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Potentially toxic metals in historic landfill sites: implications for grazing animals.

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ABSRACT

Municipal waste disposal is an increasing global problem, frequently solved by the use of landfill sites. Following closure, such sites contain a legacy of pollutants and must be managed to provide a safe and useful end life. The soils and vegetation from 4 historic landfill sites were analysed to determine the extent of pollution by potentially toxic metals (PTMs). Data were subsequently assessed to determine if post closure uses involving grazing was safe for the animals. The heaviest and most wide spread soil contamination was due to Ni. Concentrations at all sites exceeded the 95 %ile value for rural soils, in one case by a factor of 30. Cu and Pb contamination was identified at some sites, but no evidence of Al or Zn contamination was found. Oral bioaccessibility testing showed that the availability of Ni in soil was exceeding low, whilst that of Pb was consistently high. Concentrations in plant shoots differed significantly amongst the sites, but interspecific differences in shoot concentration were only significant in the case of Cu. The results indicated that exposure levels to grazers would be at or below tolerable levels, indicating that it is generally safe to graze historic landfill. However, animals could be exposed to higher levels of PTMs than would be expected from rural locations and grazing under conditions where soil consumption may be high could result in levels of exposure to Al, Ni and Pb exceeding tolerable levels.

Keywords: Metals; Soil; Shoots; Grazing; Landfill; Restoration.

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1. Introduction

The disposal of municipal and industrial solid waste in landfill sites is a ubiquitous practice, still widely used on a global scale despite legislative initiatives aimed at its reduction (e.g. EC, 1999). For example, on average in the EU 37 % of waste is disposed of to landfill, but in some member States this figure is over 90 % (DEFRA 2011). After closure, landfill sites leave a legacy of contaminated land, particularly in developing countries lacking legislative constraints on the dumping of hazardous materials and in the case of developed countries, in historic landfill sites that predate the introduction of constraints. For example, the nature of materials deposited in landfill sites was largely uncontrolled in the UK until the enactment of the Control of Pollution Act (COPA 1974). Contamination can consist of a wide range of potentially toxic substances including metals, cyanides, acids, alkalies, solvents and PCBs, presenting a pollution potential that may persist for a time scale measured in thousands of years (ICRCL, 1990, Slack et al., 2009). Elemental pollutants, such as potentially toxic metals (PTMs), will be amongst the most persistent contaminants as they cannot be broken down.

The global scale of the problem posed by historic landfills is unknown, but can be judged from the fact that approximately 100, 000 historic landfill sites exist in the USA (Suflita et al., 1992), whilst the UK has over 20,000 (Wilkinson, 2011). Globally, this problem will escalate as economic growth and increasing urbanisation in developing countries proliferates the generation of municipal solid waste, which will in turn require increasing use of landfill for disposal (Khajuria et al. 2010).

Once closed, it is necessary for landfill sites to be restored in some way to contain the pollutants encompassed within and to also provide the site with a useful end life role. For sites close to population centres, end life frequently has a recreational use such as public open space or sports facilities, while for more rural sites, agricultural grassland is more common (Simmons, 1999; Misgav et al., 2001). It is also being increasingly recognised in both developed and developing countries that ecological restoration can be combined with after-uses such as public open space to provide an opportunity to enhance nature conservation (Simmonds, 1999; Townsend et al. 2004; Rahman et al., 2011; Xiang et al., 2011).

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Containment of potentially toxic materials is usually achieved by covering the contents of landfills with impervious substrates, usually clay, which is deliberately compacted to create a seal (Simon & Mǚller, 2004). The sealing layer must then be covered with soil/soil forming material to allow restoration of vegetation (LRM, 2007), which is required to prevent erosion of the sealing layer and to facilitate useful end life. However, landfill sites are not always suitably capped, particularly in older sites (Barry et al., 2001) and this can result in the concentration of pollutants, such as PTMs, becoming elevated in the upper soil horizons (Hernández et al., 2012; Pastor & Hernández, 2012; Dao et al., 2013).

Whilst the restoration of grasslands on historic landfill sites maximises the protection of the cap and offers opportunities for wildlife conservation and agriculture, grasslands are invariably plagioclimax communities. Hence they require management by regular defoliation to prevent successional change. The two most commonly used methods for maintaining grassland plagioclimaxes are mowing and grazing. Mowing regimes can often be very difficult to implement on landfill sites because of the tendency for irregular topography to develop through subsidence and their sometimes steep slopes. Accordingly, historic landfill sites are often grazed in both ecological and agricultural end uses.

There are two principle pathways by which animals grazing on historic landfills might be exposed to pollutants. Firstly, grazing animals ingest surface soil, either through directly consuming soil or through eating soil splashed onto foliage (Thornton & Abrahams, 1983; Green et al., 1996; McGreevy et al. 2001). This can be a major pathway of exposure, potentially accounting for over 70 % of PTMs ingested (Thornton & Abrahams, 1983; Thornton, 2002). Secondly, animals can also be exposed to pollutants taken up from the soil by plants, which are subsequently translocated to the shoots. Although the root-shoot barrier generally excludes PTMs from the shoot, this is not always the case and PTM concentrations higher than in the soil may be found in shoots (Sauerbeck, 1991; Green et al., 2006). Consequently, there can be elevated concentrations of PTMs in the shoots of plants growing on landfills (Murphy et al., 2000; Hernández et al., 2012). There has, however, been no assessment made of whether grazing on historic landfill sites poses a risk either to the grazing animals or, through trophic links, to other species in the ecological community, including humans if the animals are later consumed.

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The aim of this study was to evaluate the exposure of animals grazing on historic landfills to PTMS. Our specific objectives were:

i) To establish the level and variability of soil contamination in the rooting zone of historic landfill sites

ii) To establish the oral bioaccessibility of PTMs in the soil

iii) To measure the extent to which PTMs are accumulated in the shoots of plants

iv) To estimate the relative contribution of soil and plant ingestion to PTM intake

2.0 MATERIALS & METHODS

2.1 Site description

Four historic landfill sites situated in the county of Dorset, UK were selected as case studies for this investigation. Dorset has a highly variable geology that allowed a comparison of sites representing a range of soil pH and ages since closure under the same climatic conditions. Site 1 is situated on a former salt marsh close to the coast. This site received waste from a non-industrialised conurbation between 1949 and 1990, although the area studied was active from the late 1960's until sometime before 1974. Sites 2, 3 and 4 are within a 3 miles radius and received waste from a second non-industrialised conurbation. Sites 2 and 3 are situated on a river flood plain. Site 2 was operational over several phases from the 1950's until 1981. The sampled area was active post 1974. Landfill operations at Site 3 commenced around 1945 and ceased in the early 1970's. The area sampled in the present study was active until 1951. Site 4 is situated on former heathland and was operational between 1950 and 1970. Site 1 is primarily used as a sports ground, sites 2 and 4 are designated as local nature reserves (LNR), whilst site 3 has areas used as a sports ground and designated as a LNR. Only the area of the LNR was sampled. Site 1 is managed by mechanical mowing. Sites 2 and 4 are actively managed by grazing. Site 3 was grazed, but this activity ceased in the year prior to sampling and the site was unmanaged at the time of sampling.

2.2 Soil and plant sampling

Three species of grass (*Arrhenatherum elatius* (L.) J. &. C. Presl, *Dactylis glomerata* L. & *Holcus lanatus* L.) and three forb species (*Lotus corniculatus* L., *Plantago lanceolata* L. & *Potentilla reptans* L.) were sampled in June from 5 randomly chosen locations on each of the 4 historic landfill sites. These plant species were chosen because they were abundant on each site and therefore would form the bulk of the diet of grazing animals. All 6 species are also widely naturalised outside their native ranges and so are likely to occur widely on landfill sites around the globe. Five plants of each species and soil samples taken from the rooting zone (0-10 cm) of each plant were collected at each of the 5 sampling points. At each sampling point, plants from the same species and the soil samples from the rooting zone of that species were combined to form a bulk plant and soil sample. Thus, 30 bulk plant samples (5 samples of 6 species) and 30 bulk soil samples were taken from each site. Analysis was conducted in duplicate on these bulk samples.

2.3 Chemical analysis

All analysis of the soil was carried out on the fine earth fraction. Soil pH was determined in a 2.5:1 water soil suspension. Total metal concentrations were determined by refluxing 0.3 g of soil in 10 ml of *aqua regia* for 15 hrs at 90 ^{o}C. Samples were then evaporated to dryness at 150 ^{o}C and re-suspend in 25 ml of 5 % nitric acid (Smith et al., 2006).

To estimate the oral bioaccessibility of PTMs to grazing animals ingesting soil, a physiologically based extraction test (PBET) was conducted. This involved agitating a 0.25 g soil sample in 25 ml of simulated gastric fluid (SGF) in an end-over-end shaker for 2 h. SGF was prepared according to the U.S. Pharmacopoeia recommendations (U.S. Pharmacopoeia, 1990). The temperature was maintained at 37 ^{o}C throughout the extraction procedure. Extracts were filtered through Whatman No.42 filter papers before storage at -18 ^{o}C until analysis. To reduce the analytical load, 1 of the 6 soil samples taken from each sample point was randomly selected and subjected to the PBET, i.e. 5 samples points per site were analysed.

Harvested plants were separated into roots and shoots before washing once in 0.1 % detergent solution and twice in distilled water. Washed plant material was dried to a constant weight at 70 ^{o}C and the dried shoot material finely ground in a rotary mill. 0.25 g sub-samples of the milled material were digested in 10 ml of 69 % nitric acid at 90 ^{o}C and diluted to a volume of 25 ml with deionised distilled water (Merrington et al. 1997).

The concentration of Al, Cd, Cu, Ni, Pb and Zn in all soil and plant samples was determined by ICP-OES (Varian Vista Pro). Concentrations of Cd were below the limit of detection in nearly every sample and are not reported further. Analytical quality was further ensured by the digestion of relevant certified reference material for soils (BCR 143R) and plants –(BCR 281) and process blanks in each batch of samples digested and analysed. Extraction efficiencies for BCR 134R were Al – not certified, Cu , Ni, Pb, Zn , whilst the or BCR 281 All concentrations are expressed as mg kg^{-1} dry weight.

2.4 Data analysis

Estimated intakes of PTMs by livestock from plants were calculated using a daily intake of 22 g dry weight kg^{-1} live weight. This figure is consistent with the dry matter intake for both horses and cattle (Dulphy et al. 1992), which are the two species most commonly grazed on historic landfill in the UK. It is well attested that horses directly eat soil (McGreevy et al., 2001) and, like cattle, will also eat soil adhered to plant material (Healy, 1974). There are no clear figures for the amount of soil consumed by grazing horses, but figures for cattle range between 1.1 % and 4 % of dry matter intake under usual agricultural conditions (Thornton & Abrahams, 1983; Thornton, 2002). Consequently, the intake of PTMs by both cattle and horses was estimated at soil consumption rates of 1 % and 4 % of dry matter intake to represent conditions of low and high soil consumption. Metal intake from the consumption of herbage (mg kg^{-1} l.w. d^{-1}) was estimated by multiplying the mean concentration (mg kg^{-1}) of metal in the shoots found on each site by 0.022 (d.w. consumed kg^{-1} d^{-1}), whilst intake from soil was calculated by multiplying the total concentration in the soil by 1 % and 4 % of 0.022.

Data sets were tested for the assumptions of parametric statistical tests, but in many instances these assumptions were not met. Thus, a conservative non-parametric two-way comparison, the Sheirer-Ray-

Hare (SRH) test, was used to determine the significance of differences between median values and Spearman's rank order correlation was used to determine the significance of relationships between variables. In the case of one way comparisons of means, where the assumptions were not met, ANOVA was conducted using Welch's F ratio.

3.0 RESULTS

3.1 Soils.

The mean pH values of the soils were 8.00, 7.79, 5.90 and 6.34 for sites 1 to 4 respectively, which were significantly different among the sites (Welch's F = 205, $P < 0.001$). The total concentrations of PTMs in the soils fell in the general order Al > Ni > Pb > Zn > Cu, although considerable variation amongst sites was found (Figure 1). Site 1 had the highest concentrations of Al and Ni, whilst Cu and Zn concentrations were highest in site 4. Site 2 had constantly low concentrations of all PTMs. Concentrations of each PTM showed highly significant differences among the sites (Welch's F = 33.6, 80.3, 38.1, 5.8 and 7.1 for Al, Cu, Ni, Pb and Zn respectively, $P \leq 0.001$ for all metals).

3.2 Oral bioaccessibility of PTMs in the soil.

The order in which concentrations of PTMs extracted by SGF fell was Al > Pb > Zn > Cu > Ni, demonstrating that Pb had particularly high and Ni particularly low oral bioaccessibility in comparison to the total concentration (Table 1). Al was also poorly bioaccessible based on a comparison with the total Al concentration in the soil, but concentrations were by far the highest for the PTMs studied. Both Cu and Zn showed relative high extractabilities, especially in site 1. With the exception of Cu, bioaccessibility of PTMs differed significantly amongst the study sites.

3.3 Variation in shoot PTM accumulation amongst plant species.

Concentrations of PTMs in plant shoots generally increased in the order site 1 < site 2 < site 3 < site 4 (Table 2) and exhibited significant, positive correlations to the total soil concentration in the case of Al, Cu and Zn (Al - $r_s = 0.24$, $P = 0.008$; Cu - $r_s = 0.49$, $P < 0.001$; Zn - $r_s = 0.30$, $P = 0.01$). By contrast, Ni concentration in shoots was negatively correlated with the soil concentration ($r_s = -0.34$, $P < 0.001$), whilst no significant correlation was found in the case of Pb ($r_s = 0.12$, $P = 0.21$). Two-way comparisons using the SRH test demonstrated that shoot concentration differed significantly amongst the sites in the case of all PTMS tested (Al - H = 8.55, P = 0036; Cu- H = 11.87, P = 0.037; Ni - H = 16.47, P = 0.001; Pb - H = 12, P = 0.01; Zn -H = 9.88, P = 0.02). *Arrhenatherum elatius* consistently exhibited the lowest shoot concentrations for all PTMs, whilst *L. corniculatus* and *P. reptans* generally exhibited high PTM concentrations in their shoots. However, two-way comparisons found that interspecific differences in shoot concentrations were only significant in the case of Cu (H = 11.87, P = 0.037). The interaction term between site and species was non-significant in the case of all five PTMs.

3.4 The relative contribution of soil and vegetation to oral PTM intake.

For Cu and Zn, herbage was estimated to contribute the largest proportion of intake, even when soil was consumed at a rate of 4 % of plant dry matter (Figure 2). Herbage accounted for between 72-97 % of Cu and 91-98 % of Zn intake. The relative contribution made by soil and plant material to the oral intake of the other PTMs depended on the level of soil consumption and site. At a consumption rate of 1 %, soil was estimated to make the greatest contribution to Al, Ni and Pb intake at site 1 and in the case of Ni, soil also made a slighter greater contribution to uptake than plants in site 4. With a rise in soil consumption to 4 % of herbage intake, estimates indicated that the dominant source of all three metals was the soil for all sites.

4.0 DISCUSSION

4.1 Potentially toxic metals in soils

Prior to the implementation of COPA (1974), there was little restriction on the land filling of waste in England. Only site 2 was operational under the licensing scheme that COPA (1974) brought into being. As site 2 consistently showed the lowest soil PTM concentrations, this may suggest that legislation reduced PTM concentrations in the surface soil. Hence sites that were not regulated during use may potentially pose a greater risk to grazing livestock. Without records of the material disposed of in the older sites, explaining the differences in PTM concentrations among the sites is speculative. However, site 4 is known to have received chemically contaminated waste from a cosmetics factory, which may explain the high levels of Cu, Pb and Zn found at this site. Site 1 is known to have received industrial, household and commercial waste in the area sampled (Njue, 2010) and received waste from a different conurbation and hence will have received waste of different nature to sites 2 and 3, which served the same conurbation.

Contamination was most profound in the case of Ni with the mean concentrations of Ni found in all 4 sites exceeding the 95 %ile value for rural soils (34.3 mg kg^{-1}; SHS, 2007). Indeed, on site 1, concentrations of Ni were 30 times higher than this value. All sites with the exception of site 2 exceeded the UK soil guideline value (SGV) for Ni in residential soils (130 mg kg^{-1}; Martin et al., 2009) and site 4 exceeded the higher SVG for allotments (230 mg kg^{-1}) by over 4 fold. Consequently, the heaviest and most wide spread soil contamination was due to Ni.

The only other occasion where an element exceeded the 95 %ile concentration for rural soils was Cu in site 4, where the concentration was 47.8 mg kg^{-1} compared to the 95 %ile concentration of 43.3 mg kg^{-1} (SHS, 2007). Cu concentrations at site 1 were twice the mean value for rural soils (19.8 mg kg^{-1}; SHS, 2007), also indicating possible Cu contamination of this site. Site 4 also had high levels of Pb, with a concentration marginally below the 95 %ile value for rural soils (155 mg kg^{-1} compared to 158 mg kg^{-1}). Uncontaminated rural soils typically exhibit Pb concentrations below 50 mg kg^{-1} (SCAN, 2003), hence contamination of site 4 by Pb is suggested. For all sites, Al and Zn concentrations were below or close to the mean values reported for rural soils (SHS, 2007), indicating a general lack of contamination by these elements. Sites 2 and 3 also appeared not to be contaminated by Cu and Pb, as concentrations were also close to the mean values for rural soils.

It is not clear if the contamination of sites arose from a failure of the landfill cap to separate waste from the surrounding environment or if the topsoil used in the capping was contaminated when it was brought on site. Certainly both scenarios are possible as the use of thin capping layers (~0.3 m) and of contaminated capping material were not uncommon in landfill sites of the type and age of those used in the present study (Watson & Hack, 2000; Barry et al., 2001).

4.2 Oral bioaccessibility of potentially toxic metals

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The results of the PBET showed that there were considerable differences in the percentage of PTMs that were bioaccessible amongst the sites and amongst the individual PTM elements. These differences did not relate to the total concentration of PTM in the soil. This is a common finding for bioaccessibility tests (Oomen et al., 2002) and highlights the need for this type of testing when assessing the risks of contaminated land. However, some caution is required in interpreting the results of PBETs. Determinations of oral bioaccessibility by *in vitro* digestion models cannot truly reflect the *in vivo* bioaccessibility of PTMs in soils, as such models are not able to fully reproduce complex conditions of the alimentary canal. The PBET used to determine bioaccessibility in the present study only simulated the gastric compartment and bioaccessibility may potentially be lowered by the less acidic conditions in the small intestine, where majority of PTM uptake will occur (Oomen et al., 2002). Nevertheless, dissolution in the gastric compartment is a crucial step in the mobilisation of PTMs into bioaccessible forms (Oomen et al., 2002). Modelling only the gastric compartment is thus appropriate and is particularly valid when a precautionary approach to the assessment of the risk posed by contaminated soils is required.

Pb was the most bioaccessible PTM according to the PBET, followed by Cu and Zn. For site 1, a very high proportion of the Cu, Pb and Zn in the soil were potentially bioaccessible. Indeed, the bioaccessibility of Pb and Cu exceeded 100 %, but this is an artefact of sub-sampling the soils samples for the PBET as the process blanks showed no contamination (<0.006 mg kg^{-1}). A very high level of mobilisation in the gastric fluid is not unusual for Pb as bioaccessibilities of ca. 90 % have been reported (Oomen et al., 2002) and this seems a likely level for Pb bioaccessibility in site 1. This is also consistent with the reported high bioavailability of Pb in the topsoil covering landfill (Dao et al., 2013). This is cause for concern as the concentration of Pb found in the SGF exceeded the statutory limit set by the EC directive on undesirable substances in animal feed (10 mg kg^{-1}; EC, 2003) by a factor of nearly 10. This is reinforced by the relatively large contribution made by soil borne Pb to the estimated total Pb intake by grazing animals for site 1.

In the case of Cu and Zn, the concentrations of bioaccessible metal were similar to those reported in the herbage. Given this and the very low percentage of total uptake accounted for via the consumption of soil, this was not a critical exposure pathway. The proportion of the total Al concentration that was bioaccessible was the second lowest, but the actual concentration of Al was by far the highest. Indeed, for site 2, the Al concentration in the SGF just exceeded the maximum tolerable limit (MTL – the concentration of a substance in an animal's diet that will not affect health or performance; NRC, 2005) of 1,000 mg kg^{-1}, indicating some cause for concern. The bioaccessibility of Ni was the lowest of the PTMs studied in terms of both the percentage of the total concentration and the concentration in the SGF. The slight exception to this was site 2, which had the lowest total concentration, but the largest concentration in the SGF. The overall picture is one that suggests that Ni was in very unavailable forms, even where very high levels of contamination were evident.

4.3 PTM levels in plant shoots

Cu was the only PTM for which significant differences in concentration were found among the plant species. However, concentrations in the shoots were low, despite relatively high soil-root transfer (data not shown) and concentrations were generally below the mean value reported for rural herbage (7.22 mg kg^{-1}; SHS, 2007). Nevertheless, the three forb species exceeded this value in site 4, as did *P. reptans* in site 3. Indeed *P. reptans* particularly accumulated Cu in its shoots, resulting in a concentration close to the 95 %ile value for herbage (11.5 mg kg^{-1}; SHS, 2007).

Of the remaining PTMs, Zn concentrations were consistently the highest in herbage relative to reported rural concentrations. All forb species in all sites exceeded the reported mean concentration (33.6 mg kg^{-1}; SHS, 2007) except in the case of *P. lanceolata* in site 1 and *L. corniculatus* in site 2. Concentrations in *L. corniculatus* and *P. reptans* from site 3 and *H. lanatus*, *P. lanceolata* and *P. reptans* from site 4 exceeded the 95 %ile value for herbage (53.6 mg kg^{-1}; SHS, 2007). As there was no evidence of Zn contamination, this element appeared to have a high availability on the landfill sites. Soil pH and total metal concentration in the soil are the prime determinant of Zn availability to plants (Sauerbeck, 1991; Kabata-Pendias & Pendias, 2001). Sites 3 and 4 had the lowest pH and highest total Zn concentration, which partially accounts for the high shoot concentrations in these two sites.

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Aluminium concentrations in herbage were within the reported range for forage plants (6.5-3,400 mg kg^{-1}; Kabata-Pendias & Pendias, 2001), but concentrations in pasture reported to be typically below 100 mg kg^{-1} (SCAN, 2003). Herbage with Al concentrations above the typical level was found in all sites. *Holcus lanatus* and *P. reptans* exhibited the highest concentrations of Al, but even so, concentrations were less than a third of the MTL for horses and cattle Al stated by the NRC (2005).

There was very low transfer of Ni from the soil to the plants, indicating along with the very low oral bioaccessibility, that Ni was predominately in non-available forms. This is consistent with findings from sequential extraction studies conducted on landfill sites (Murphy et al., 2000). Shoot concentrations were generally below the mean value reported for herbage of 1.72 mg kg^{-1} (SHS, 2007). Although Ni concentrations were higher in sites 3 and 4, exceeding 1.72 mg kg^{-1} in most cases, the highest concentration was less than 2.4 mg kg^{-1}. Moreover, there was a negative relationship between the total concentration of Ni in the soil and the shoot. Thus, contamination was effectively locked away from the edible parts of the plant, either in the root or within the soil.

Pb concentrations in shoots differed significantly among the sites, but exhibited no relationship with the Pb total concentration in the soil. This was not unexpected as Pb has been demonstrated to have very low soil-shoot mobility (Sauerbeck, 1991). Site 4 showed the highest concentrations in all species except *H. lanatus* and all species except *A. elatius* exceeded the mean value reported for of herbage (1.87 mg kg^{-1}; SHS, 2007) in site 4. Moreover, *P. reptans* exceeded and *H. lanatus* came close to the 95 %ile value (5.43 mg kg^{-1}) at this site. However, all concentrations in shoots were below the 10 mg kg^{-1} limit for undesirable substances in animal feed for feed materials (EC, 2003).

Overall, there was a general pattern of falling PTM concentrations in grasses in the order *H. lanatus*>*D. glomerata*>*A. elatius*. Concentrations in forbs were generally higher than in grasses, which is consistent with other reports (Sauerbeck, 1991). PTM concentrations in the forbs did not show a general pattern as they did in the grasses, although with the exception of Al, *P. reptans* showed the greatest tendency to accumulate PTMs in its shoots and *P. lanceolata* showed a tendency to accumulate the lowest PTM concentrations. Consequently, a historic landfill site could be managed to minimise the transfer of

PTMs, particularly Cu, to herbivores by selecting plant species for restoration, such as *A. elatius* and *P. lanceolata*, which show a tendency to accumulate less PTMs in their shoots.

4.4 PTM uptake and risk to grazing live stock

The results of the present study showed that the tested PTMs differ in the major route through which grazing animals could be exposed. For Cu and Zn, consumption of herbage was clearly the main route of exposure. McDonald et al. (1988) stated that Cu is a cumulative toxin to which ruminant animals are more susceptible than non-ruminants. However, Cu toxicity is associated with a herbage concentration between 10-20 mg kg^{-1}, but only when this occurs in conjunction with low levels of Mo (McDonald et al. 1988). Even on the most contaminated site (site 4) and in the species showing the highest Cu concentration (*P. reptans*), Cu concentrations were below this level. In terms of soil contamination, site 4 had concentrations above the Cu MTL for cattle of 40 mg kg^{-1} stated for conditions of sufficient Mo and S supply (NRC, 2005). As soil makes such a small contribution to Cu ingestion, the intake rate for site 4 from both soil at 4% consumption and herbage was estimated as 0.21 mg kg^{-1} (l.w.) d^{-1}, which is less than a quarter of the intake rate at the MTL (0.88 mg kg^{-1} l.w. d^{-1}).

Most animals are highly tolerant of Zn (McDonald et al., 1988), with doses exceeding 2,000 mg kg^{-1} required to induce chronic toxicity in large animals (Merck, 2005) and concentrations up to 500 mg kg^{-1} in the diet are considered tolerable for cattle and horses (NRC, 2005). Even at the site with the highest level of Zn (site 4), concentrations were well below the tolerable limit in both soil and plants and the estimated intake of Zn from soils at 4 % ingestion and herbage combined did not exceed 12 % of the intake at the suggested MTL (NRC, 2005).

Soil was estimated to make a substantial contribution to the exposure of grazing animals to Ni even at a low (1 %) soil consumption rate. Given the high level of Ni contamination in the soil, this PTM-pathway combination has the potential to pose the greatest risk to grazers. However, despite causing toxicity through a number of pathways, including interfering with the normal metabolism of several other trace elements, participation in reactions producing reactive oxygen species and causing DNA lesions (NRC, 2005; Das, et al., 2008), Ni is considered to have a low toxicity (McDonald et al., 1988).

The MTL for Ni is 100 mg kg^{-1} for cattle (NRC, 2005). The concentration of Ni in the soils of sites 1, 3 and 4 exceeded this value, by a factor of over 12 in the case of site 1. However, Ni showed very low oral bioaccessibility, such that concentration extracted by the simulated gastric juice did not exceed $1/40^{th}$ of the MTL. This can not be taken as evidence that this extractable concentration is safe, as Ni generally exhibits a low availability in the digestive tract (McDonald et al., 1988). Nevertheless, the total estimated intake rate at site 4 with high soil consumption was 43 % of the rate at the MTL. Ingestion of soil would have to take place at a rate of 10 % of herbage consumption for the intake rate to exceed the MTL. However, as soil ingestion rates of up to 18 % have been reported in cattle in grazing in late April (Abrahams & Thornton, 1994), it is possible for grazing animals to be subjected to potentially harmful levels of Ni on this site.

At low soil consumption rates (1 %), herbage was estimated to be the principle source of Al intake, although this was only moderately the case at site 3. At high consumption rates (4 %) soil was estimated to be the predominant source of Al intake, especially at sites 1 and 3. Al toxicity in grazing animals is rare, but does occur (Fogerty et al., 1998) and the NRC (2005) quoted the MTL for Al as 1,000 mg kg^{-1} for horses and cattle. The highest estimated total intake for Al was found for site 3. Here, intake was 64 % of that at the MTL when soil consumption was 4 % of plant dry matter intake. However, the MTL would be exceeded on site 3 if consumption of soil reached 8 % and this is in combination with a relatively high bioaccessibility. In addition, Al bioaccessibility on site 2 exceeded the MTL. Consequently, despite total soil concentrations showing little evidence of Al contamination, there was still a potential for Al to cause harm.

The relative contribution to Pb intake rate made by soil and herbage also differed with site and soil consumption rate. At low soil consumption (1 %), soil and plants were estimated to make similar contributions to Pb intake for sites 1 and 3, whilst plants were estimated to be the principle source for sites 2 and 4. At high (4 %) soil consumption rates, the soil was estimated to be the principle source of Pb intake at all sites. For Pb, the MTL for cattle is 100 mg kg^{-1} and the estimated intake did not exceed 10 % of that at the MTL even for site 4 (the most contaminated). Moreover, the PBET indicated that site 4 had the lowest percentage of bioaccessible Pb. A very high percentage of Pb in the soil of site 1 appeared to be bioaccessible, but the low total concentration of Pb in the soil meant that intake would be only 4 % of that at the MTL. Consequently, cattle should be safe whilst grazing all sites, even considering the high bioaccessibility of the Pb in some sites.

The Pb MTL for young horses it is 10 mg kg^{-1} (NRC, 2005), which reflects the vulnerability of young horses to Pb toxicity (Casteel, 2001). This low limit would be reached on site 4 (the most contaminated) if soil consumption was at 4 % of dry matter intake. Consequently, young horses are potentially vulnerable as a small increase in the level of soil consumed would lead to Pb intake exceeding the MTL. In a worse case scenario where ingested soil reaches 18 % of ingested plant matter, the MTL for young horses would be exceeded by a factor of over 3 on site 4. Furthermore, a soil ingestion rate of 11% would see the MTL for young horses exceeded at all sites. Consequently, grazing of young horses on historic landfill sites should be avoided, particularly under conditions that are likely to lead to high soil ingestion rates. These include situations where the sward is sparse or short (Healy, 1968), where there is over grazing, abundant worm casts or the sward is dominated by clover (Dewes, 1996).

5.0 CONCLUSIONS

Historic landfill sites can provide highly useful areas for productive agriculture or ecological reserves. The peri-urban location of landfill sites, combined with increasing pressure on land use from global population increase and urbanisation, means that such sites will become increasingly useful for these purposes. However, the present study has demonstrated that the topsoil in historic landfill sites may be contaminated with PTMs. Contamination was variable and was most pronounced in the case of Ni and least in the case of Al and Zn. Legal constraints on landfill appeared to lower the levels of soil contamination. The risk to grazers from consuming contaminated soil was reduced as oral bioaccessibility of PTMs in the soil tended to be low where total concentration was high. PTM concentration in the shoots of plants that grazers are likely to consume was found to vary significantly with site for every PTM, but inter-specific differences were only significant in the case of Cu. Copper and Zn were the most labile metals in the soil-plant system and consumption of plant matter was estimated to be the primary intake route for grazers in the case of these two PTMs. Plants were generally estimated as the dominant sources of Al, Ni and Pb at low levels of soil ingestions, but soil dominated intake at high soil consumption levels. Overall, intake of all tested PTMs was estimated to be at or below the MTL, even at relatively high levels of soil consumption. Consequently, the health of grazing animals and humans consuming them should be safe, at least in terms of PTM exposure. Nevertheless, some caution is still required as there are certain circumstances where grazing animals would be exposed to Al, Ni and Pb at intake rates above tolerable levels. Accordingly, as long as conditions where soil consumption is likely to be high are avoided, historic landfill sites can be safely grazed.

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Tables

Table 1. Concentration of orally bioaccessible potentially toxic metals extracted from the soil of historic landfill sites by simulated gastric fluid (mg kg^{-1} dry soil; mean ± 1SE) and bioaccessibility expressed as % of the total soil concentration.

Site	Al		Cu		Ni		Pb		Zn	
	Conc.	%	Conc.	%	Conc.	%	Conc.	%	Conc.	%
1	737 ± 61	5.7	40.6 ± 2.2	102	2.1 ± 0.7	0.2	95.3 ± 7.1	106	61.7 ± 5.3	87
2	1019 ± 94	14	9.6 ± 0.4	82	2.3 ± 0.2	3.8	31.7 ± 3.8	48	35.5 ± 2.5	57
3	765 ± 100	6.1	7.7 ± 0.5	46	0.8 ± 0.1	0.5	46.9 ± 3.4	71	29.2 ± 4.9	34
4	555 ± 132	9.1	9.0 ± 2.2	18	2.3 ± 0.3	1.0	36.8 ± 0.4	24	28.4 ± 3.8	23
Signif.	F = 3.34		F = 3.17†		F = 8.73†		F = 5.30		F = 3.36	
	P = 0.04		P = 0.07		P = 0.001		P = 0.008		P = 0.04	

† - Welch's F ratio

Table 2. Potentially toxic metal concentrations (mg kg^{-1}, mean ± 1 SE) in herbage grown on historic landfill sites (H. lan – *Holcus lanatus*, A. ela - A*rrhenatherum elatius,* D. Glo -*Dactylis glomerata*, *L. cor* - *Lotus corniculatus*, P. lan - *Plantago lanceolata* and P. rep - *Potentilla reptans*).

Site	**Species**					
	H. lan	**A. ela**	**D. glo**	**L. cor**	**P. lan**	**P. rep**
Al						
1	88.2 ±13.3	41.4 ± 4.4	31.6 ± 5.1	70.2 ± 9.3	35.9 ± 7.7	126 ± 34
2	226 ± 44	46.4 ± 6.4	117 ± 42	215 ± 13	185 ± 31	181 ± 24
3	147 ± 20	92.6 ± 14.1	124 ± 46.	255 ± 75	175 ± 36	152 ± 18
4	259 ± 37	51.3 ± 6.8	179 ± 60	198 ± 41	297 ± 57	178 ± 49
Cu						
1	3.32 ± 0.17	2.54 ± 0.32	2.84 ± 0.52	5.99 ± 0.33	4.42 ± 0.52	6.32 ± 0.29
2	4.56 ± 0.22	2.69 ± 0.29	3.91 ± 0.37	7.16 ± 0.47	5.49 ± 0.52	6.29 ± 0.52
3	5.73 ± 0.45	4.85 ± 0.44	6.63 ± 1.38	8.34 ± 1.52	6.68 ± 0.84	7.43 ± 0.50
4	6.57 ± 0.35	5.40 ± 0.67	5.20 ± 0.60	7.60 ± 0.90	9.56 ± 0.86	10.3 ± 0.95
Ni						
1	1.49 ± 0.16	1.04 ± 0.04	0.84 ± 0.09	2.04 ± 0.20	0.95 ± 0.10	1.24 ± 0.08
2	1.13 ± 0.10	0.81 ± 0.05	1.20 ± 0.10	1.24 ± 0.10	1.00 ± 0.11	1.14 ± 0.09
3	2.06 ± 0.19	1.98 ± 0.17	2.34 ± 0.12	2.20 ± 0.25	1.77 ± 0.18	2.28 ± 0.27
4	2.35 ± 0.15	1.93 ± 0.21	1.98 ± 0.19	1.68 ± 0.33	1.86 ± 0.24	1.97 ± 0.26
Pb						
1	1.39 ± 0.20	0.54 ± 0.14	0.70 ± 0.29	0.95 ± 0.33	1.03 ± 0.20	2.04 ± 0.34
2	3.40 ± 0.91	0.88 ± 0.40	0.75 ± 0.37	1.96 ± 0.19	1.02 ± 0.29	0.75 ± 0.24
3	1.38 ± 0.33	0.82 ± 0.26	1.17 ± 1.07	0.69 ± 0.40	0.34 ± 0.25	0.61 ± 0.21
4	2.80 ± 0.49	1.18 ± 0.52	5.25 ± 2.54	3.81 ± 1.33	4.13 ± 1.58	6.19 ± 2.65
Zn						
1	23.2 ± 1.5	12.6 ± 1.0	15.8 ± 1.3	37.0 ± 4.3	33.3 ± 9.0	40.6 ± 4.3
2	23.7 ± 0.9	12.4 ± 1.4	22.3 ± 1.0	26.6 ± 1.7	36.1 ± 7.2	38.3 ± 3.5
3	37.7 ± 3.2	31.1 ± 6.8	41.9 ± 9.2	83.4 ± 21.8	47.8 ± 10.5	72.6 ± 6.7
4	54.7 ± 19.8	34.8 ± 5.3	44.2 ± 7.6	52.1 ± 10.9	65.7 ± 5.3	74.6 ± 11.8

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Figures

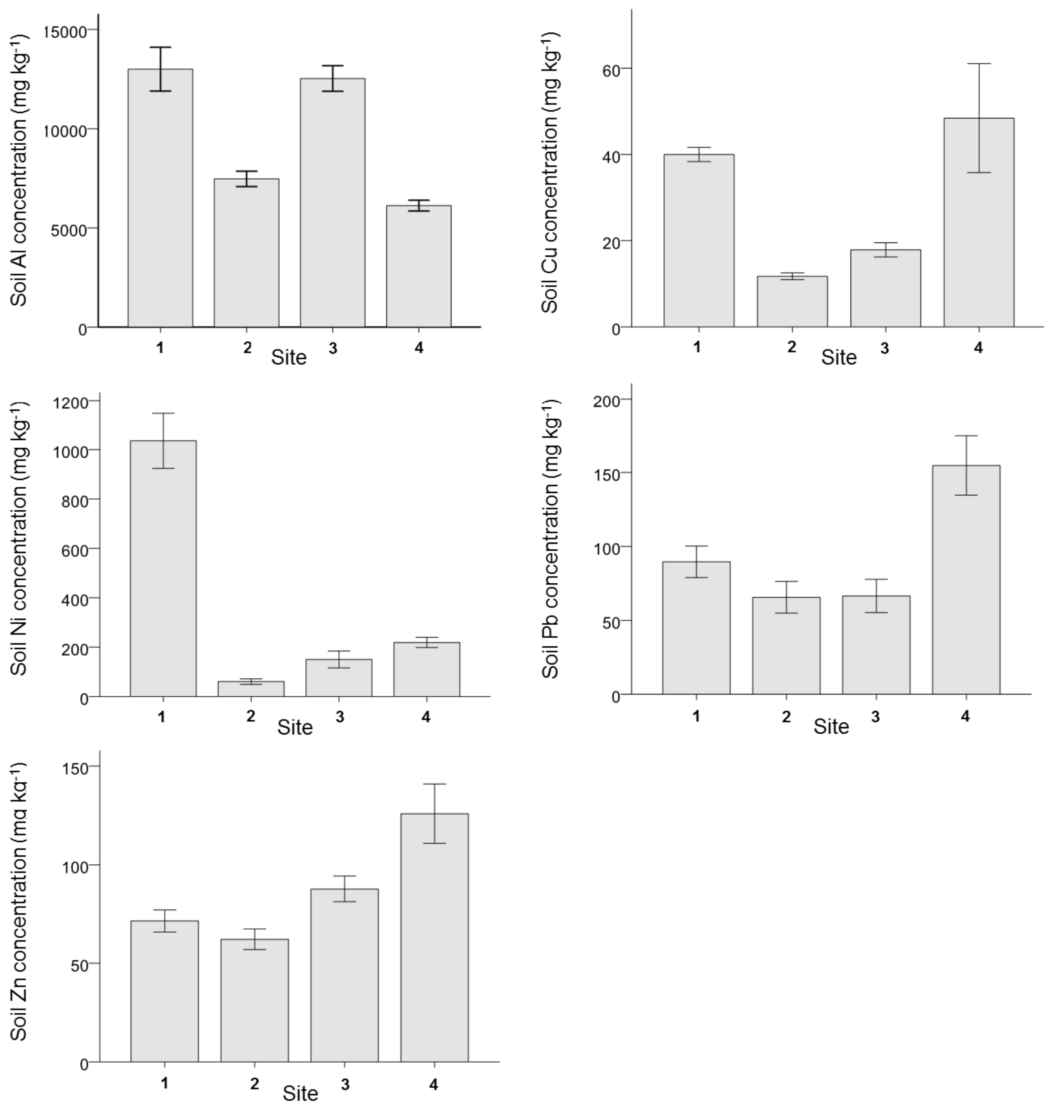

Figure 1. Concentrations (mg kg^{-1}) of potentially toxic metals in the soils of four historic landfill sites (mean ± 1 SE).

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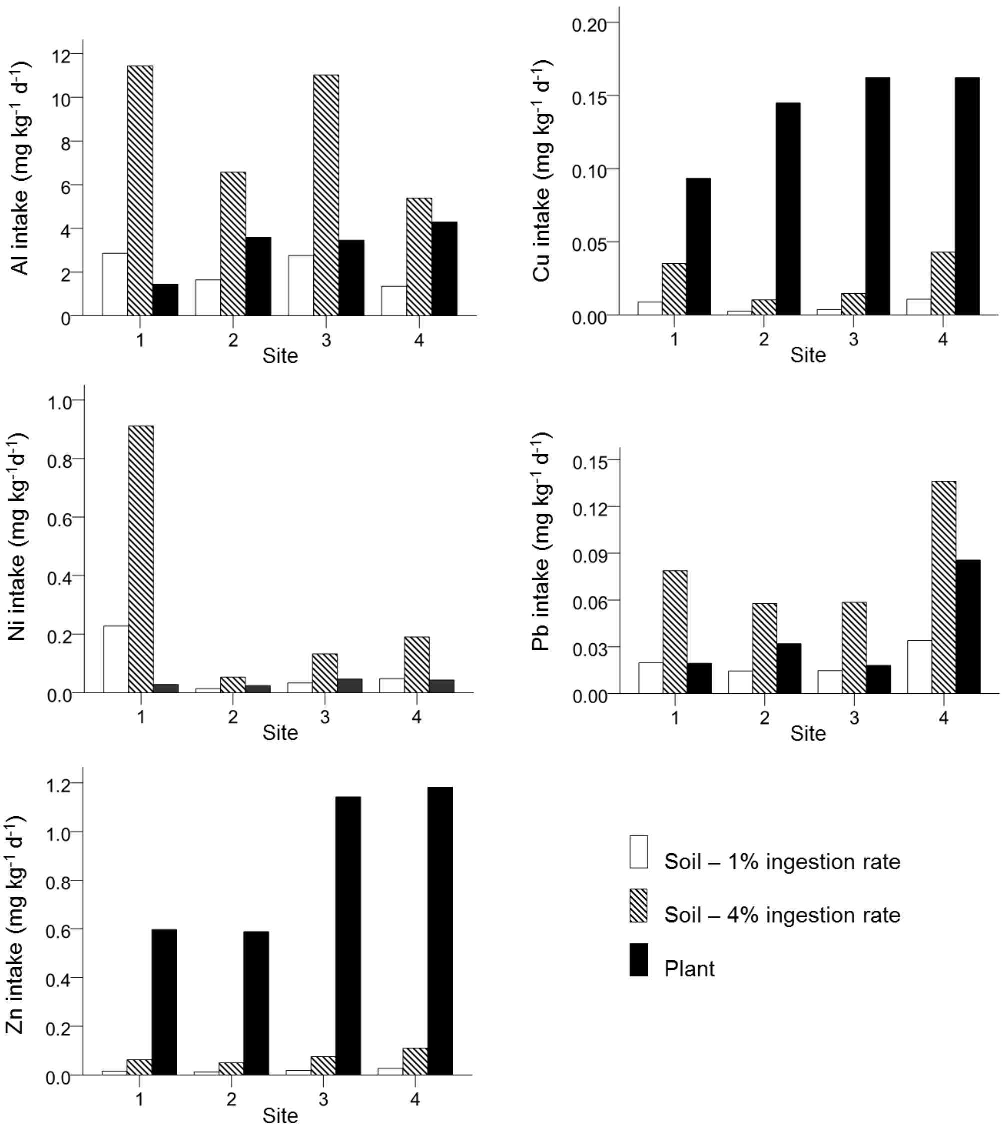

Figure 2. Estimated intakes (mg kg^{-1}(l.w.) d^{-1}) of potentially toxic metals by large grazing mammals from the ingestion of soil and herbage from four historic landfill sites at soil ingestion rates of 1 % and 4 % plant dry matter consumption.

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