

## Field-scale study of the influence of differing remediation strategies on trace metal geochemistry in metal mine tailings from the Irish Midlands

Perkins, W.T.; Bird, G.; Jacobs, S.R.; Devoy, C.

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1 Field-scale study of the influence of differing remediation strategies on trace metal geochemistry in metal mine  
2 tailings from the Irish Midlands.

3  
4 William T. Perkins<sup>a</sup>, Graham Bird<sup>b\*</sup>, Suzanne R. Jacobs<sup>c</sup>, Cora Devoy<sup>d</sup>

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7 <sup>a</sup>Department of Geography and Earth Sciences, Aberystwyth University, Aberystwyth, Ceredigion, SY23 3DB, UK. Tel.:  
8 +44 (0)1970 622636, email: [www@aber.ac.uk](mailto:www@aber.ac.uk)

9 <sup>b</sup>School of Environment, Natural Resources and Geography, Bangor University, Bangor, Gwynedd, LL57 2UW, UK.  
10 Tel.: +44 (0)1248 383222, email: [g.bird@bangor.ac.uk](mailto:g.bird@bangor.ac.uk).

11 <sup>c</sup>Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Kreuzeckbahnstraße 19, 82467  
12 Garmisch-Partenkirchen, Germany. Tel.: +49 8821 183309, email: [Suzanne.jacobs@kit.edu](mailto:Suzanne.jacobs@kit.edu).

13 <sup>d</sup>Lundin Mining UK Ltd, Hayworthe House, Haywards Heath, West Sussex, RH16 1DB, UK

14  
15 \*corresponding author

## ABSTRACT

Mine tailings represents a globally-significant source of potentially harmful elements (PHEs) to the environment. The management of large volumes of mine tailings represents a major challenge to the mining industry and environmental managers. This field-scale study evaluates the impact of two highly contrasting remediation approaches to the management and stabilisation of mine tailings. The geochemistry of the tailings, overlying amendment layers and vegetation are examined in the light of the different management approaches. Pseudo-total As, Cd, and Pb concentrations and solid-state partitioning (*speciation*), determined via sequential extraction, were established for two Tailings Management Facilities (TMFs) in Ireland subjected to: 1) a 'walk-away' approach (Silvermines) and 2) application of an amendment layer (Galmoy). PHE concentrations in roots and herbage of grasses growing on the TMFs were also determined. Results identify very different PHE concentration profiles with depth through the TMFs and the impact of remediation approach on concentrations and their potential bioavailability in the rooting zone of grass species. Data also highlight the importance of choice of grass species in remediation approaches and the benefits of relatively shallow-rooting *Agrostis capillaris* and *Festuca rubra* varieties. In addition, data from the Galmoy TMF indicate the importance of regional soil geochemistry for interpreting the influence of the PHE geochemistry of capping and amendment layers applied to mine tailings.

**KEY WORDS:** mine tailings, metals, phytoremediation, speciation, plant uptake

## 1. INTRODUCTION

The processing of metal ores produces significant quantities of fine-grained mine tailings, making the metal mining industry one of the largest waste producers in the world (Moncur et al., 2005). Mine tailings can contain highly elevated quantities of potentially harmful elements (PHEs), notably As, Cd and Pb (Bird et al., 2010; Nash and Fey, 2007). The storage of mine tailings has been a significant worldwide challenge for the mining industry for many years (CDC, 2007; Shu et al., 2001). Indeed, it is estimated that the production of solid mine waste, such as tailings, is in the region of several thousand million tonnes per year worldwide (Lottermoser, 2010). Challenges arise in relation to ensuring the physical and chemical stability of stored tailings (Hudson-Edwards et al., 2011), which have been described by Sima et al. (2011) as being one of the major sources of hazardous materials leading to the release of metals into the environment.

Metal contamination arising from the release of mine tailings into the environment has been demonstrated following: major tailings dam failures (e.g. Bird et al., 2008), aeolian transport of unconsolidated tailings (e.g. Grandlic et al., 2008) and the chemical leaching of metals (e.g. Palumbo-Roe et al., 2008). Surface and groundwater environments have been shown to be particularly vulnerable to contamination by the release of metals from deposits of mine tailings (Sharma and Al-Busaidi, 2001) as well as other mine drainage (Bearcock and Perkins, 2007; Perkins et al., 2006). In Europe, the environmental risk posed by mine tailings has been further highlighted by the development of the EU Mine Waste Directive (2006/21/EC), which has introduced new requirements for mine waste management in order to improve sustainability of practices, prevent accidents and reduce environment impact. This European legislation is not retrospective so that older, abandoned, mine sites are not subject to its control.

Inherent within effective management of mine tailings are attempts to ensure the physical and chemical stability of tailings and to minimize the release of metals into the local environment (Kim and Jung, 2011; Meggyes et al., 2008). Establishing networks to monitor metal release from tailings facilities is relatively straightforward, however, a much greater challenge is found in attempts to establish methods for effectively remediating mine tailings and minimizing long-term environmental impacts. Work by Pyatt et al. (2000) has demonstrated that metal release from unmanaged mine tailings can continue over 10s to 1000s of years. Remediation of mine tailings has commonly focused on ensuring physical and chemical stability; in the case of the latter, particularly on lowering oxidation rates in pyritic tailings. Revegetation has been identified as a potentially viable approach to tailings remediation (Tordoff et al., 2000). Approaches to this have ranged from direct hydro-seeding of tailings (Martínez-Ruiz et al., 2007), to capping with soil amendments (Palmer, 2006), geotextile membranes (Callery and Courtney, in press), rock backfill (Shu and Bradshaw, 1995).

Given their sedimentological, mineralogical and geochemical properties; mine tailings are very complex and highly reactive materials. Furthermore, they are often present within geochemically dynamic environments. Studies of approaches to tailings remediation have been carried out at a laboratory- and trial-scale (Lindsay et al., 2011; Mench et al., 2003; Mench et al., 2010; Moreno-Jimenez et al., 2011); however, relatively few have sought to evaluate the impact of remediation techniques on tailings geochemistry at the field-scale. The aims of this work are to investigate the longer-term impact of remediation practices on the geochemistry of mine tailings at two sites that have been subject to very different remediation strategies. The study focuses particularly upon the geochemistry of As, Cd and Pb given their noted environmental concern.

## 2. STUDY AREA

Sample collection focused upon two tailings management facilities (TMFs) in Ireland. The Pb/Zn mine at Galmoy in the Irish Midlands features a TMF under differing stages of remediation, ranging from active settling ponds to revegetated tailings (Figure 1). Mining at Galmoy primarily focused on the extraction of Zn and Pb ores in rock matrix

breccias at or towards the base of the Waulsortian Limestone (Lowther et al. 2003) (Balassone et al., 2008). The stratabound ore lenses are predominantly massive sulphides (Balassone et al., 2008), with ore grades ranging from c.10-13.5% (Zn) and c. 0.5-5.5% Pb during the operation of the mine. The sequence of mineralisation at Galmoy consists of a coarse-grained pyrite/marcasite assemblage followed by first, second and third generation sphalerite followed by late pyrite (Lowther et al., 2003). Galmoy's TMF became operational in 1997 and covers an area of c. 0.35 km<sup>2</sup>. This study focused upon Phase 1 of the TMF, which has been filled to capacity with tailings and has been capped with a minimum 30 cm layer of diamicton and vegetated. The capping with diamicton was proscribed by local government with the material sourced from 'borrow pits' adjacent to the TMF. The site also contains thirteen 10 m<sup>2</sup> trial plots that were established in 2002 to evaluate the suitability of differing soil amendments and vegetation species (Table 1) as options for developing a long-term remediation solution.

The Gortmore TMF near Silvermines village (Figure 1) is an older facility than Galmoy, and was constructed in 1967 to store tailings from the processing of Zn and Pb ores at Garryard within the Silvermines mining district. Mining at Garryard produced 10.7 m tonnes of ore grading 7.4% Zn and 2.7% Pb, which produced 9 m tonnes of tailings; 7.7 m tonnes of which were stored in the Gortmore TMF (Stanley et al., 2010). The paragenetic sequence at Silvermines has early hematite/magnetite and barite followed by pyrite/marcasite before the development of sphalerite and galena together with Cu-Ag-As sulphides (Hitzman and Beaty, 2003). The TMF covers an area of 0.77 km<sup>2</sup> and contains a volume of ca. 5 m<sup>3</sup> of material (Stanley et al., 2010). Following the cessation of mining activity in 1982, the TMF was effectively abandoned with little attention paid to remediation efforts. A dust-blow event in 1985 prompted attempts to vegetate the TMF surface through the simple addition of grass seed (Stanley et al., 2010), however, the vegetative cover is generally in poor condition, with evidence of ponding of rainwater. Release of metals from the site via drainage and wind-blown material have been the focus of environmental concerns (e.g. Aslibekion et al., 1999) and Pb concentrations in the upper 10 cm of the TMF have been previously reported as being in excess of 5000 mg kg<sup>-1</sup> (McGrath et al., 2004). Mineralization at Silvermines is hosted predominantly within the basal Waulsortian Limestone and the underlying Ballysteen Limestone which lies on the basement rocks consisting of Silurian and Devonian Old Red Sandstone (Hitzman and Beaty, 2003). The geology of the area is dominated by the Silvermines Fault complex that was active during sedimentation and mineralization (Taylor and Andrew, 1978). The Zn and Pb sulphide ores are associated with non-sulphide deposits and are generally present in a stratabound morphology (Balassone et al., 2008).

### 3. SAMPLING AND ANALYTICAL METHODS

Sampling focused upon three broad locations: 1) the remediated phase of the Galmoy TMF, 2) the 13 trial plots established at Galmoy Mine, and 3) the Gortmore TMF near Silvermines. At Silvermines and the Galmoy trial plots push cores of a minimum 17 cm depth were collected through the overlying material and into the underlying tailings. At Silvermines, samples sites (n = 5) were spaced equidistantly along the centre of the TMF (Figure 1). On the Galmoy TMF (n = 4), given the depth of diamicton coverage, a pit was dug through this material to allow sampling through the overburden and the recovery of a core through the base of the pit into the underlying tailings. Samples of vegetation cover (roots and herbage) were collected from the Galmoy and Silvermines TMFs at the site of each core. Herbage refers to the above-ground portion of the plant.

#### 3.1. Analysis of particulate samples

All cores were cut into 2 cm sections and all samples were air-dried, disaggregated and sieved through a stainless steel mesh to isolate the <2mm fraction, which was retained for subsequent analysis. The pH of samples was determined by pH electrode (Hannah Instruments pH209) in a solution containing sample and deionized water in a 1:2.5 (w:v) ratio. Organic matter content was quantified in a sub-set of samples (providing on average 4 determinations per core) by the ignition of sample material at 375°C for 16 hours (Ball, 1964), the ash residue was

193 then further ignited at 850°C for 1 hour with any further loss taken as being representative of carbonate content  
194 (Avery and Bascomb, 1974). Whilst commonly being termed organic matter content, it must be noted that ignition of  
195 the sample may also cause mass loss from sulphides, especially in samples of tailings. Samples were digested in  
196 concentrated aqua regia (HCl and HNO<sub>3</sub> in a 3:1 v/v ratio) with pseudo-total concentrations of As, Cd and Pb  
197 determined by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). Accuracy (Table 2) and precision of  
198 analyses was monitored by the repeat analysis of the CANMET Till2 certified reference material (CRM). Precision was  
199 found to be 8.4% (As), 9.4% (Ca), 13.5% (Cd with concentrations < 0.5 mg kg<sup>-1</sup>) and therefore generally below the  
200 10% threshold commonly adopted by analysts (Hamilton, 1980).

201  
202 A selection of samples (n = 155) were digested in 0.11 Moles L<sup>-1</sup> acetic acid to provide an indication of As, Cd and Pb  
203 concentrations that could be considered as being potentially mobile and available for plant uptake (Bjerre and  
204 Schierup, 1985; Loring, 1981). Elemental concentrations were determined by ICP-MS. Analytical precision was  
205 monitored by the analysis of duplicate samples and found to be 9.5% (As and Pb) and 9.4% (Cd). Instrumental  
206 accuracy, determined by analysis of standard solutions was 1.6% (As), 3.1% (Cd) and 7.2% (Pb).

### 207 208 **3.2. Analysis of herbage samples**

209 The herbage samples were divided into root and above ground portions. Sediment was removed from the roots by  
210 repeated washing in milli-Q H<sub>2</sub>O. All herbage samples were then subjected to sonication in a 0.05 % (v/v) solution of  
211 Triton X100 for 10 minutes before being rinsed three times with milli-Q H<sub>2</sub>O. The samples were dried at <40°C before  
212 being milled to < 1 mm in an IKA MF 10.1 mill. Sub-samples of the milled herbage (0.25 g) were subjected to a rapid  
213 digestion procedure after Hustead (2004), where 5 mL of 50% (v/v) HNO<sub>3</sub> was added to the sample, in a 50 mL pyrex  
214 boiling tube, which was heated to 180-190°C for 10 minutes. The tubes were then cooled and 2.5 mL of  
215 concentrated HNO<sub>3</sub> was added before the tubes were covered and heated at 100°C for 1 hour. Finally the cooled  
216 solutions were filtered through Whatman number 1 filter papers and made up to 50 mL before being transferred to  
217 30 mL LDPE bottles for storage.

### 218 219 **3.3. Sequential extraction procedure**

220 Finally, 28 samples were subjected to the BCR (Bureau of Community Reference) sequential extraction procedure  
221 (SEP) in order to evaluate the solid-state partitioning or *speciation* of PHEs (Quevauviller et al., 1993; Rauret et al.,  
222 1999). The four extractants used were: 1) 0.11 Moles L<sup>-1</sup> acetic acid, 2) 0.5 Moles L<sup>-1</sup> NH<sub>2</sub>OH.HCl, 3) 8.8 Moles L<sup>-1</sup>  
223 H<sub>2</sub>O<sub>2</sub>, and 4) concentrated *aqua regia*. This gave partitioning in four operationally-defined phases analogous to: 1)  
224 exchangeable, 2) Fe/Mn oxides, 3) organic matter/sulphides, and 4) residual metal forms. All supernatants were  
225 decanted into acid-washed plastic bottles and refrigerated prior to analysis. Between each phase of the SEP,  
226 samples were washed using 10 mL Milli-Q water. All reagents used were of Analar quality and reactions were  
227 performed in acid-washed 50 mL HDPE centrifuge tubes. Recovery of the SEP was determined by comparison of  
228 summed concentration in the four phases with values determined by a single *aqua regia* digest of blind duplicate  
229 samples (Bird et al., 2003; Li and Thornton, 2001). Recovery rates for the SEP ranged from 96 - 120 with a mean  
230 recovery of 111%. Precision of the SEP, determined by analysis of duplicate samples (n = 5) was found to be 9.9%  
231 (As), 9.3% (Cd) and 8.3% (Pb).

## 232 233 **4. RESULTS AND DISCUSSION**

### 234 235 **4.1. pH, organic matter and carbonate content**

236  
237 The pH of material in the Silvermines TMF is generally lower than that at Galmoy (Table 3) with minimum (5.71),  
238 median (6.61) and maximum (7.38) pH values all lower than those at Galmoy (6.75, 7.39 and 8.37 respectively). This  
239 may be explained by lower carbonate content in material from the Silvermines TMF (4.8-18.7%) as well as the  
240 greater abundance (32.8%) of pyrite within the Silvermines tailings (Jordan and Mullen, 2006), compared to that in

241 ore at Galmoy (5-17%) (Hallewell et al., 2005). . Whilst the carbonate contents of material at the two locations are  
242 not statistically significantly different (Mann Whitney U Test;  $p = 0.1055$ ), the Galmoy TMF and Galmoy trial plots  
243 contain higher mean and maximum carbonate content, which reflects the carbonate-dominated host geology  
244 (Balassone et al., 2008). Down profile trends in organic matter content are similar in all core samples from Galmoy,  
245 with highest organic matter content in the upper cores. At Galmoy maximum organic matter content ranges from 10  
246 % to 18.5 % within the soil layers, reducing to less than 2 % in the underlying tailings material. The organic matter  
247 content of the Galmoy trial plots (Figure 2), which were constructed with 10-15 cm soil covering is generally higher  
248 than that of the Silvermines tailings pond (Figure 3) and certainly contains higher organic matter content at depth.  
249 For example, at 8-10 cm depth, mean organic matter content in the Galmoy trial plots is 6.4% compared to 0.7 % at  
250 Silvermines. The Galmoy TMF has organic matter content of 0.1-22% with greatest amounts in the upper 15 cm of  
251 the introduced capping material. On the basis of the mean % organic matter content, soils present on the Galmoy  
252 trial plots and Galmoy and Silvermines TMFs could be classed as mineralized, whereas peak % organic matter values  
253 in the upper profiles would be classified as humose (Ball, 1964). Lower organic matter content at Silvermines  
254 compared to Galmoy is likely to reflect both the differences in treatment and associated differences in vegetation  
255 development and creation of soil organic matter. The cores collected at Silvermines are characterised by an orange  
256 Fe-rich (average Fe content of 0.23%) layer (Munsell colour classification 5YR 6/5) of up to 15 cm thick that is located  
257 from approximately 5cm depth in the cores. This layer was clearly observable during sampling.  
258

#### 259 **4.2. Pseudo-total PHE concentrations**

260  
261 In the Galmoy trial plots PHE concentrations range from 11-2440 mg kg<sup>-1</sup> As, 0.7-39 mg kg<sup>-1</sup> Cd and 31-2600 mg kg<sup>-1</sup>  
262 Pb. The peak concentrations in the trial plots all occur in the lower profiles at 8-10 cm depth or below (Figure 4).  
263 Non parametric significant different analysis (Kruskall-Wallis H-Test) indicates that there is no significant difference  
264 in As or Pb concentrations between the thirteen different trial plots. Whilst higher concentrations in the underlying  
265 tailings are common to all plots, the analysis suggests that the type of amendment layer and vegetation cover has  
266 not resulted in statistically significant differences in As and Pb concentrations throughout the whole cores. The same  
267 analysis indicates that Cd concentrations are significantly lower ( $p < 0.05$ ) in trial plots GT4 and GT10, although there  
268 is no significant difference in Cd concentrations amongst the remaining eleven plots. Unfortunately sample  
269 populations are too small to robustly analyse for significant differences between PHE concentrations in the  
270 amendment layers. However, non-parametric significant difference analysis (Mann-Whitney U Test), indicates that  
271 pseudo-total PHE concentration in the amendment layers are significantly lower ( $p < 0.05$ ) than in the underlying  
272 tailings.  
273

274 In samples collected from the Galmoy TMF concentrations range from 2-3200 mg kg<sup>-1</sup> As, 0.25-122 mg kg<sup>-1</sup> Cd and  
275 11-21400 mg kg<sup>-1</sup> Pb (Figure 5). The peak Pb concentration represents a single value of that magnitude, with the  
276 upper value in the remainder of samples being 9700 mg kg<sup>-1</sup>. As with the trial plots, maximum values occur at depth  
277 (below 50 cm) within the tailings material; characterized by higher carbonate content, indicative of the carbonate  
278 gangue material that constitutes much of the tailings material. The chemical data presented here demonstrate that  
279 the volume percentage of galena and sphalerite in the tailings material analysed range up to 2.3 and 4 % respectively  
280 with typical values being c.0.7 and c.2.2%, respectively. At Silvermines, mean (492 mg kg<sup>-1</sup>) and peak (1040 mg kg<sup>-1</sup>)  
281 As concentrations are lower than those at Galmoy, however minimum, mean and peak, Cd and Pb concentrations  
282 are higher at Silvermines (Table 3). Data indicate that the Silvermine tailings contain volume percentages of galena  
283 and sphalerite with typical values c. 0.12% and c.1.5%, respectively. Non-parametric significant difference analysis  
284 (Mann-Whitney U Test) indicates that Cd ( $p=0.0007$ ) and Pb ( $p=0.0009$ ) concentrations in Silvermines and Galmoy  
285 samples are significantly different.  
286

287 Arsenic and Pb concentrations in the Galmoy trial plots and TMF are strongly positively correlated carbonate content  
288 (Table 4). Reference to Figs. 3 and 4 show that in the trial plots this correlation has a clear vertical pattern which we

289 interpret to indicate the boundary between the amendment layer and the underlying tailings (at the time of  
290 sampling). The strength of correlation coefficients for the relationships between trace metal concentrations and pH,  
291 organic matter and carbonate content are notably lower for Silvermines than Galmoy. For samples for which loss on  
292 ignition data is available, there are statistically significant correlation relationships between organic matter content  
293 and Pb concentration ( $r = 0.69$ ) and carbonate content and Cd concentration ( $r = -0.70$ ).

294  
295 The presence of elevated As concentrations, particularly within the tailings material, suggests the presence of  
296 arsenic-bearing minerals within the mined and processed material. Hitzman and Beaty (1996) state that iron  
297 sulphides are abundant in Silvermines and Galmoy with ores containing from 10 to 20% Fe and that most Irish zinc  
298 deposits contain minor arsenic-rich, antimony-poor tennantite as well as a number of Pb-As-Ag sulphosalt minerals.  
299 Elevated Pb concentrations, certainly within tailings material, are to be expected given the presence of Pb  
300 mineralization, whilst elevated Cd is believed to present in association with ZnS mineralization.

301  
302 In the Galmoy trial plots and TMF, samples collected in the upper 10 cm and 50 cm, respectively comprise those  
303 collected within the layers of applied overburden. Within the trial plots, concentrations of As (20-2440 mg kg<sup>-1</sup>), Cd  
304 (0.7-32 mg kg<sup>-1</sup>) and Pb (11-1540 mg kg<sup>-1</sup>) in the upper 10 cm are generally lower than those in material below. In the  
305 Galmoy TMF, concentrations of As (3-267 mg kg<sup>-1</sup>) Cd (0.3-5.7 mg kg<sup>-1</sup>) and Pb (19-985 mg kg<sup>-1</sup>) are generally lower  
306 than in material from greater than 50 cm depth; certainly in the case of maximum concentrations. However, it is  
307 apparent that whilst concentrations in the coverings applied to the tailings material concentrations are lower than  
308 material below, particularly As concentrations in these upper layers often exceed critical concentrations for soils  
309 reported by Kabata-Pendias and Pendias (2001) (Table 5). Of the total number of samples collected between 0 and  
310 10 cm or 0 and 50 cm depth in the trial pits and TMF respectively ( $n=80$ ), only 23% of samples have As  
311 concentrations below 20 mg kg<sup>-1</sup>. Exceedence of critical Cd (30% of samples) and Pb (52% of samples) concentrations  
312 is lower, but still present. Concentrations of As, Cd and Pb in the applied soil layers at Galmoy also exceed the  
313 national average concentrations for Irish soils (Table 5) by up to 24 (As), 8 (Cd) and 10 (Pb) times with respect to  
314 average concentrations.

315  
316 Cadmium and Pb concentrations at Silvermines are higher than at Galmoy and mean PHE concentrations at  
317 Silvermines are 54 (As), 52 (Cd) and 73 (Pb) times higher than average concentrations determined in Irish soils. All  
318 samples from the Silvermines TMF contain As, Cd and Pb at concentrations above the critical range for soils (Table  
319 5). Unlike at Galmoy, in cores recovered from the Silvermines TMF, peak concentrations occur in the upper 5 cm  
320 (Figure 6). These peak concentrations constitute enrichment factors of 115 (As), 256 (Cd) and 561 (Pb) times above  
321 Irish average concentrations. Whilst the Silvermines TMF has not been subject to extensive capping with  
322 overburden, one may expect highest metal concentrations to be associated with tailings material at depth. However,  
323 the presence of peak metal and As concentrations in the upper 5 cm of the Silvermines TMF indicates that there has  
324 been the enrichment of metal levels within material in the upper core. Importantly, these highly elevated  
325 concentrations will be in the rooting zones for vegetation cover and may help to explain the generally poor nature of  
326 vegetation cover on the Silvermines TMF (Environmental Protection Agency, 2004). The exact cause of enrichment in  
327 the upper profile is unknown, however, it possible that the Fe-rich layer identified previously may be acting as a  
328 focus for PHE-enrichment, perhaps from pore-water.

#### 329 330 **4.3. Acetic Acid-soluble PHE concentrations and speciation**

331 Within the Galmoy trial plots acetic acid-soluble PHE concentrations are in the range <0.1-3.4 mg kg<sup>-1</sup> (As), 0.1-16 mg  
332 kg<sup>-1</sup> (Cd) and 0.2-1340 mg kg<sup>-1</sup> (Pb). These concentrations are broadly similar in the Galmoy TMF (Table 3), however  
333 the maximum Pb concentration in the TMF is somewhat higher at 6800 mg kg<sup>-1</sup>. As seen with pseudo-total  
334 concentrations, acetic acid-soluble As is lower in the Silvermines TMF (<0.1-1.9 mg kg<sup>-1</sup>), whilst Cd (1.2-33 mg kg<sup>-1</sup>)  
335 and Pb (30-4100 mg kg<sup>-1</sup>) concentrations are similar to, or moderately higher, at Silvermines. Calculating the acetic-  
336 acid soluble concentration, i.e. that which could be termed potentially bioavailable (Loring, 1981), as a percentage of

337 the pseudo total concentration (Table 3) indicates that on average acetic acid-soluble As concentrations are less than  
338 2% of the pseudo-total concentrations. Importantly, coupled with the relatively low acetic-acid-soluble As  
339 concentrations, this would suggest that As will be largely unavailable for plant uptake. This is further supported by  
340 speciation data that indicated As is predominantly present in the residual phase at all sites (Figure 7). Highest  
341 percentage partitioning of As in the residual phase generally occurs in material with the highest total As  
342 concentrations, which in the case of the Galmoy trial plots and TMF is the tailings material at depth and at  
343 Silvermines material in the upper 10 cm. Exceptions to the dominance of the residual phase occur in the upper parts  
344 of the Galmoy trial plots and TMF (Figure 7). Overall, it is apparent that As is strongly bound within mineral  
345 structures, will be relatively immobile and be of lower environmental significance (c.f. Bird et al., 2003) than the  
346 pseudo-total concentrations alone may suggest. It should be noted however, that acid generation in tailings may  
347 increase the potential for the dissolution of some tightly-bound PHEs. For example, tailings at Silvermines have been  
348 reported as having an acid producing potential of 221-474 kg CaCO<sub>3</sub>/tonne of tailings (Golder Associates,  
349 unpublished).

350  
351 On average acetic acid-soluble Cd concentrations are 28% (Galmoy trial plots), 22% (Silvermines TMF) and 9%  
352 (Galmoy TMF) of pseudo-total concentrations. Cadmium is known to be a generally mobile element (Beesley et al.,  
353 2010) and therefore its greater presence in the more loosely-bound exchangeable phase (Figure 8) is unsurprising.  
354 Importantly, the depth of maximum acetic acid-soluble concentrations in each core is on average 16 cm in the  
355 Galmoy trial plots, 10 cm on the Silvermines TMF and at >1 m depth on the Galmoy TMF. Certainly in the case of  
356 Galmoy, this would mean that material containing the highest weakly-bound Cd occurs in the lower part of the  
357 profiles. In the upper profiles at Galmoy, Cd is mostly associated with the Fe/Mn oxides and organic matter/sulphide  
358 phases. At Silvermines, whilst the maximum Cd partitioning occurs at 0-2 cm depth in core SC4 (90% associated with  
359 the Fe/Mn oxide phase), mean Cd partitioning at Silvermines is greatest with the organic matter/sulphide phase  
360 (Figure 8). The low organic matter content in sub-surface samples (0.8%) at Silvermines, may indicate that this  
361 partitioning is associated particularly with sulphides (Bird et al., 2008).

362  
363 Lead is generally predominantly associated with the Fe/Mn oxide phase in the surface samples (< 10 cm) at both  
364 Galmoy and Silvermines (Figure 9) and mirrors findings of other studies into the speciation of Pb (e.g. Gomez-Alvarez  
365 et al., 2011; Reis et al., 2012). The importance of Fe/Mn oxides in the partitioning of Pb is particularly dominant in  
366 higher pH environments (Terzano et al., 2007) such as those found at Galmoy (pH range of 7.02-8.1). With increasing  
367 depth the importance of the Fe/Mn oxide phase reduces, with greater proportions of Pb present in the  
368 'exchangeable' at all sites (Figure 9), mirroring in the case of Galmoy, an increase in PHE concentrations. The role of  
369 the organic matter/sulphide phase and residual phases also increases at depth at Galmoy, with the former phase  
370 likely to be residues of Pb sulphide minerals present within tailings material. On average acetic acid-soluble Pb  
371 concentrations peak at 20 cm depth in the Galmoy trial plots and >1 m depth on the Galmoy TMF. For Silvermines,  
372 peak acetic acid-soluble Pb concentrations occur on average at 8 cm depth with these concentrations representing  
373 0.4-94% of the pseudo total concentration.

#### 374 **4.4. Potential uptake to plants and implications for TMF remediation**

375  
376 In samples of roots and herbage from the Galmoy and Silvermines TMFs, PHE concentrations are lower in the  
377 herbage than in roots (Figure 10). At Silvermines PHE concentrations in herbage are 0.6 – 57 times greater in the  
378 roots, whilst at Galmoy the enrichment in the roots compared to the herbage is lower (0.5 - 11). The much higher  
379 PHE concentrations in the root matter on the Silvermines TMF (e.g. up to 670 mg kg<sup>-1</sup> Pb), is very likely to reflect the  
380 location of peak Pb concentrations in the growing media, which occur within the upper 5 cm. In contrast, maximum  
381 PHE concentrations in root material growing on the Galmoy TMF, subject to a ≥30 cm amendment layer and with  
382 maximum PHE concentrations at >50 cm depth, are 7 – 13 times lower than those at Silvermines (Figure 10).  
383 Calculation of a bioconcentration factor (BCF) (equation 1) suggests no accumulation of PHEs in the roots of grass  
384 growing on the Galmoy and Silvermines TMF (Table 6), as BCFs are <1 (Serbula et al., 2014), indeed, whilst root PHE

385 concentrations are higher at Silvermines, maximum BCFs are lower than for Galmoy, given the very high PHE  
386 concentrations in the growing medium. The data suggest that grass species growing on the Silvermines and Galmoy  
387 TMFs are relatively successful in excluding PHEs, taken up by the roots, from transferring to the remainder of the  
388 plant. Translocation factors (TF; equation 2) are <1 at Silvermines suggesting that there has not been transfer of  
389 PHEs from roots to herbage. At Galmoy all TFs <1, with the exception of one site each for Cd (TF = 1.19) and Pb (TF =  
390 2.12), which suggests that there has been some limited uptake of Cd and Pb to herbage. With the exception of Pb in  
391 herbage at Silvermines, maximum PHE concentrations in herbage on the Galmoy and Silvermines TMFs are within  
392 the normal ranges for plants (Table 5) and all maximum PHE concentrations are below the upper threshold of the  
393 concentration ranges that could be considered excessive in leaf tissue (Table 5). Low TFs bode well for potential  
394 future use of remediated TMFs for uses including pastoral agriculture even at Silvermines where the soil layer is very  
395 thin.

$$BCF = C_{root}/C_{soil} \quad \text{Equation 1}$$

399 Where  $C_{root}$  is the PHE concentration in the roots and  $C_{soil}$  is the PHE concentration in soil.

$$TF = C_{shoot}/C_{root} \quad \text{Equation 2}$$

403 Where  $C_{shoot}$  is the PHE concentration in the shoots and  $C_{root}$  is the PHE concentration in roots.

405 Whilst there is no As and Cd herbage data for the Galmoy trial plots, analysis of Pb concentrations in herbage from  
406 the Galmoy trial plots (Galmoy Mines Ltd, unpublished) indicates that these are highest in herbage collected in the  
407 spring-time (Figure 11). Average Pb concentrations in the herbage of the different plots ranged from 7.4 mg kg<sup>-1</sup> to  
408 27.1 mg kg<sup>-1</sup>, with the highest average (and maximum concentration: 94 mg kg<sup>-1</sup>) occurring in plot 7, which had a 15  
409 cm coverage of topsoil but no addition of compost. The lowest average concentration is found in herbage from plot  
410 4, which also has the lowest variability in concentrations between sample periods (standard deviation of 3.1). Plot 4  
411 has thicker (15 cm) addition of topsoil and compost and was sown with the *Festuca rubra Pernille* grass variety. This  
412 variety was also sown in plots 6A and 6B (along with *Poa compressa Reubens*) but with thinner top soil additions of 8  
413 cm and 13 cm, respectively. However, mean Pb concentrations in plots 6A and 6B are still lower than those in eight  
414 other trial plots that were given thicker amendment layers, but sown with different grass varieties. Lead  
415 concentrations were found to be generally highest in April, previous studies of Pb uptake to grasses grown on  
416 contaminated soils and tailings have found concentrations to be highest in winter months (e.g. Crilly et al., 1998;  
417 Smith et al., 2009), which may influence the suitability of such land for use in grazing at certain times of the year.  
418 What is also apparent is that ingestion of PHEs by animals grazing on such grass may occur from soils adhering to the  
419 grass as much as from PHEs within the plant.

421 The lower concentrations in the Galmoy TMF herbage, and in the trial plots compared to herbage grown on metal  
422 rich soils reported by other studies, are indicative of the importance of soil cover thickness and plant species in  
423 influencing the potential for plant uptake. The thicker amendment layer of the TMF, with its lower Pb  
424 concentrations, provides a more effective barrier against plant uptake of Pb (and other PHEs) in underlying tailings.  
425 Data collated by Canadell et al. (1996) for over 90 species of temperate grass growing on various soil types  
426 demonstrates a maximum rooting depth of 1.2-6.3 m, which would potentially give rise to root penetration into  
427 underlying tailings material. However, *Agrostis capillaris* and *Festuca rubra*, which were the species planted at  
428 Galmoy are species that have predominantly shallow root systems. Bolinder et al. (2002) reported that *Agrostis*  
429 *capillaris* has 80% of its root volume within the upper 15cm of the soil profile, whilst Brown et al. (2010)  
430 demonstrated that the root volume of *Festuca rubra* in the upper 7.6 cm of the soil profile ranged from 61-66%.  
431 Data presented by Courtney (2013) for Pb concentrations in *Agrostis capillaris* and *Festuca rubra* growing on bare  
432 tailings were on average 1243 mg kg<sup>-1</sup>, much higher than at Galmoy and demonstrating the benefits of an

433 amendment layer. The data from Galmoy indicate that a 15 cm amendment layer may not be sufficient to prevent  
434 Pb uptake into herbage exceeding normal levels and that a thicker, although more expensive, amendment layer is  
435 preferable. What is apparent, is that whilst mean PHE concentrations in herbage from the Galmoy TMF are within  
436 the normal range for leaf tissue, despite a  $\geq 30$  cm amendment layer, detectable PHE concentrations are present.  
437 Data have shown that the amendment layer on the Galmoy TMF does contain As concentrations above critical soil  
438 concentration (Table 5). Whilst it is possible that the As, and other PHEs, are sourced from the underlying tailings, it  
439 is also possible that the PHEs represent natural geogenic loading to the material in its source area. It is unknown  
440 exactly where the diamicton used for the amendment layer was sourced from, however, the Galmoy mine lies on the  
441 north-west edge of an area of higher soil As concentrations; as identified in the Soil Geochemical Atlas of Ireland (Fay  
442 et al., 2007). Soil As concentration in the Galmoy area ( $9.1\text{-}12\text{ mg kg}^{-1}$ ), generally lie within the 75th percentile of  
443 nationally-monitored concentrations, with soil As levels increasing to  $>15\text{ mg kg}^{-1}$  within c. 50 km. Whilst, further  
444 work is required firmly to establish the source of As in amendment layers; the data highlight the importance of  
445 awareness of the geochemistry of amendments layers during remediation projects, as well as the geochemistry of  
446 waste material.

## 447 448 **5. CONCLUSIONS**

449  
450 Determination of PHE concentrations from two differently-managed and remediated TMFs, has identified clear  
451 resultant differences in the geochemistry of TMF materials and vegetation growing upon them. A walk-away  
452 approach results in a PHE-rich environment, notably within the upper portions of the tailings material and resulted in  
453 high PHE concentrations particularly in the roots of grasses growing on the TMF, despite relatively low % occurrence  
454 of more loosely-bound species. Application of an amendment layer has been shown to create a rooting zone with  
455 much lower PHE concentrations and result in grasses growing in that material having PHE burdens of up to 13 times  
456 less. Data from this study suggest that remediation strategies should carefully consider the depth and geochemistry  
457 of applied amendment layers, particularly in relation to the rooting characteristics of vegetation intended for  
458 planting; and that shallow-rooting (grass) species offer distinct advantages in reducing metal uptake from material  
459 below amendment layers. In addition, Pb concentrations in grass varieties grown upon amended tailings have  
460 demonstrated a tendency for higher concentrations during spring months; this may be of relevance where  
461 revegetated tailings is intended for future use for animal grazing.

## 462 463 **ACKNOWLEDGEMENTS**

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468 research and during fieldwork at Galmoy.  
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481 Table 1. Grass types and organic substrates used in trial plots at Galmoy mine.

Plot	Substrate	Grass variety	Plot	Substrate	Grass variety
1	Bare tailings	Bardot, Barclay, Providence, Merlin	7	Topsoil (15 cm)	Bardot, Barclay, Providence, Merlin
2	Topsoil & compost (10cm)	Barclay	8	Topsoil & compost (13 cm)	Highland
3	Topsoil & compost (13 cm)	Barcrown	9	Topsoil & compost (15 cm)	Bardot
4	Topsoil & compost (15 cm)	Pernille	10	Topsoil & compost (15 cm)	Providence
5	Topsoil & compost (13 cm)	Merlin	11	Topsoil & compost (15 cm)	Heriot
6a	Topsoil & compost (13 cm)	Pernille & Reubens	12	Topsoil & compost (15 cm)	Reubens
6b	Topsoil (8 cm)	Pernille & Reubens			

482 Bardot: Colonial Bentgrass (*Agrostis capillaris*)

483 Barclay: Perennial Ryegrass (*Lolium perenne*)

484 Providence: Bentgrass (*Agrostis capillaris*)

485 Merlin: Bentgrass (*Agrostis capillaris* 'merlin')

486 Barcrown: Red Fescue (*Festuca rubra*)

487 Pernille: Red Fescue (*Festuca rubra*)

488 Reubens: Canada Bluegrass (*Poa compressa*)

489 Highland: Highland Bentgrass (*Agrostis capillaris*)

490 Heriot: Browntip Bentgrass (*Agrostis capillaris*)

491

492 Table 2. Analytical Quality Control of aqua regia digest versus CANMET Till2 CRM.

	As	Cd	Pb
Aqua Regia digests of CANMET Till2 CRM			
Certified (mg kg <sup>-1</sup> )	22	0.3	21
Measured (mg kg <sup>-1</sup> )	17±1.4	0.37±0.04	26±2.3

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512 Table 3. Mean\* and range of soil properties and PHE concentrations in samples from Galmoy and Silvermines.

	Galmoy trial plots	Galmoy TMF	Silvermines TMF
<i>Soil properties</i>			
<i>n</i>	66	26	30
pH	7.47 (7.02 – 8.1)	7.39 (6.75 – 8.37)	6.61 (5.71 – 7.38)
Organic matter (%)	6.6 (0.2 - 18.5)	5.1 (0.1 – 22)	3.36 (0.1 – 29.6)
Carbonates (%)	15.6 (4.2 – 32)	16 (6.1 - 36)	11.3 (4.8 – 18.7)
<i>Pseudo-total PHE content</i>			
<i>n</i>	127	46	56
As (mg kg <sup>-1</sup> )	820 (11 – 2450)	1040 (2 – 3230)	500 (190 – 1040)
Cd (mg kg <sup>-1</sup> )	11 (0.7 – 40)	22 (0.2 – 120)	31 (13 – 150)
Pb (mg kg <sup>-1</sup> )	930 (31 – 2600)	2760 (12 – 21500)	2280 (620 – 125200)
<i>Acetic acid-soluble PHE content</i>			
<i>n</i>	67	30	30
As (mg kg <sup>-1</sup> )	0.8 (0.1 – 3.4)	0.9 (<0.1 – 4.5)	0.2 (<0.1 – 1.9)
Cd (mg kg <sup>-1</sup> )	3.8 (0.1 – 17)	4.2 (<0.1 – 10)	7 (1.2 – 33)
Pb (mg kg <sup>-1</sup> )	99 (<0.1 – 1340)	2013 (5 – 6800)	1320 (30 – 4120)

513 \*median in the case of pH

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Table 4. Correlation coefficients for the relationship between pH, organic matter (OM) and carbonate content with PHE concentrations

	Galmoy trial plots			Galmoy TMF			Silvermines TMF		
	As	Cd	Pb	As	Cd	Pb	As	Cd	Pb
pH	-0.48**	-0.56**	-0.51**	-0.57**	-0.62**	-0.62**	-0.32	-0.14	0.12
OM	-0.82**	-0.75**	-0.77**	-0.35	-0.32	-0.26	0.3	0.33	0.71**
Carbonate	0.78**	0.79**	0.70**	-0.51**	-0.58**	-0.56**	-0.47**	-0.72**	-0.29

519 \*Significant at 95% confidence level.

520 \*\*Significant at 99% confidence level.

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Table 5. Summary of mean (with range in brackets) PHE concentrations in Irish soils and threshold PHE concentrations in soils and plants (concentrations in mg kg<sup>-1</sup> except for pH).

Sample	As	Cd	Pb	pH
Irish soils <sup>a, b</sup>	9.04 / 7.25 (0.2-122.7)	0.56 / 0.33 (0.02-15)	31 / 24.8 (1.1-2634)	5.33 / 5.3 (3.2-7.7)
Critical soil concentration <sup>c</sup>	20-50	3-8	100-400	--
Excessive concentrations in leaf tissue <sup>d</sup>	5-20	3-30	30-300	--
Normal range in plants <sup>c</sup>	0.02-7	0.1-2.4	0.2-20	--

529 <sup>a</sup>Environmental Protection Agency. Samples digested in a mixture of HF, HClO<sub>4</sub>, HCl and HNO<sub>3</sub> acids with analysis by ICP-MS (n = 1310).

530 <sup>b</sup>50<sup>th</sup> percentile value given in italics

531 <sup>c</sup>Kabata-Pendias and Pendias (2001)

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533 <sup>d</sup>Bowen (1979)

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536  
537 Table 6. Range of bioconcentration factors (BCF) and, translocation factors (TF) for grass growing on the Galmoy and  
538 Silvermines TMFs.

	BCF	TF
	Galmoy TMF	
As	0.13-0.34	0.08-0.24
Cd	0.18-0.25	0.36-1.19
Pb	0.07-0.23	0.19-2.12
	Silvermines TMF	
As	<0.01-0.06	0.02-0.63
Cd	0.08-0.16	0.07-0.18
Pb	<0.01-0.25	0.04-0.59

539  
540  
541 **Figure captions**

542  
543 Figure 1. Schematic and location of the Galmoy and Silvermines TMFs and the location of TMF sample sites.

544  
545 Figure 2. Down-core pH, organic matter and carbonate content in samples from the Galmoy trial plots.

546  
547 Figure 3. Down-core pH, organic matter and carbonate content in samples from the Silvermines TMF.

548  
549 Figure 4. Down-core PHE concentrations in the samples collected from the Galmoy trial plots.

550  
551 Figure 5. Down-core PHE concentrations in the samples collected from the Galmoy TMF.

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553 Figure 6. Down-core PHE concentrations in samples collected from the Silvermines TMF.

554  
555 Figure 7. Down-core speciation of As in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial  
556 plots.

557  
558 Figure 8. Down-core speciation of Cd in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial  
559 plots.

560  
561 Figure 9. Down-core speciation of Pb in samples collected from the Galmoy and Silvermines TMFs and Galmoy trial  
562 plots.

563  
564 Figure 10. Minimum, mean and maximum PHE concentrations in root and herbage material sampled from the  
565 Silvermines (n = 5) and Galmoy (n = 4) TMFs.

566  
567 Figure 11. Pb concentrations in herbage sampled from the Galmoy trial plots. Pb concentrations were determined  
568 following an aqua regia digest; data from Galmoy Mines Limited (unpublished). Grey shading represents the 0.2-20  
569 mg kg<sup>-1</sup> normal range for Pb in plants Kabata-Pendias and Pendias (2001).

573 **REFERENCES**

574

575

576 Aslibekion, O., Childs, P., Moles, R., 1999. Metal concentrations in surface water in the vicinity of the Silvermines  
577 abandoned mine site. *Environmental Geochemistry and Health* 21, 347-352.

578 Avery, B.W., Bascomb, C.L., 1974. *Soil Survey Laboratory Methods*, Soil Survey Technical Monograph No. 6. Soil  
579 Survey of Great Britain, Harpenden.

580 Balassone, G., Rossi, M., Boni, M., Stanley, G., McDermott, P., 2008. Mineralogical and geochemical characterization  
581 of nonsulfide Zn–Pb mineralization at Silvermines and Galmoy (Irish Midlands). *Ore Geology Reviews* 33, 168-186.

582 Ball, D.F., 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. *Journal*  
583 *of Soil Science* 15, 84-92.

584 Bearcock, J.M., Perkins, W., 2007. The use of green rust to accelerate precipitation of ochre for mine water  
585 remediation, in: Cidu, R., Frau, F. (Eds.), *IMWA Symposium 2007: Water in Mining Environments*. Mako Edizioni,  
586 Cagliari, Italy, pp. 135-139.

587 Beesley, L., Moreno-Jimenez, E., Clemente, R., Lepp, N., Dickinson, N., 2010. Mobility of arsenic, cadmium and zinc in  
588 a multi-element contaminated soil profile assessed by in-situ soil pore water sampling, column leaching and  
589 sequential extraction. *Environmental Pollution* 158, 155-160.

590 Bird, G., Brewer, P.A., Macklin, M.G., Balteanu, D., Driga, B., Serban, M., Zaharia, S., 2003. The solid-state partitioning  
591 of contaminant metals and As in river channel sediments of the mining affected Tisa drainage basin, northwestern  
592 Romania and eastern Hungary. *Applied Geochemistry* 18, 1583-1595.

593 Bird, G., Brewer, P.A., Macklin, M.G., Nikolova, M., Kotsev, T., Mollov, M., Swain, C., 2010. Contaminant-metal  
594 dispersal in mining-affected river catchments of the Danube and Maritsa drainage basins, Bulgaria. *Water Air and*  
595 *Soil Pollution* 206, 105-127.

596 Bird, G., Brewer, P.A., Macklin, M.G., Serban, M., Balteanu, D., Driga, B., Zaharia, S., 2008. River system recovery  
597 following the Novaț-Roșu tailings dam failure, Maramureș County, Romania. *Applied Geochemistry* 23, 3498-3518.

598 Bjerre, G.K., Schierup, H.H., 1985. Influence of waterlogging on availability and uptake of heavy metals by oat grown  
599 in different soils. *Plant and Soil* 88, 45-56.

600 Bolinder, M.A., Angers, D.A., Belanger, G., Michaud, R., Laverdiere, M.R., 2002. Root biomass and shoot to root ratios  
601 of perennial forage crops in eastern Canada. *Canadian Journal of Plant Science* 82, 731-737.

602 Bowen, H.J.M., 1979. *Environmental Chemistry of the Elements*. Academic Press, New York.

603 Brown, R.N., Percivalle, C., Narkiewicz, S., DeCuollo, S., 2010. Relative rooting depths of native grasses and amenity  
604 grasses with potential for use on roadsides in New England. *HortScience* 45, 393-400.

605 Callery, S., Courtney, R., in press. Assessing metal transfer to vegetation and grazers on reclaimed pyritic Zn and Pb  
606 tailings. *Environmental Science & Pollution Research* DOI: 10.1007/s11356-015-5149-4.

607 Canadell, J., Jackson, R.B., Ehleringer, J.R., Mooney, H.A., Sala, O.E., Schulze, E.D., 1996. Maximum rooting depth of  
608 vegetation types at the global scale. *Oecologia* 108, 583-595.

609 CDC, 2007. Recommendations for Preventing Lead Poisoning among the Internally Displaced Roma Population in  
610 Kosovo from the Centers for Disease Control and Prevention. U. S. Centers for Disease Control and Prevention,  
611 Atlanta, p. 12.

612 Courtney, R., 2013. Mine tailings composition in a historic site: implications for ecological restoration. *Environmental*  
613 *Geochemistry and Health* 35, 79-88.

614 Crilly, J., Kinsella, A.J., Johnson, M.S., Brady, E., 1998. Evaluation of blood and tissue lead as estimators of exposure in  
615 sheep. *Irish Journal of Agricultural and Food Research* 37, 17-28.

616 Environmental Protection Agency, 2004. Final Report of Expert Group for Silvermines County Tipperary: Lead and  
617 Other Relevant Metals. Environmental Protection Agency, Johnstown, Ireland, p. 68.

618 Fay, D., Kramers, G., Zhang, C., McGrath, D., Grennan, E., 2007. *Soil Geochemical Atlas of Ireland*. Teagasc &  
619 Environmental Protection Agency, Dublin.

620 Gomez-Alvarez, A., Valenzuela-Garcia, J.L., Meza-Figueroa, D., de la O-Villanueva, M., Ramirez-Hernandez, J.,  
621 Almendariz-Tapia, J., Perez-Segura, E., 2011. Impact of mining activities on sediments in a semi-arid environment:  
622 San Pedro River, Sonora, Mexico. *Applied Geochemistry* 26, 2101-2112.

623 Grandlic, C.J., Mendez, M.O., Chorover, J., Machado, B., Maier, R.M., 2008. Plant growth-promoting bacteria for  
624 phytostabilization of mine tailings. *Environmental Science & Technology* 42, 2079-2084.

625 Hallewell, M., Macdonald, N., Thorpe, R., Laframboise, P., 2005. Stabilization of lead and zinc flotation circuits at  
626 Galmoy mine, Kilkenny, Ireland. *SGS Mineral Services Technical Paper 2005-15*, Geneva.

627 Hamilton, E.I., 1980. Analysis for Trace Elements. Sample treatment and laboratory quality control, in: Davies, B.E.  
628 (Ed.), Applied Soil Trace Elements. J. Wiley and Sons, Chichester, pp. 21-48.

629 Hitzman, M.W., Beaty, D.W., 1996. The Irish Zn-Pb-(Ba) orefield, in: Sangster, D.F. (Ed.), Carbonate-Hosted Lead-Zinc  
630 Deposits. SEG Special Publication, pp. 112-143.

631 Hitzman, M.W., Beaty, D.W., 2003. The Irish Zn-Pb (Ba-Ag) orefield, in: Kelly, J.G., Andrew, C.J., Ashton, J.H., Boland,  
632 M.B., Earls, G., Fusciardi, L., Stanley, G. (Eds.), Europe's major base metal deposits. Irish Association for Economic  
633 Geology, Dublin, pp. 499-532.

634 Hudson-Edwards, K.A., Jamieson, H.E., Lottermoser, B.G., 2011. Mine wastes: past, present and future. Elements 7,  
635 375-380.

636 Hustead, S., Mikkelsen, B.F., Jensen, J., Nielsen, N.E., 2004. Elemental fingerprint analysis of barley plants using ICP-  
637 MS, IR-MS and multivariate statistics. Analytical and Bioanalytical Chemistry 378 171-182.

638 Jordan, S., Mullen, G.L., 2006. Characterization of pyritic lead-zinc tailings, Silvermines, Co. Tipperary, in: Moles, R.  
639 (Ed.), Proceedings of ENVIRON 2006 Conference, Dublin, pp. 38-39.

640 Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants, 3rd ed. CRC Press, Boca Raton.

641 Kim, J.-W., Jung, M.C., 2011. Solidification of arsenic and heavy metal containing tailings using cement and blast  
642 furnace slag. Environmental Geochemistry and Health 33, 151-158.

643 Li, X.D., Thornton, I., 2001. Chemical partitioning of trace and major elements in soils contaminated by mining and  
644 smelting activities. Applied Geochemistry 16, 1693-1706.

645 Lindsay, M.B.J., Wakeman, K.D., Rowe, O.F., Grail, B.M., Ptacek, C.J., Blowes, D.W., Johnson, D.B., 2011. Microbiology  
646 and Geochemistry of Mine Tailings Amended with Organic Carbon for Passive Treatment of Pore Water.  
647 Geomicrobiology Journal 28, 229-241.

648 Loring, D.H., 1981. Potential bioavailability of metals in eastern Canadian estuarine and coastal sediments. Rapports  
649 et procès-verbaux des réunions; conseil international pour l'exploration de la mer 181, 93-101.

650 Lottermoser, B.G., 2010. Mine Wastes: Characterization, Treatment and Environmental Impacts, 3rd ed. Springer-  
651 Verlag Berlin Heidelberg.

652 Lowther, J.M., Balding, A.B., McEvoy, F.M., Dunphy, P., MacEoin, P., Bowden, A.A., McDermott, P., 2003. The Galmoy  
653 Zn-Pb orebodies: structure and metal distribution - clues to the genesis of the deposits, in: Kelly, J., Andrew, C.J.,  
654 Ashton, J.H., Boland, M.B., Earls, G., Fusciardi, L., Stanley, G. (Eds.), Europe's major base metal deposits. Irish  
655 Association for Economic Geology, Dublin, pp. 437-454.

656 Martínez-Ruiz, C., Fernández-Santos, B., Putwain, P.D., Fernández-Gómez, M.J., 2007. Natural and man-induced  
657 revegetation on mining wastes: Changes in the floristic composition during early succession. Ecological Engineering  
658 30, 286-294.

659 McGrath, D., Zhang, C.S., Carton, O.T., 2004. Geostatistical analyses and hazard assessment on soil lead in  
660 Silvermines area, Ireland. Environmental Pollution 127, 239-248.

661 Meggyes, T., Niederleithinger, E., Witt, K.J., Csovari, M., Kreft-Burman, K., Engels, J., McDonald, C., Roehl, K.E., 2008.  
662 Enhancing the safety of tailings management facilities. Soil & Sediment Contamination 17, 323-345.

663 Mench, M., Bussiere, S., Boisson, J., Castaing, E., Vangronsveld, J., Ruttens, A., De Koe, T., Bleeker, P., Assuncao, A.,  
664 Manceau, A., 2003. Progress in remediation and revegetation of the barren Jales gold mine spoil after in situ  
665 treatments. Plant and Soil 249, 187-202.

666 Mench, M., Lepp, N., Bert, V., Schwitzguebel, J.P., Gawronski, S.W., Schroder, P., Vangronsveld, J., 2010. Successes  
667 and limitations of phytotechnologies at field scale: outcomes, assessment and outlook from COST Action 859.  
668 Journal of Soils and Sediments 10, 1039-1070.

669 Moncur, M.C., Ptacek, C.J., Blowes, D.W., Jambor, J.L., 2005. Release, transport and attenuation of metals from an  
670 old tailings impoundment. Applied Geochemistry 20, 639-659.

671 Moreno-Jimenez, E., Vazquez, S., Carpena-Ruiz, R.O., Esteban, E., Penalosa, J.M., 2011. Using Mediterranean shrubs  
672 for the phytoremediation of a soil impacted by pyritic wastes in Southern Spain: A field experiment. Journal of  
673 Environmental Management 92, 1584-1590.

674 Nash, J.T., Fey, D.L., 2007. Mine Adits, Mine-Waste Dumps and Mill Tailings as Sources of Contamination, in: Church,  
675 S.E., Von Guerard, P., Finger, S.E. (Eds.), Integrated Investigations of Environmental Effects of Historical Mining in the  
676 Animas River Watershed, San Juan County, Colorado. USGS Professional Paper 1651, pp. 315-345.

677 Palmer, J.P., 2006. Dealing with water issues in abandoned metalliferous mine reclamation in the United Kingdom,  
678 Water in Mining Conference, Brisbane, pp. 1-10.

679 Palumbo-Roe, B., Klinck, B., Banks, V., Quigley, S., 2008. Prediction of the long-term performance of abandoned lead  
680 zinc mine tailings in a Welsh catchment. Journal of Geochemical Exploration 100, 169-181.

681 Perkins, W., Hartley, S., Pearce, N., Dinelli, E., Edyvean, R., Sandlands, L., 2006. Bioadsorption in remediation of metal  
682 mine drainage: the use of dealginated seaweed in the BIOMAN project. *Geochimica Et Cosmochimica Acta* 70, A482-  
683 A482.

684 Pyatt, F.B., Gilmore, G., Grattan, J.P., Hunt, C.O., McLaren, S., 2000. An imperial legacy? An exploration of the  
685 environmental impact of ancient metal mining and smelting in Southern Jordan. *Journal of Archaeological Science*  
686 27, 771-778.

687 Quevauviller, P., Ure, A.M., Muntau, H., Griepink, B., 1993. Improvement of analytical measurements within the BCR-  
688 programme: single and sequential extraction procedures applied to soil and sediment analysis. *International Journal of*  
689 *Analytical Chemistry* 51, 129-134.

690 Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C.M., Ure, A.M., Quevauviller, P., 1999.  
691 Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and  
692 soil reference materials. *Journal of Environmental Monitoring* 1, 57-61.

693 Reis, A.P., Patinha, C., Ferreira da Silva, E., Sousa, A.J., 2012. Metal fractionation of cadmium, lead and arsenic of  
694 geogenic origin in topsoils from the Marrancos gold mineralisation, northern Portugal. *Environmental Geochemistry*  
695 *and Health* 34, 229-241.

696 Serbula, S.M., Radojevic, A.A., Kalinovic, J.V., Kalinovic, T.S., 2014. Indication of airborne pollution by birch and  
697 spruce in the vicinity of copper smelter. *Environmental Science & Pollution Research* 21, 11510-11520.

698 Sharma, R.S., Al-Busaidi, T.S., 2001. Groundwater pollution due to a tailings dam. *Engineering Geology* 60, 235-244.

699 Shu, J.M., Bradshaw, A.D., 1995. The containment of toxic wastes: I. Long term metal movement in soils over a  
700 covered metaliferous waste heap at Parc lead-zinc mine, North Wales. *Environmental Pollution* 90, 371-377.

701 Shu, W., Ye, Z., Lan, C., Zhang, Z., Wong, M., 2001. Acidification of lead/zinc mine tailings and its effects on heavy  
702 metal mobility. *Environment International* 26, 389-394.

703 Sima, M., Dold, B., Frei, L., Balteanu, D., Zobrist, J., 2011. Sulfide oxidation and acid mine drainage formation within  
704 two active tailings impoundments in the Golden Quadrangle of the Apuseni Mountains, Romania. *Journal of*  
705 *Hazardous Materials* 189, 624-639.

706 Smith, K.M., Abrahams, P.W., Dalgleish, M.P., Steigmajer, J., 2009. The intake of lead and associated metals by sheep  
707 grazing mining-contaminated floodplain pastures in mid-Wales, UK: I. Soil ingestion, soil-metal partitioning and  
708 potential availability to pasture herbage and livestock. *Science of the Total Environment* 407, 3731-3739.

709 Stanley, G., Gallagher, V., Ní Mhairtín, F., Brogan, J., Lally, P., Doyle, E., Farrell, L., 2010. Historic Mine Sites -  
710 Inventory and Classification. Volume 1: Geochemical Characterization and Environmental Matters. Irish  
711 Environmental Protection Agency, Dublin, p. 160.

712 Taylor, S., Andrew, C.J., 1978. Silvermines orebodies, County Tipperary, Ireland. . *Transactions, Institution of Mining*  
713 *and Metallurgy (Section B, Applied Earth Science)* 87, 111-124.

714 Terzano, R., Spagnuolo, M., Vekemans, B., De Nolf, W., Janssens, K., Falkenberg, G., Flore, S., Ruggiero, P., 2007.  
715 Assessing the origin and fate of Cr, Ni, Cu, Zn, Pb, and V in industrial polluted soil by combined microspectroscopic  
716 techniques and bulk extraction methods. *Environmental Science & Technology* 41, 6762-6769.

717 Tordoff, G.M., Baker, A.J.M., Willis, A.J., 2000. Current approaches to the revegetation and reclamation of  
718 metalliferous mine wastes. *Chemosphere* 41, 219-228.

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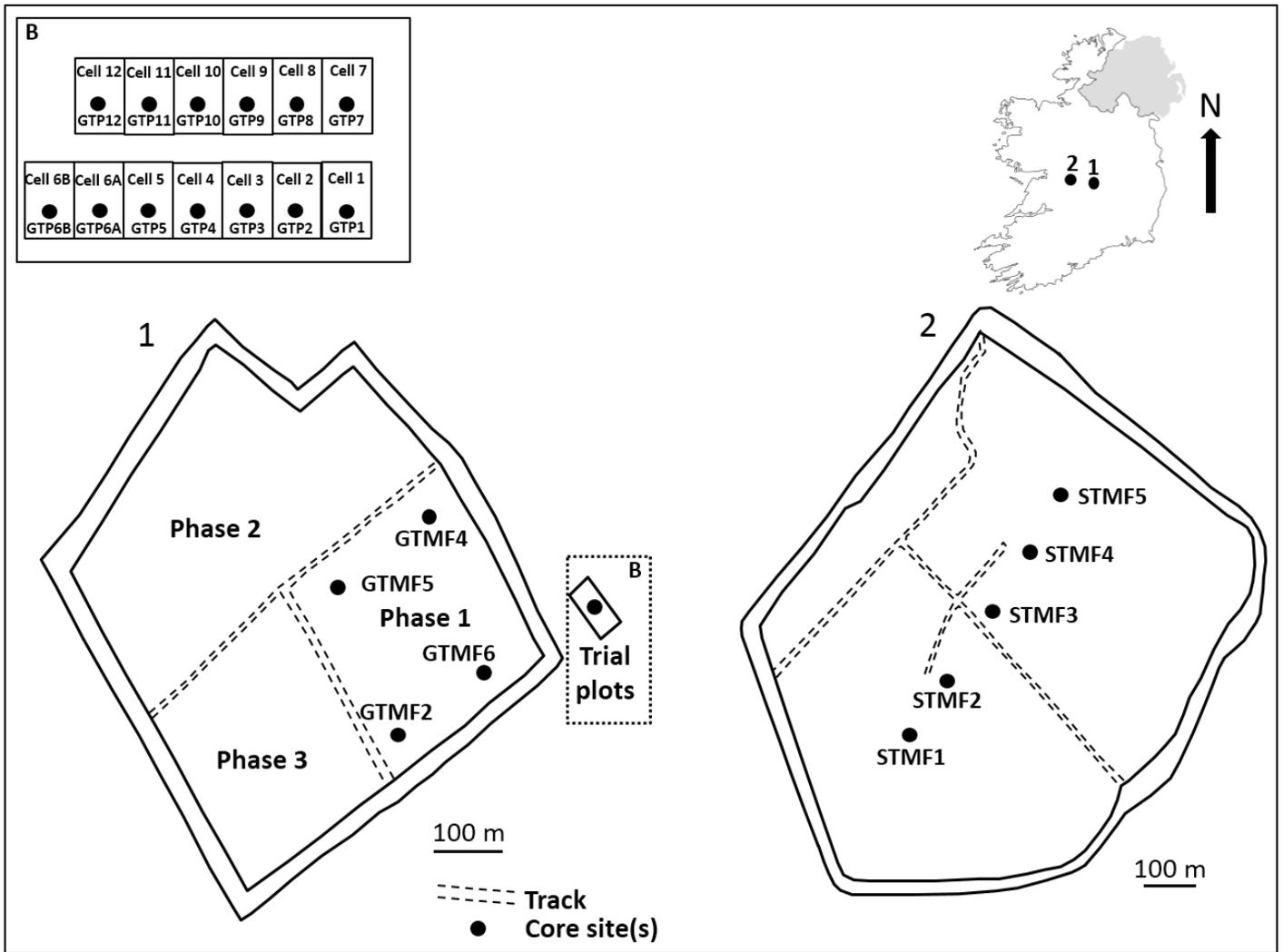
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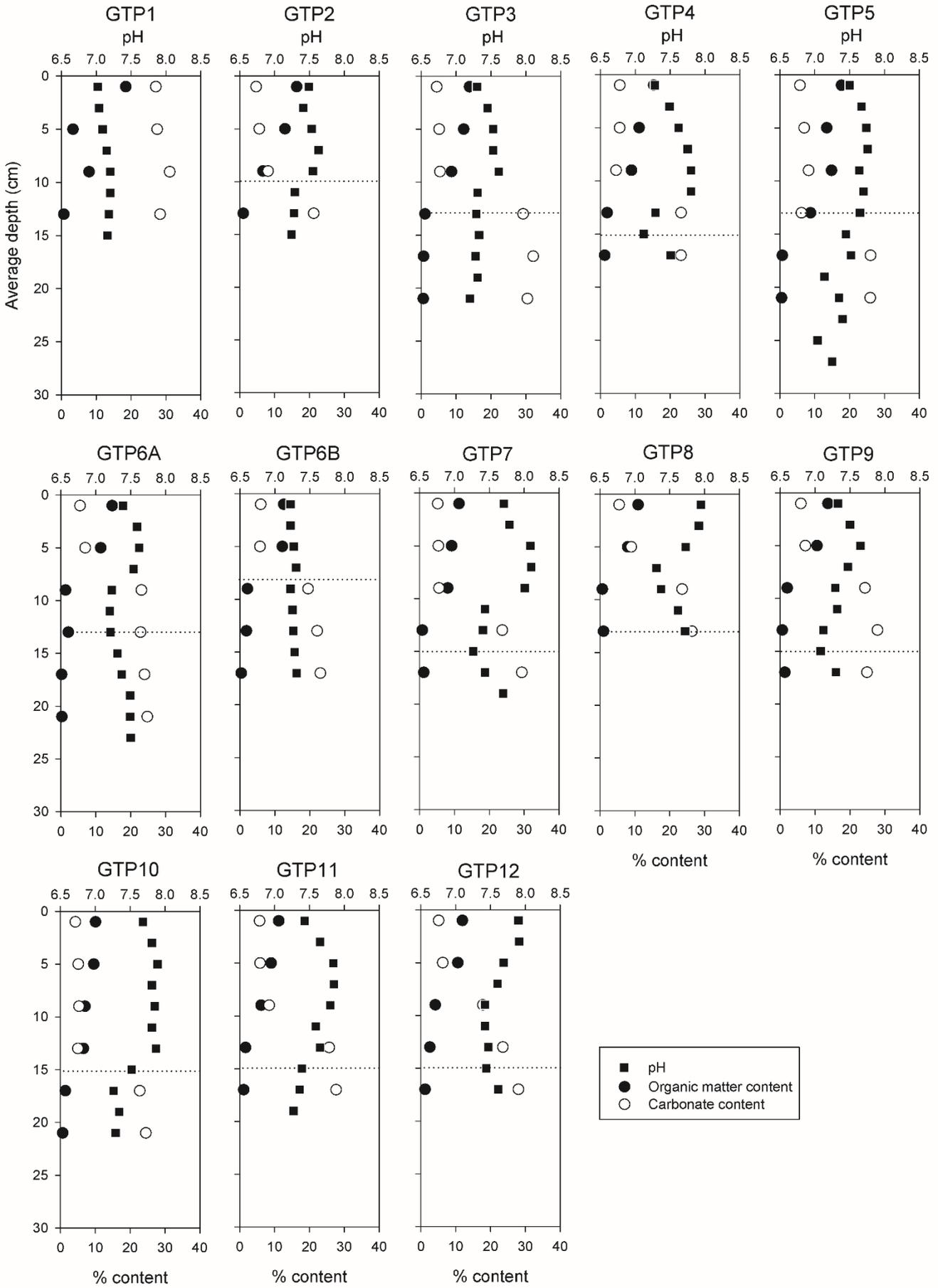
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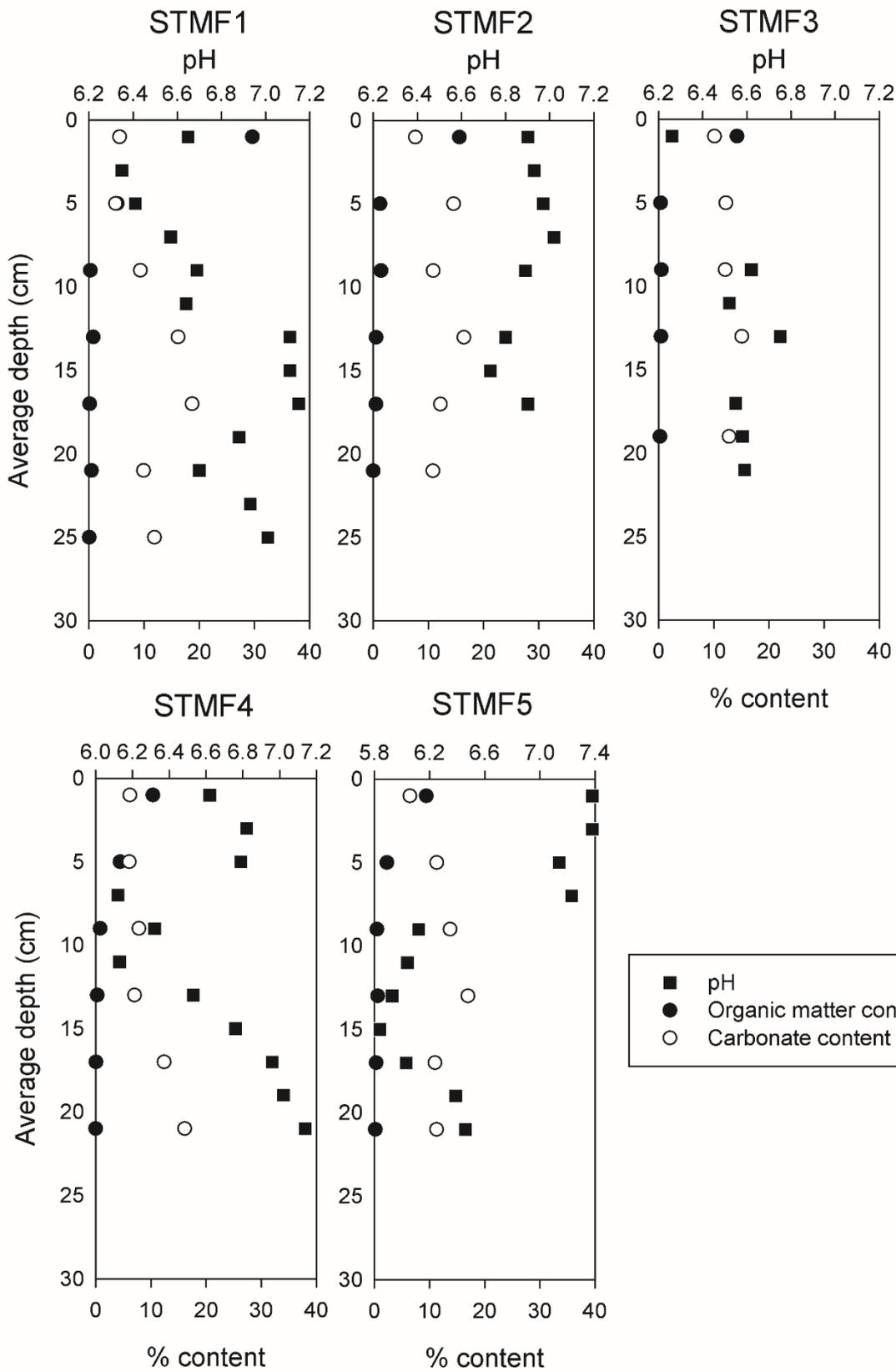


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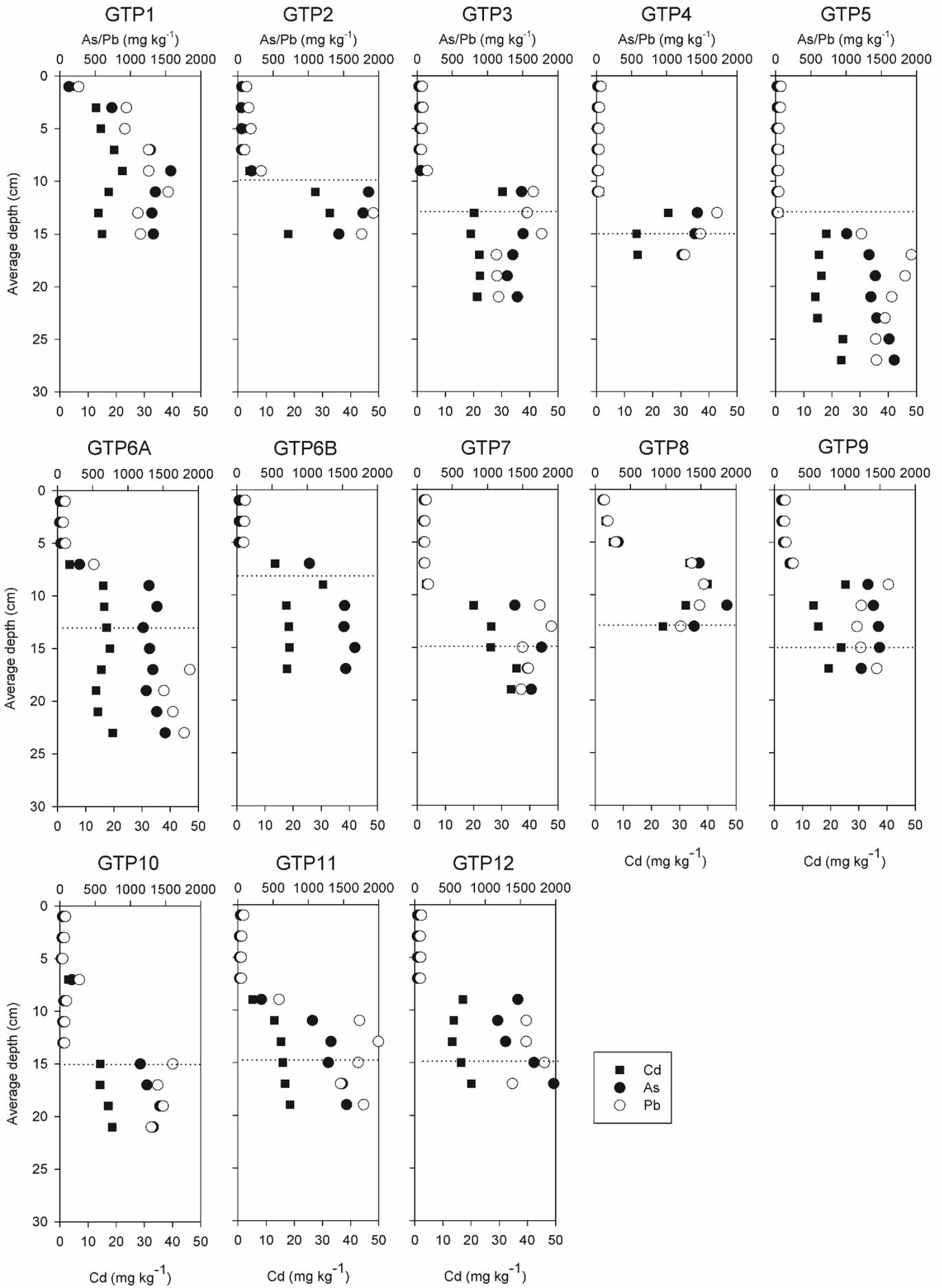
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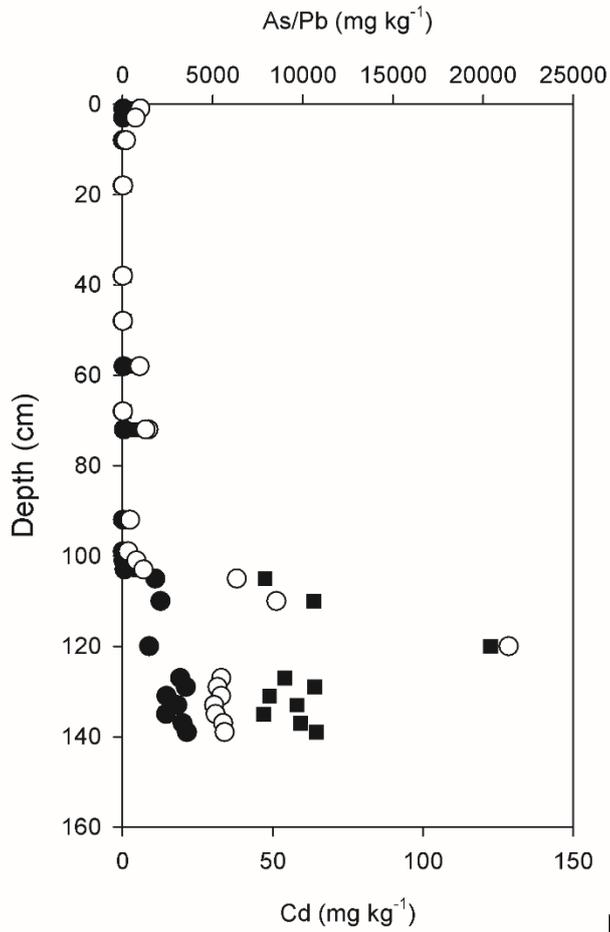
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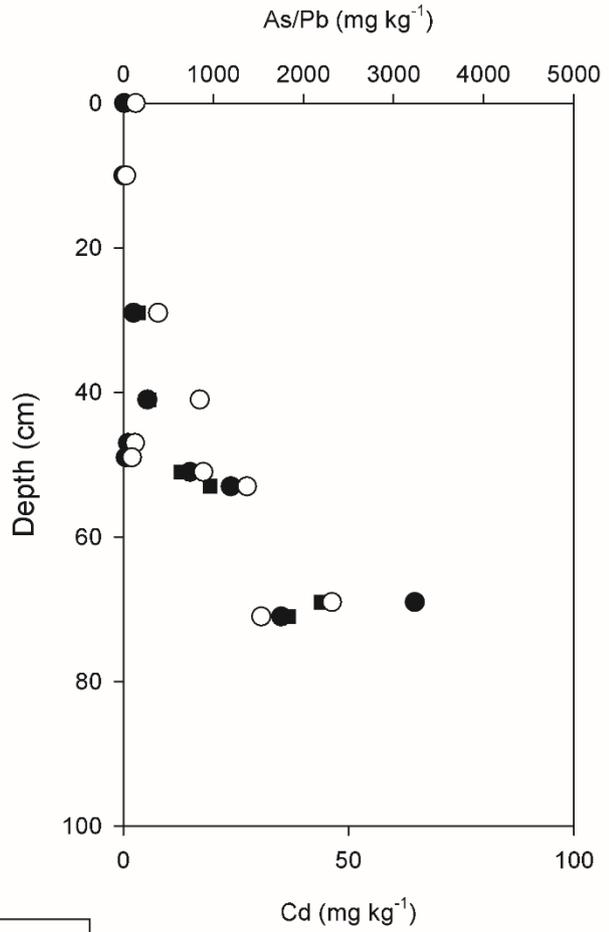
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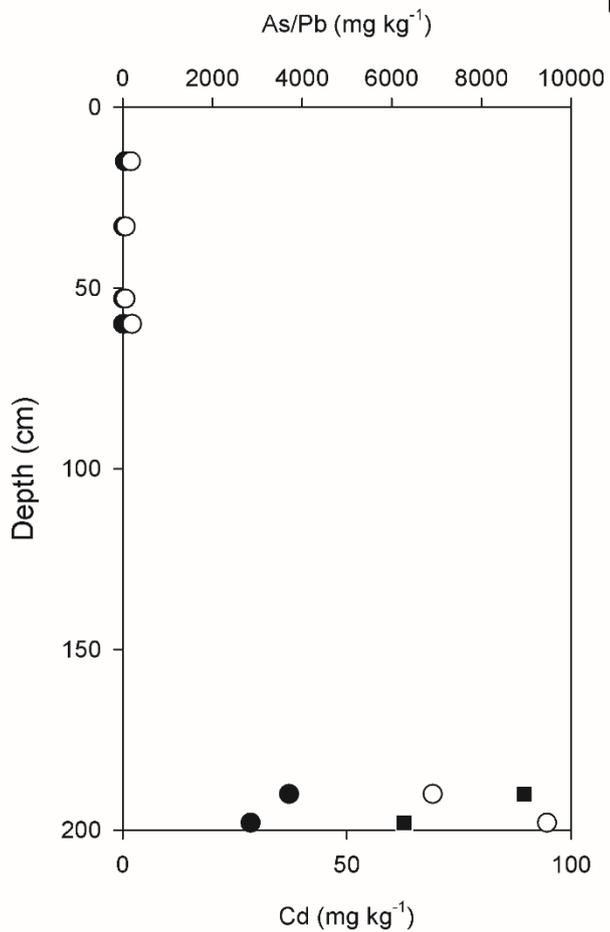
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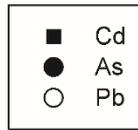
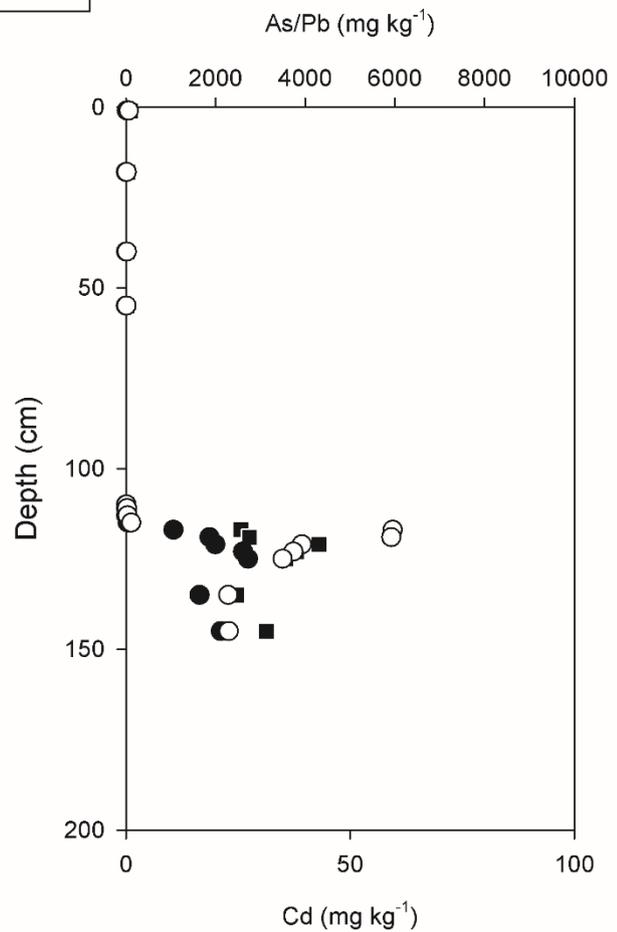
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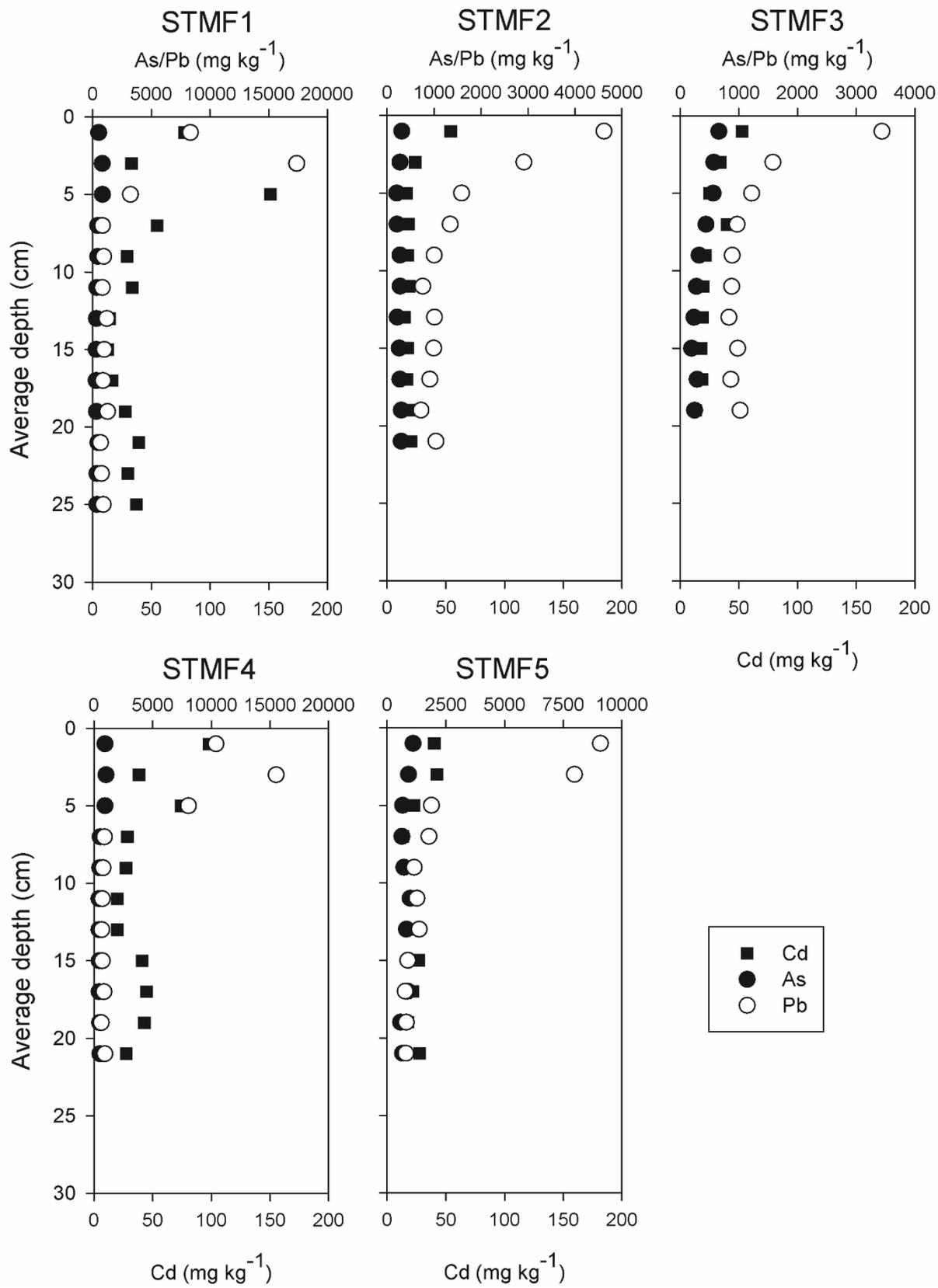


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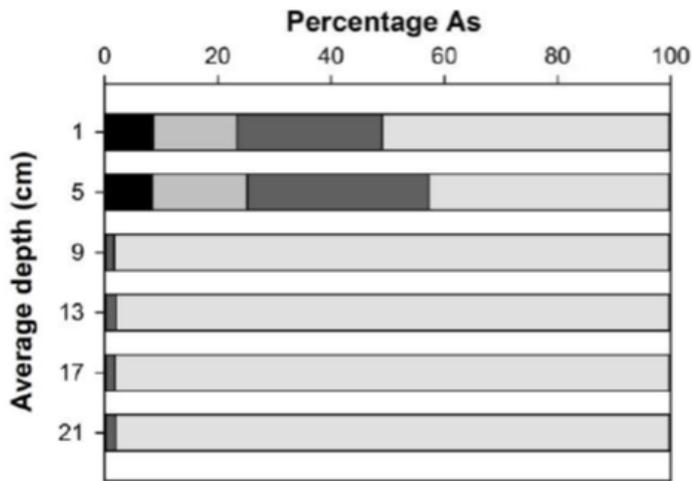
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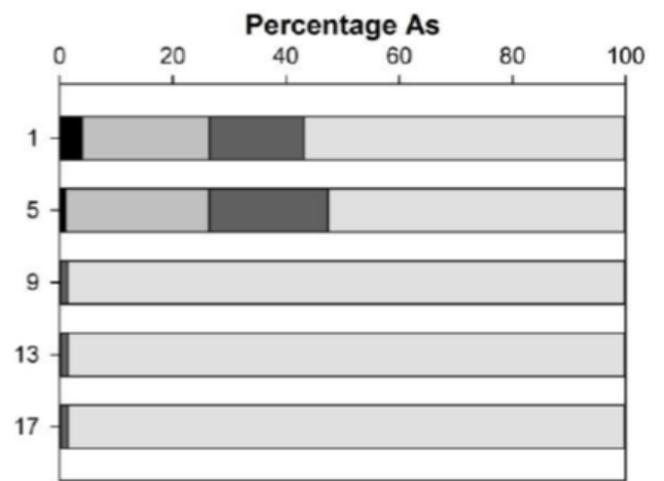


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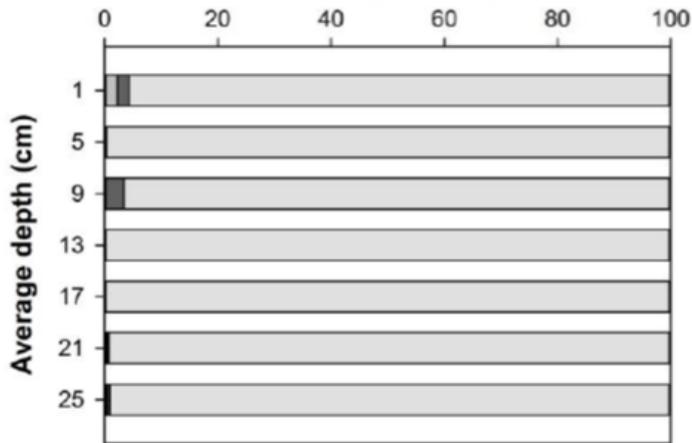
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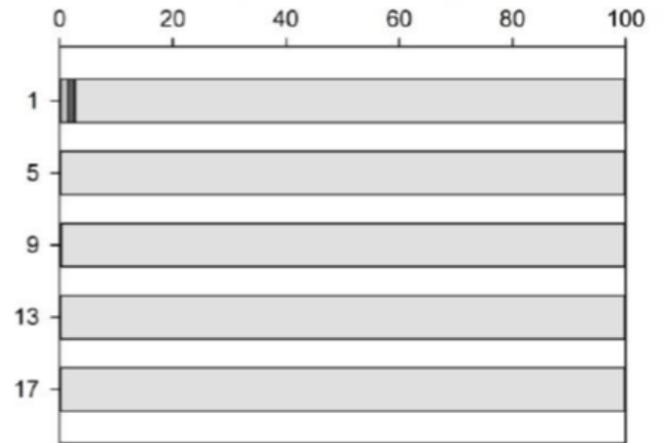
**Galmoy trial plots GT6B**



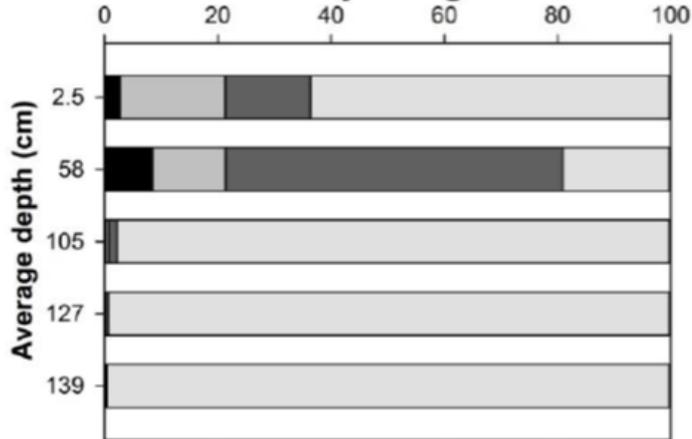
**Silvermines SC1A**



**Silvermines SC4A**

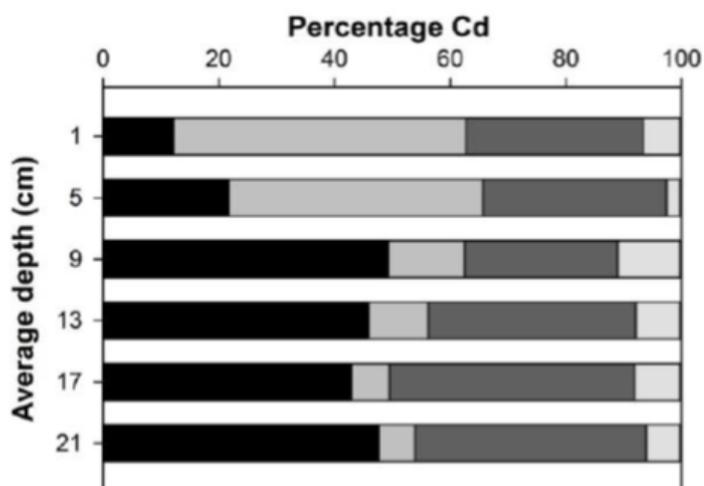


**Galmoy tailings G2**

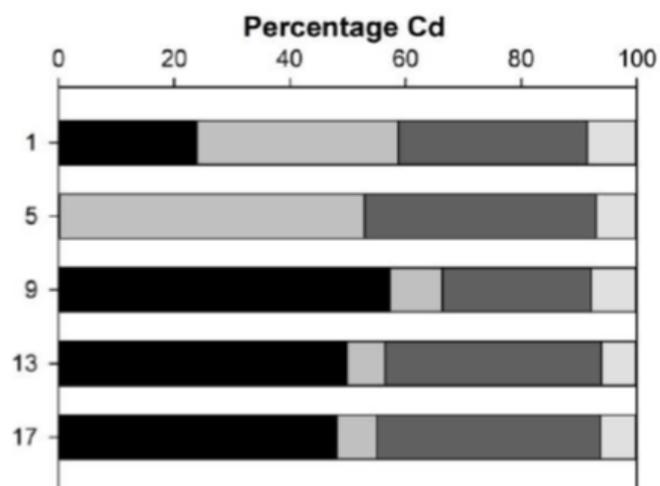


- Exchangeable
- Fe/Mn oxides
- Organic matter/sulphides
- Residual

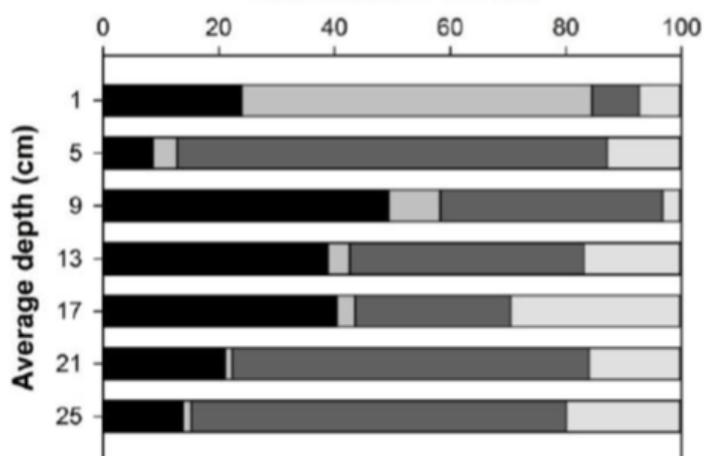
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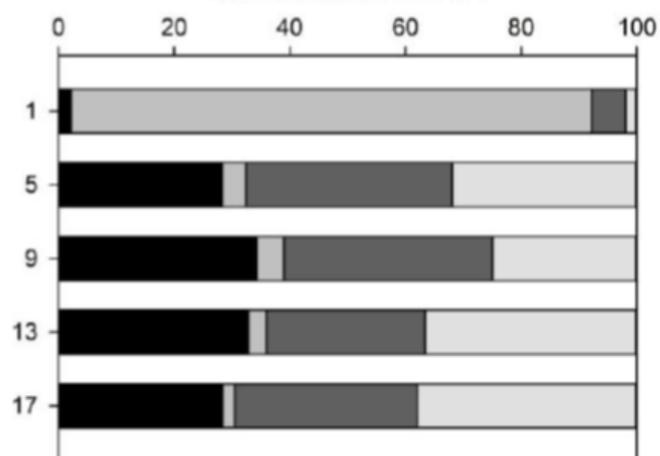
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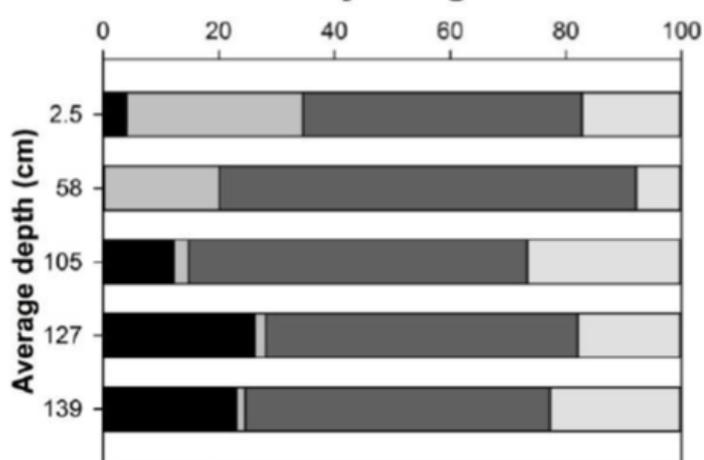
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**Silvermines SC4A**

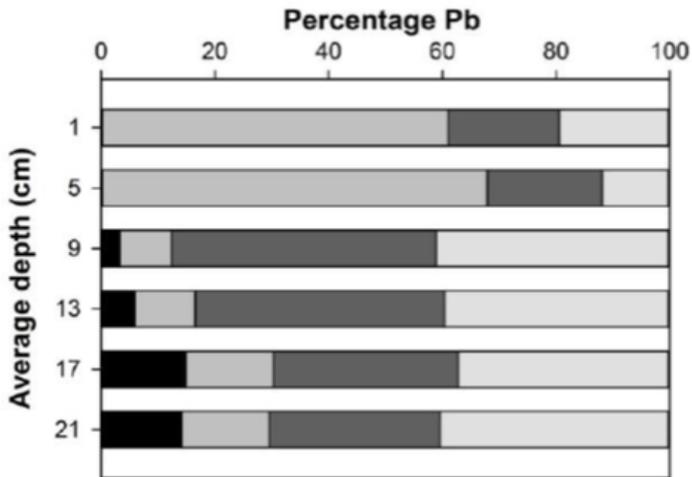


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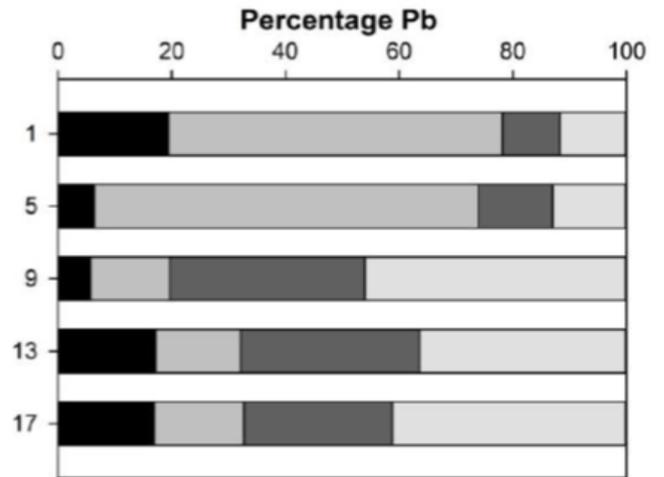


- Exchangeable
- Fe/Mn oxides
- Organic matter/sulphides
- Residual

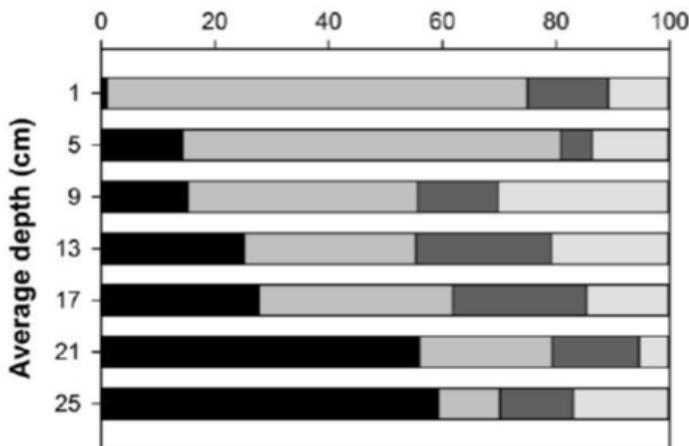
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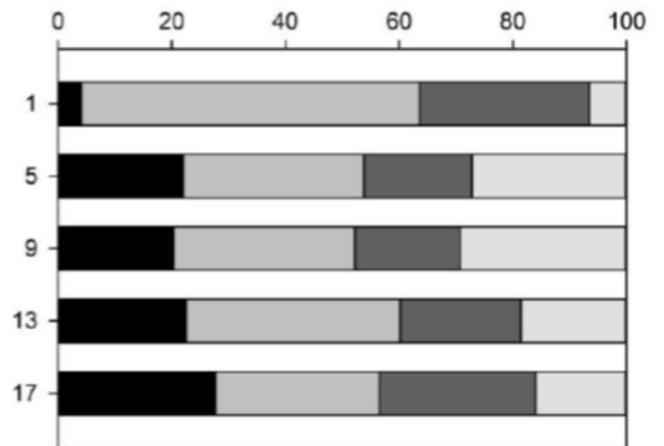
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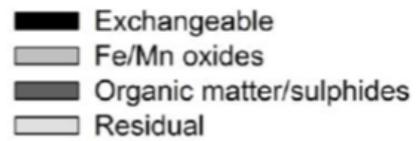
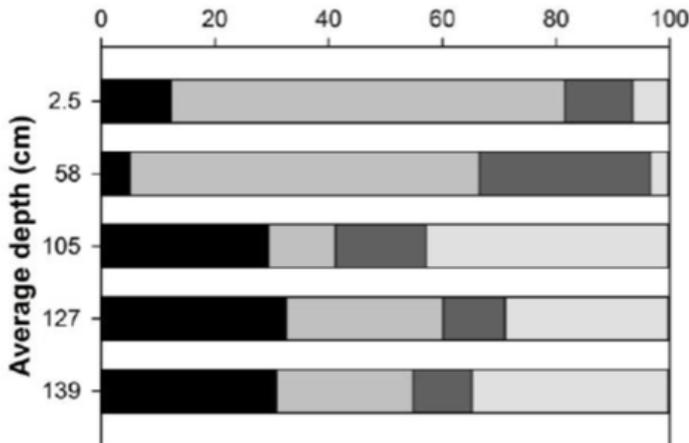
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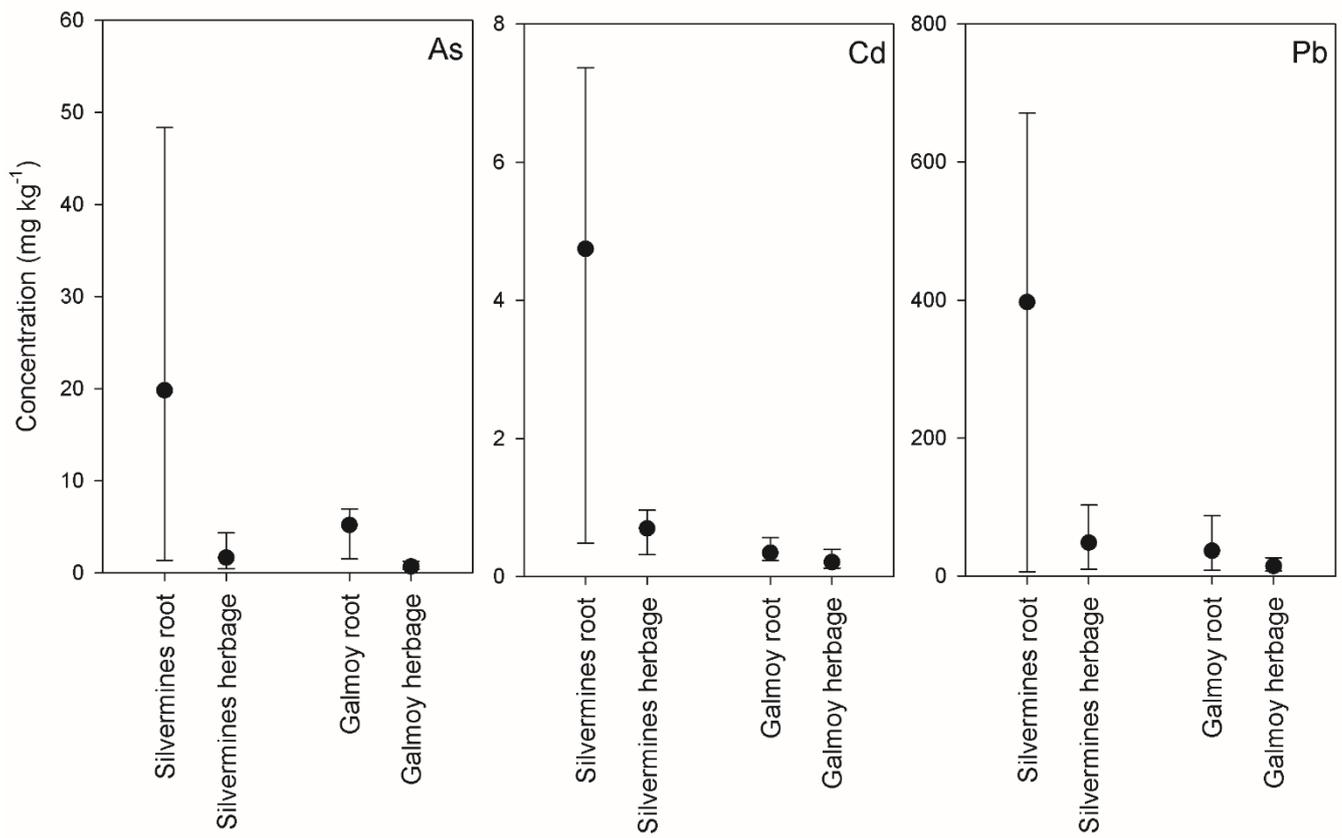


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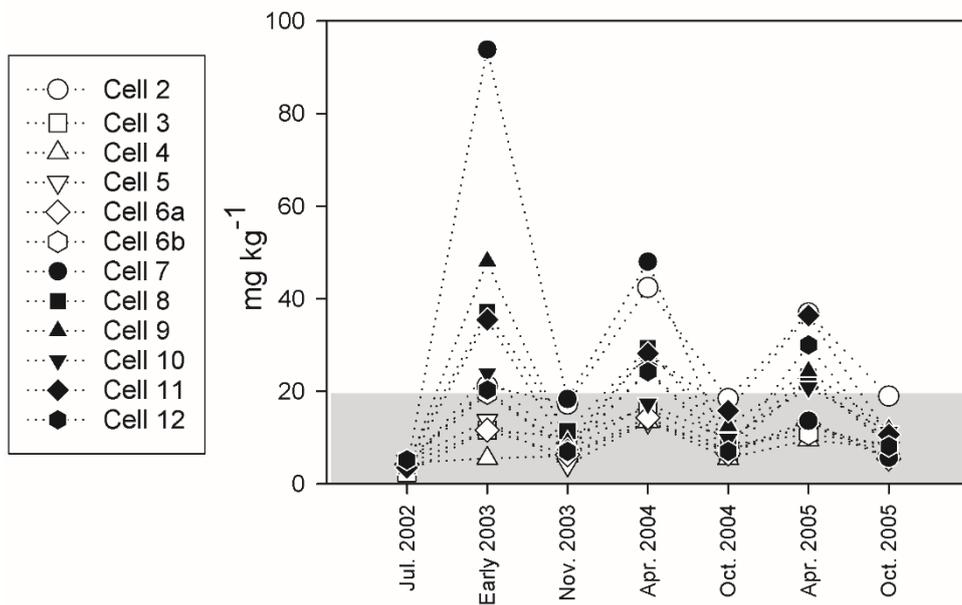


**Galmoy tailings G2**





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