Hunt et
490 al., 2006).

491

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

500

501 Studies reviewed by the Environmental Protection Agency have resulted in best estimates for
502 daily soil and dust ingestion (including inhalation and subsequent swallowing) of 100 mg for
503 children (between 1 and 21 years old) and 50 mg for adults (U.S. EPA, 2011). These values
504 have also been adopted in the Contaminated Land Exposure Assessment (CLEA) model for
505 different land uses and form the basis of soil guideline values (Environment Agency, 2009b).
506 Thus, an adult visiting DGC for a period of six hours and ingesting 12.5 mg of material
507 containing 13,000 $\mu\text{g g}^{-1}$ As (the median concentration determined by XRF) is exposed to
508 163 μg of the metalloid; this is equivalent to 2.3 $\mu\text{g kg}^{-1} \text{ bw day}^{-1}$ for a body weight of 70 kg,
509 or well in excess of the Index dose of minimal risk. For children of 9.8 kg and 19.7 kg,
510 representing average female body weights for age ranges of 1-2 years and 5-6 years,

511 respectively, and employed as default values in the CLEA model, ingestion of 25 mg of
512 material results in a total As exposure of 325 μg which is equivalent to 33 $\mu\text{g kg}^{-1} \text{ bw day}^{-1}$
513 and 16 $\mu\text{g kg}^{-1} \text{ bw day}^{-1}$, respectively, and more than an order of magnitude greater than the
514 dose of minimal risk. Factoring in for median oral or inhalation bioaccessibilities would
515 reduce exposure estimates but would still result in significant exceedances of this risk,
516 especially for young children.

517

518 There is more uncertainty regarding the risk arising from dermal exposure to As from soils
519 and other geosolids, largely because current models assume that uptake is equal to intake, or
520 that all of the contaminant is available to traverse the skin into the systemic circulation
521 (Environment Agency, 2009b; U.S. EPA, 2011). The factors determining uptake according
522 to CLEA are the total concentration of contaminant in soil, the exposed area of skin, the
523 sediment to skin adherence factor and a chemical-specific dermal absorption factor (= 0.03
524 for As). For an As concentration of 13,000 $\mu\text{g g}^{-1}$ and an exposure period of six hours, data
525 reported by the U.S. EPA for an adult 70 kg adult (a passive outdoor adherence factor of 0.1
526 mg cm^{-2} and exposed area of skin consisting of the face, hands, forearms and lower legs of
527 0.53 m^2) yields an intake of 103 $\mu\text{g g}^{-1}$, or about 1.5 $\mu\text{g kg}^{-1} \text{ bw d}^{-1}$. For a child of six years
528 old (a passive outdoor adherence factor of 0.1 mg cm^{-2} and exposed area of skin of 0.21 m^2),
529 a daily intake of 41 $\mu\text{g g}^{-1}$, or about 2 $\mu\text{g kg}^{-1} \text{ bw d}^{-1}$, is predicted. Clearly, the importance of
530 the dermal route of exposure relative to the ingestive pathway depends on the ability of As to
531 mobilise from soil to the skin surface. Nevertheless, it could represent a significant risk if a
532 child or pet were to play in or become covered by wet, contaminated soil, or for a mountain-
533 biker who takes a fall on the spoil heaps.

534

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

537 Monuments and Sites, 2006) and trails management code of conduct (Tamar Valley AONB,
538 2010) mention the potential toxicity of the spoil heaps, with the former document also
539 calling for contamination control to be implemented. That said, significant As contamination
540 is observed more widely, presumably because of the extensive disturbance of the site and the
541 mobility of As-rich waste material, and extends to areas used for car parking, walking and
542 cycling. Clearly, therefore, there is a general risk of As exposure to members of the public
543 on the trails around DGC which is greatest for frequent visitors (as well as maintenance
544 volunteers and workers in the timber industry) and during windy conditions, and for
545 occupants of vehicles and households where contaminated material is regularly tracked in.

546

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

556

557 Any risk to health arising directly from recreational or occupational access to DGC may also
558 exacerbate the long-term exposure of As to residents within the wider region of the
559 Devon/Cornwall mining area. For example, Middleton et al. (2017) reported 69% of soils at
560 residential properties in Cornwall ($n = 127$) exceeded the relevant $37 \mu\text{g g}^{-1}$ As C4SL, and
561 highlighted the potential vulnerability of infants and small children. In addition, a survey of
562 512 private water supplies (out of an estimated 3500) in Cornwall found that nearly 6%

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

565

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

577

578 **5. Conclusions**

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

589

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593

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