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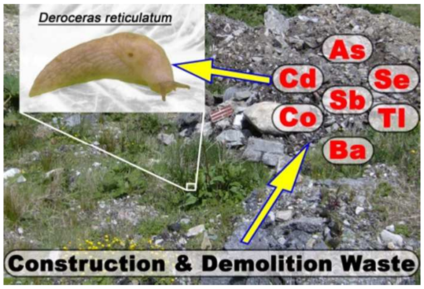

This study employs *Deroceras reticulatum* as the first biomonitor of priority pollutant metals on construction and demolition waste.

Large quantities of construction and demolition waste (C&D) are produced globally every year, with little known about potential environmental impacts. *Deroceras reticulatum* (Mollusca: Gastropoda) was used as the first biomonitor of metals (Ag, As, Ba, Cd, Co, Cr, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V and Zn) on wetlands infilled with construction and demolition (C&D) waste. The bioaccumulation of As, Ba, Cd, Co, Sb, Se and Tl were significantly elevated in slugs collected on C&D waste when compared to unimproved pastures (control sites), while Mo, Se and Sr had significantly higher concentrations in slugs collected on C&D waste when compared to known contaminated sites (mining locations), indicating the potential hazardous nature of C&D waste.

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Assessing metal contamination from construction and demolition (C&D) waste used to infill wetlands: using *Deroceras reticulatum* (Mollusca: Gastropoda).

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Large quantities of construction and demolition waste (C&D) are produced globally every year, with little known about potential environmental impacts. In the present study, the slug, *Deroceras reticulatum* (Mollusca: Gastropoda) was used as the first biomonitor of metals (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Se, Ti, Tl, V and Zn) on wetlands post infilling with construction and demolition (C&D) waste. The bioaccumulation of As, Ba, Cd, Co, Sb, Se and Tl were found to be significantly elevated in slugs collected on C&D waste when compared to unimproved pastures (control sites), while Mo, Se and Sr had significantly higher concentrations in slugs collected on C&D waste when compared to known contaminated sites (mining locations), indicating the potential hazardous nature of C&D waste to biota. Identifying exact sources for these metals within the waste can be problematic, due to its heterogenic nature. Biomonitors are a useful tool for future monitoring and impact studies, facilitating policy makers and regulations in other countries regarding C&D waste infill. In addition, improving separation of C&D waste to allow increased reuse and recycling is likely to be effective in reducing the volume of waste being used as infill, subsequently decreasing potential metal contamination.

Introduction

Wetlands are among the world's most important habitats, providing many ecologically and economically important ecosystem services including water storage and filtration, flood control, carbon fixation, and habitat provision.[1,2] Covering an estimated nine million km^2 globally, they include habitats such as swamps, bogs, fens, marshes and wet grasslands which occur from polar to tropical latitudes.[2] Despite their importance, many wetlands have been and continue to be significantly impacted by anthropogenic activities, including draining, dredging and infilling.[1] While draining is responsible for the largest amount of wetland loss, infilling is also a significant contributor[1], with construction and demolition (C&D) waste often being used under license[3] for this purpose.[4]

Construction and demolition waste results from the construction, renovation or demolition of any structures, such as buildings, roads and bridges.[5,6] For example C&D wastes produced on building sites is dependent on factors such as variations in regional building practices, such as the increased use of timber in Scandinavian countries,[7] and the structure, size and nature of source activity.[5,8] The contents of C&D waste are therefore variable and can include materials such as soil, stones, concrete, timber, plastics, gypsum, metal and bitumen,[5,9] some of which may contain potentially hazardous metals (e.g. Cu, As, Pb, Cd) and other environmentally important compounds such as benzene and chromates.[8] Globally, large quantities of this waste are generated on an annual basis with production linked to economic growth.[10] The most recent European Union data suggest over 870 million tonnes of C&D waste was produced in 2008.[10] However, this figure may be unreliable, as weight/volume estimation techniques are open to biased reporting, and even among countries different materials are reported as C&D waste.[7] The rate of production in many eastern European countries are also known to be under-reported[10] and significant amounts of unregulated C&D waste disposal are known to occur in Spain, Hungary,[7] Italy[11] and the United States.[12] Most of the waste is disposed of in unlined landfills,[5,9] but there is no published information on the habitat types these landfills affect, or the areas covered. Although all European wetlands listed as Natura 2000 sites are protected under the Habitats Directive,[13] local authorities in Ireland issue permits for infilling of unprotected wetlands with C&D waste, and only a small number of these applications require the completion of an Environmental Impact Assessment (EIA).[3]

Although any hazardous material should be removed from the waste prior to infilling in unlined landfills, some of it inevitably fails to be adequately removed during the sorting process.[14] Leachate from C&D waste can contain elevated levels of metals including Al, Fe and Mn,[8,15] and priority pollutants[16] such as As, Cd, Cu and Pb.[8,14,15,17] These elevated metal concentrations in C&D waste leachate can pose a risk to human health if they enter water supplies.[14,15] The generation of this leachate occurs as surface and groundwaters move through the waste, mobilising both organic and inorganic compounds.[18] However, leachate pollutant concentrations can vary according to waste permeability and depth, age of the waste and exposure time. As the C&D waste is typically heterogeneous in nature, there are logistical difficulties in obtaining representative samples for analysis of contaminant content. In addition, the evaluation of temporal variations in contaminant concentrations is restricted by sampling leachate at one point in time. Furthermore, the direct chemical analysis of the waste or the waste leachate limits the provision of information on contaminant bioavailability and ultimately potential toxicity.[19]

The use of biomonitors is a well-established technique for monitoring bioavailable levels of environmental contaminants in terrestrial[20,21,22] and aquatic[23,24] ecosystems. There is little published information on the ecology of C&D waste in wetlands globally except one recent study[25] (from Ireland) which showed that infilling of wetlands with C&D waste significantly altered the plant and dipteran communities present. However, to date organisms have never been employed for monitoring potentially toxic metal contamination from C&D waste. Terrestrial molluscs,[26,13] in particular slugs,[27,28] have been shown to bioaccumulate metals and have been used as cost effective[29] biomonitors of metals at locations contaminated as a result of mining activities.[30,31] *Deroceras reticulatum* (Müller, 1774) is found extensively on wetlands infilled with C&D waste in Ireland. This slug fulfils the prerequisites considered to be essential for a useful biomonitor,[32] including; being geographically widespread (including Europe, North America, Australasia and Central Asia), possessing an annual life cycle (in temperate areas adults die in late autumn or winter[33]), limited active dispersal ability,[34,35] easily collectable[27,30,31] and identifiable,[33] and amenable to laboratory studies.[28] Metal uptake can occur directly from soil by absorption through the dermis or through the digestive tract (ingested soil).[36] However, molluscs tend to accumulate the majority of metals from ingested food[36,37,38,39,40] with their tissue metal content being indicative of ambient plant and soil metal concentrations.[39]

The primary aim of this study was to assess the environmental impact of infilling wetlands with C&D waste, in terms of metal bioavailability by employing for the first time *D. reticulatum* as a biomonitor of metal contamination. Nine sampling locations (Fig. 1), subdivided into three categories (wetlands infilled with C&D waste, known contaminated mining sites and pristine unimproved pasture) (Table 1) were selected on the basis of representing different levels of metal contamination which should be reflected in the metal content of the slug tissue.

Methods

Study area

Slug samples were collected from nine sites in Ireland (see details in Fig. 1 and Table 1) which consisted of three C&D waste sites (CD), three known contaminated sites (KC), and three sites which were considered pristine (PR). *Deroceras reticulatum* was present on all nine sites and the presence of short vegetation permitted the use of slug refuge traps (see below). The CD sites which are typical of C&D waste infill sites on wetlands throughout Ireland and indeed Europe, included C&D waste on wet grassland (CD1), reed and large sedge swamps (CD2) and peatland (CD3). These wetland habitats are now heavily modified and considered damaged wetlands with altered flora and fauna communities and a lower soil moisture content[25]. All three sites were licensed after 2001, and contained, for the most part, concrete, bitumen, soil and stone. CD2 was still being actively infilled at the time of this study, but none of the sites had been levelled or covered with topsoil. The PR sites, located in rural areas, > 5km from municipal and industrial centres were pastures where no chemical treatments including, fertilisers and pesticides had been applied for at least 50 years and hence were considered pristine and selected as controls for comparative purposes. These locations were selected over matching wetlands (for CD1-3) because *D. reticulatum* was abundant on these pastures which were removed from potential sources of contamination.

Table 1 Categorisation of study sites.

Category	Description	Label
C&D waste	C&D waste on wetland (wet grassland)	CD1
C&D waste	C&D waste on wetland (reed and large sedge swamp)	CD2
C&D waste	C&D waste on wetland (peatland)	CD3
Considered pristine	Unimproved pasture	PR1
Considered pristine	Unimproved pasture	PR2
Considered pristine	Unimproved pasture	PR3
Known contaminated	Closed mine (Silvermines – Magcobar)	KC1
Known contaminated	Closed mine (Silvermines – Shallee)	KC2
Known contaminated	Closed mine (Tynagh)	KC3

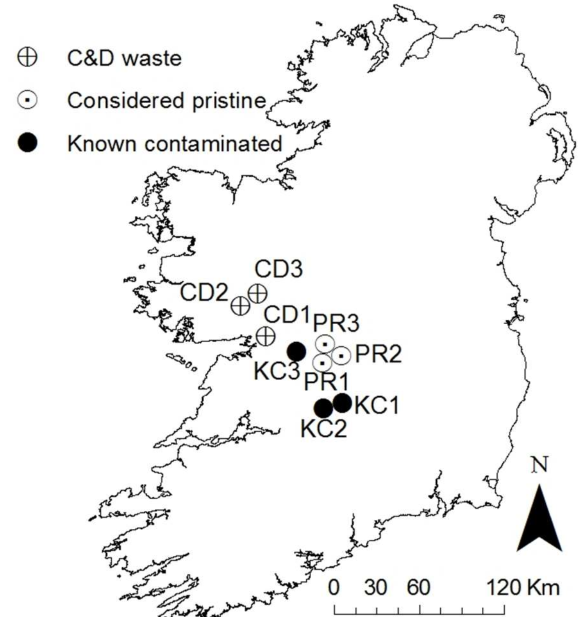

Fig. 1 Site locations in Ireland. CD = construction and demolition waste; PR = considered pristine (unimproved pasture); KC = known contaminated (mine).

Experimental procedure

The variability in metal concentrations for small samples of slugs has been documented[37] for Cd, Pb and Zn. Standard deviations often larger than the mean concentrations have been recorded with sample sizes of only three specimens.[37] Relatively smaller standard deviations were found in other studies[20,30,31,41,42] with sample sizes of up to 18. To address the limitations of previous studies, a larger sample size (n = 30) and parametric range (18 elements) were used in the present study. At each site adult *D. reticulatum* (n = 30; average length - 23mm ± 4mm; mean wet and dry weights of 0.87 g (± 0.2 g) and 0.079 g (± 0.02 g) respectively) were collected over 2 days in September, 2011 using 36 (60 x 60 cm) refuge traps placed 2 m apart in a 6 x 6 grid. Samples were transported to the laboratory in clean polythene bags (one slug per bag; at 4 °C during transportation) and rinsed using Milli-Q (Millipore, Bedford, USA) water. Depuration was allowed (48 hours at 4 °C) in clean plastic containers (1 slug per container) using damp filter paper (changed after 24 hours to minimise coprophagy[31]). The slugs were further rinsed with Milli-Q and freeze dried (Freezone 12, Labconco, Kansas City, USA) at -50 °C. Sample decomposition was performed using a microwave sample preparation system (Multiwave 3000, Anton Paar, Graz, Austria). Samples (individual slugs) were digested in a class 10,000 (ISO class 7) clean room using 4 cm^3 of HNO_3 (Trace Metal Grade, 67-69%, Fisher, UK) and 2 cm^3 of H_2O_2 (*Trace*SELECT® Ultra ≥30%, SIGMA-ALDRICH, USA). Metal concentration (Ag, As, Ba, Cd, Co, Cu, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn) was determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS; ELAN DRC-e, Perkin Elmer, Waltham, USA) in a class 1000 (ISO class 6) clean room.

Quality assurance

Certified Reference Materials (CRMs) of TORT-2 (lobster hepatopancreas; National Research Council Canada) and NIES No.6 (*Mytilus edulis*; National Institute for Environmental Studies Japan) were used with method blanks to validate the accuracy of data for quality assurance purposes. All analytical batches (20 samples) contained four procedural blanks and 4 CRMs and the precision of the methodology was assessed through the performance of duplicate analysis at a frequency of one to every ten samples and the analysis of calibration check standards after every ten samples.

Statistical analysis

The Anderson-Darling test was used to test for data normality. The Kruskal-Wallis test with a Dunn's multiple comparison post-hoc test was used to determine where significant differences in slug metal concentration occurred among site categories. All statistical calculations ($P < 0.05$ and $P < 0.01$) were performed using Minitab (version 16) and SPSS (version 20). Non-detects were treated as zero to avoid positively skewing the analyses. One-way ANOVA Power Analysis was used to determine the most efficient minimum sample sizes for potential future biomonitoring studies using *D. reticulatum*. SigmaPlot (version 12.0) was used to create graphs.

Results and Discussion

All previous studies employing *D. reticulatum* as a biomonitor of environmental contamination have focused on Cd, Cu, Pb and Zn.[20,30,31,41,42] In addition to these EU-List Priority Substances[49] the present study included a further 13 metals (Ag, As, Ba, Co, Cr, Cr, Mo, Ni, Sb, Se, Ti, Tl, V) considered a significant risk to environmental quality and included in the EU-List II Priority Substances (Mn was also included, though not a Priority Substance). At elevated concentrations, all 18 elements are potentially toxic to the biota.[43]

The results (As, Cd, Co, Cu, Mn, Mo, Ni, Pb, Se, Sr and Zn) from the analysis of the *Mytilus edulis* and lobster hepatopancreas reference tissues (Table 2) are in good agreement with their respective certified ranges. In the case of Ag in NIES NO.6, the observed values and the recoveries obtained are likely a function of their close proximity to the LOD of the analytical technique. These reference materials represent the closest possible matrix match for slug tissue which is currently commercially available. Metal concentrations are similar to what was potentially expected in the present study, based on previous investigations on the metal content of *D. reticulatum* tissue from a range of sites.[30,31,41]

Table 2 Observed results from analysis of Certified Reference Materials, with certified and reference values. All values are µg g^{-1}. n = 30.

Element	TORT-2 certified value (± SD)	Observed this study (± SD)
Ag	-	-
As	21.6 (± 1.8)	21.53 (± 1.02)
Cd	26.7 (± 0.6)	27.82 (± 1.24)
Co	0.51 (± 0.09)	0.47 (± 0.05)
Cu	106 (± 10)	110 (± 9.63)
Mn	13.6 (± 1.2)	13.82 (± 2.03)
Mo	0.95 (± 0.10)	0.98 (± 0.05)
Ni	2.50 (± 0.19)	2.30 (± 0.31)
Pb	0.35 (± 0.13)	0.34 (± 0.08)
Se	5.63 (± 0.67)	6.09 (± 0.57)
Sr	45.2 (± 1.9)	52.41 (± 7.51)
Zn	180 (± 10)	180 (± 10.2)
Element	**NIES no.6 certified value (±SD)**	**Observed this study (± SD)**
Ag	2.7×10^{-3} (± 3×10^{-3})	4.4×10^{-2} (± 4×10^{-2})
As	9.2 (± 0.5)	9.56 (± 0.56)
Cd	0.82 (± 0.03)	0.85 (± 0.03)
Co	0.37 (reference value)	0.30 (± 0.04)
Cu	4.90 (± 0.30)	6.18 (± 1.05)
Mn	16.3 (± 1.2)	15.2 (± 1.44)
Mo	0.95 (± 0.10)	0.85 (± 0.05)
Ni	0.93 (± 0.06)	0.80 (± 0.10)
Pb	0.91 (± 0.04)	0.81 (± 0.12)
Se	1.5 (reference value)	1.65 (± 0.57)
Sr	17 (reference value)	17.4 (± 1.30)
Zn	106 (± 6)	106 (± 7.74)

Metal concentrations in *D. reticulatum* are presented for each site category (mean value from three sites in each category) in Table 3, while Figs 2, 3 and 4 show individual site data. Zinc exhibited the highest median concentration of all elements measured across all C&D waste site samples (207.83 µg g^{-1}), while Mn had the highest median value across all mine (731 µg g^{-1}) and unimproved pasture site samples (226.3 µg g^{-1}). As micronutrients, both Mn and Zn[44] are broadly more abundant in biological tissue when compared to other metals.[45] Kruskal-Wallis tests performed on the data showed that all 18 metals displayed some significant ($P < 0.05$) differences between samples recovered from the different site categories (Table 4). There were 11 significant ($P < 0.05$) differences for data comparisons between C&D waste and pasture samples, while comparisons of both 'C&D waste vs mining' and 'mining vs pasture' samples each showed 16 significant ($P < 0.05$)

differences.

Table 3 Median metal concentrations in *Deroceras reticulatum* for each site category (n = 90 per site category). Interquartile range in parentheses. All values are µg g^{-1}. LOD = Limit of detection.

Element	Mining	C&D	Pasture
Ag	0.45 (0.85)	< LOD of 1.9 x 10^{-4}	0.036 (0.045)
As	0.38 (1.1)	0.19 (0.10)	0.13 (0.062)
Ba	79 (71)	9.9 (5.8)	2.6 (4.5)
Cd	37 (29)	6.5 (4.6)	3.8 (3.5)
Co	0.61 (0.66)	0.39 (0.27)	0.31 (0.16)
Cu	104 (52)	46 (18)	50 (24)
Mn	731 (803)	97 (119)	226 (382)
Mo	1.8 (0.91)	3.1 (1.3)	2.8 (2.6)
Ni	1.8 (1.51)	1.1 (0.52)	1.3 (0.93)
Pb	7.3 (59)	0.31 (0.41)	0.34 (0.24)
Sb	0.054 (0.11)	0.015 (0.023)	0.0095 (0.015)
Se	0.70 (0.74)	1.9 (1.4)	0.71 (0.62)
Sr	43 (21)	48 (38)	54 (28)
Ti	38 (6.8)	31 (5.6)	38 (10.8)
Tl	0.43 (0.94)	0.017 (0.012)	0.011(0.0077)
V	0.10 (0.075)	0.12 (0.054)	0.13 (0.051)
Zn	795 (519)	207 (70)	197 (96)

Concentrations of As, Ba, Cd, Co, Sb, Se and Tl were significantly ($P < 0.05$) elevated in slugs from C&D waste sites when compared to unimproved pasture (Table 4). Arsenic and Cd[8,15] have been reported at elevated concentrations in C&D leachate, from simulations used in the laboratory, small field test cells and full scale C&D waste infill sites.[8,15,17] Isolating the source(s) of the increased metal concentrations within the C&D waste in this study is difficult due to its variable nature. They are generally known to originate from permitted substances such as pigments used on C&D waste materials (for Cd and Sb), wood treated with preservatives (As), and cement (Tl).[8,43] Another likely source of these metals is from unpermitted items or substances mixed through the C&D waste, some of which may be hazardous, such as municipal waste (As, Cd), electrical equipment (Cd, Sb, Tl) and pesticide / paint containers (As, Cd, Sb).[8,14,43] Determining the abundance of these unpermitted items present in C&D waste is not feasible due to the volume and associated cost, but the presence of such items was noted frequently at the C&D waste sites.

Concentrations of three essential[43] metals (Mo, Se, Sr) were significantly higher ($P < 0.05$) in the slugs from C&D waste sites than from mines (KC 1, 2 and 3). A nationwide soil geochemical atlas[46] suggests that the C&D waste sites have higher background levels for Mo, Se and Sr, compared to KC1 and KC2, and this is reflected in the slug tissue concentrations. Soil S (in the form of sulphate) and P compete for the same uptake pathways as Mo in plants,[47] and as a result, uptake of Mo by plants may be reduced in mining locations with higher concentrations of S and P. Likewise a correspondingly lower concentration of Mo would, therefore be expected in herbivorous slugs such as *D. reticulatum* on these sites. A similar scenario could be expected for Se which is known to share similar uptake pathways in plants as S.[48] The significantly higher Sr concentrations in slugs collected on C&D waste (compared to mines) is likely to be a result of elevated background soil Sr concentrations at these C&D waste locations.[46] All of the metals which showed significantly elevated levels in the slug samples from C&D waste (compared to mines and unimproved pasture) are EU priority contaminants.[49]

Table 4 Comparison (between site categories; n = 90 per site category) of metal concentrations in *Deroceras reticulatum*, using Kruskal-Wallis test with Dunn's multiple comparison post hoc test. Values shown are test statistic 'K'; * indicates significant difference at $P \leq 0.05$; ** indicates significant difference at $P \leq 0.01$. [a]Most efficient sample size determined using one way ANOVA Power analysis with power value of 0.95 (P = 0.05).

Between sites	Mining vs Pasture	Mining vs C&D	C&D vs Pasture	Minimum sample size for future studies[a]
Ag	100**	160**	59**	40
As	116**	72**	-42**	23
Ba	166**	101**	-65**	11
Cd	156**	109**	-47**	15
Co	84**	53**	-30*	14
Cu	120**	127**	6.7	13
Mn	75**	136**	60**	16
Mo	-63**	-87**	-24	20
Ni	58**	95**	36**	12
Pb	134**	135**	0.96	10
Sb	118**	87**	-30**	17
Se	-2.03	-89**	-87**	9
Sr	-56**	-39**	16	15
Ti	-10	91**	102**	9
Tl	153**	114**	-38**	43
V	-44**	-26	17	20
Zn	142**	127**	-14	11

Overall metal concentrations in slugs were generally found to be significantly ($P < 0.05$) lower from both C&D waste (Ag, As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Sb, Ti, Tl, Zn) and unimproved pasture (Ag, As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Sb, Tl, Zn) when compared to mine sites. In particular, concentrations of Tl, Sb, Mn, Zn, Ba, Cd, Cu and Pb were elevated in *D. reticulatum* from the mine sites (Figs 2, 3 and 4). Environmental contamination associated with past mining operations at these locations have been widely documented.[50,51,52,53] The significantly lower concentrations in *D. reticulatum* from the C&D waste and pasture sites, compared with the mine sites coincided with metals that were known to exist at elevated concentrations in soils at KC3 – Tynagh Mines[50,51] (As, Ba, Cd, Cu, Ni, Pb, Zn) and Silvermines KC1 and 2[50,52] (Cd, Pb, Zn). All slug samples were collected on vegetated mine tailings, with KC2 having a disused smelting plant and laboratories adjacent to the sampling location.

Compared to C&D waste, only four metals (Ag, Mn, Ni, and Ti) had significantly ($P < 0.05$) higher concentrations in slugs collected on pasture sites (Table 3), with two of these (Mn and Ti) significantly ($P < 0.05$) elevated in specimens from one site (PR2) in particular (compared to PR1 and PR3; Fig 2 & 3). In addition Mo, Sr and V also displayed significantly higher concentrations in slugs from the unimproved pasture than from mining sites. Previous studies with the aquatic snail *Lymnaea stagnalis* (Linneus L.) and the slug *Arion ater* (Linnaeus, 1758)

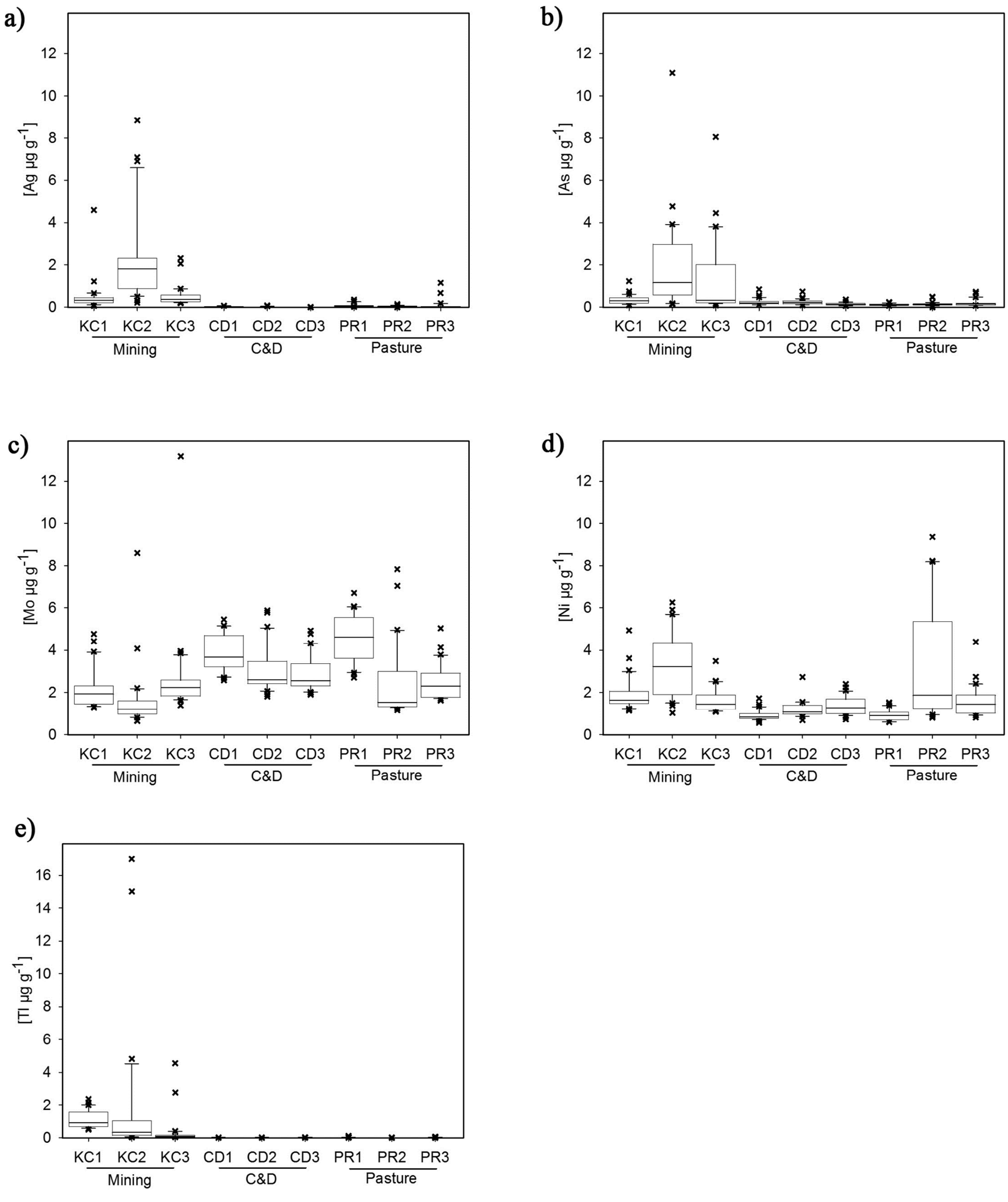

Fig. 2 (a-e) Boxplots showing median metal concentrations and outliers for Ag, As, Mo, Ni and Tl (data separated by site and sites grouped by category; n = 30 for each site).

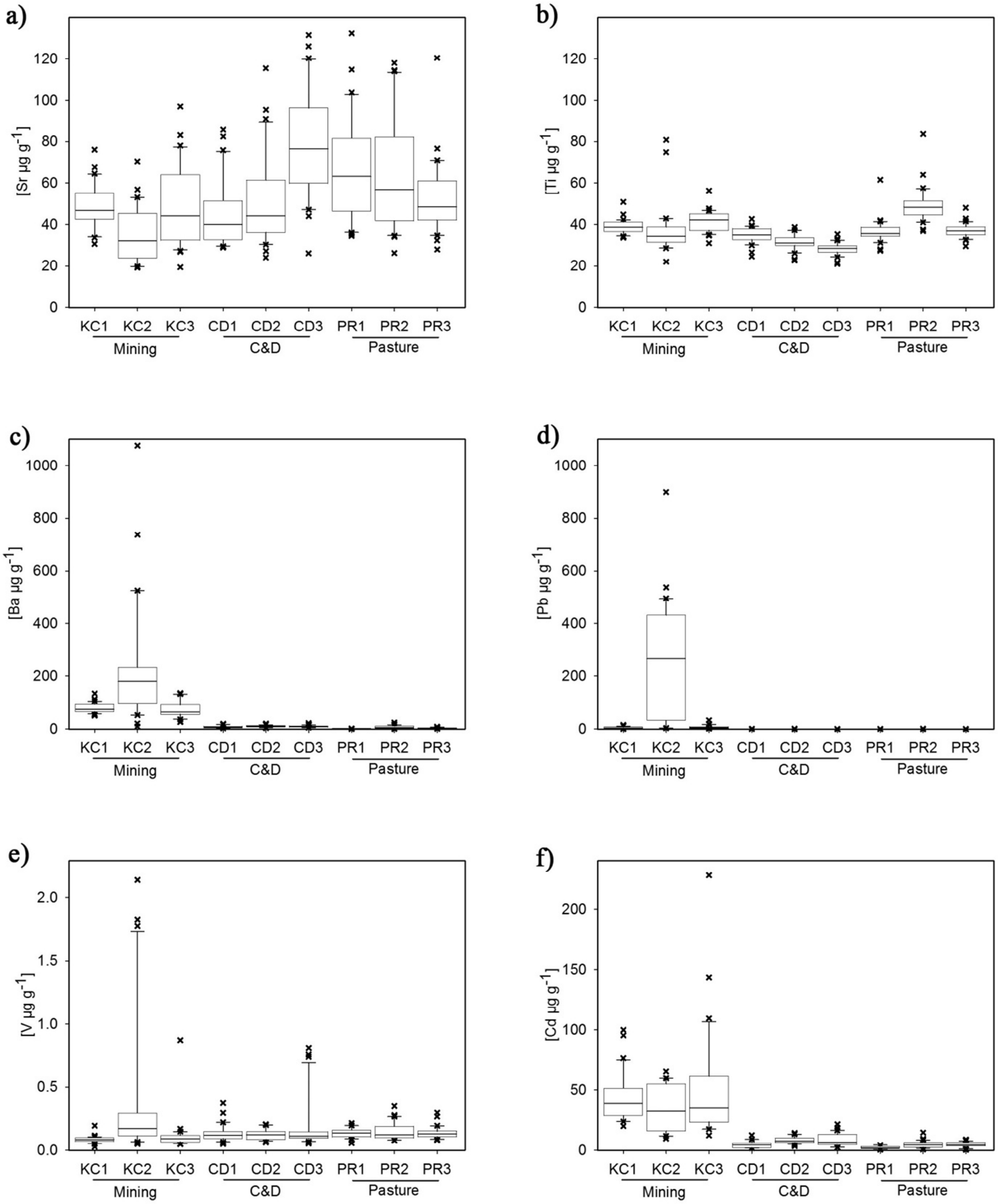

Fig. 3 (a-f) Boxplots showing median metal concentrations and outliers for Sr, Ti, Ba, Pb, V and Cd (data separated by site and sites grouped by category; n = 30 for each site).

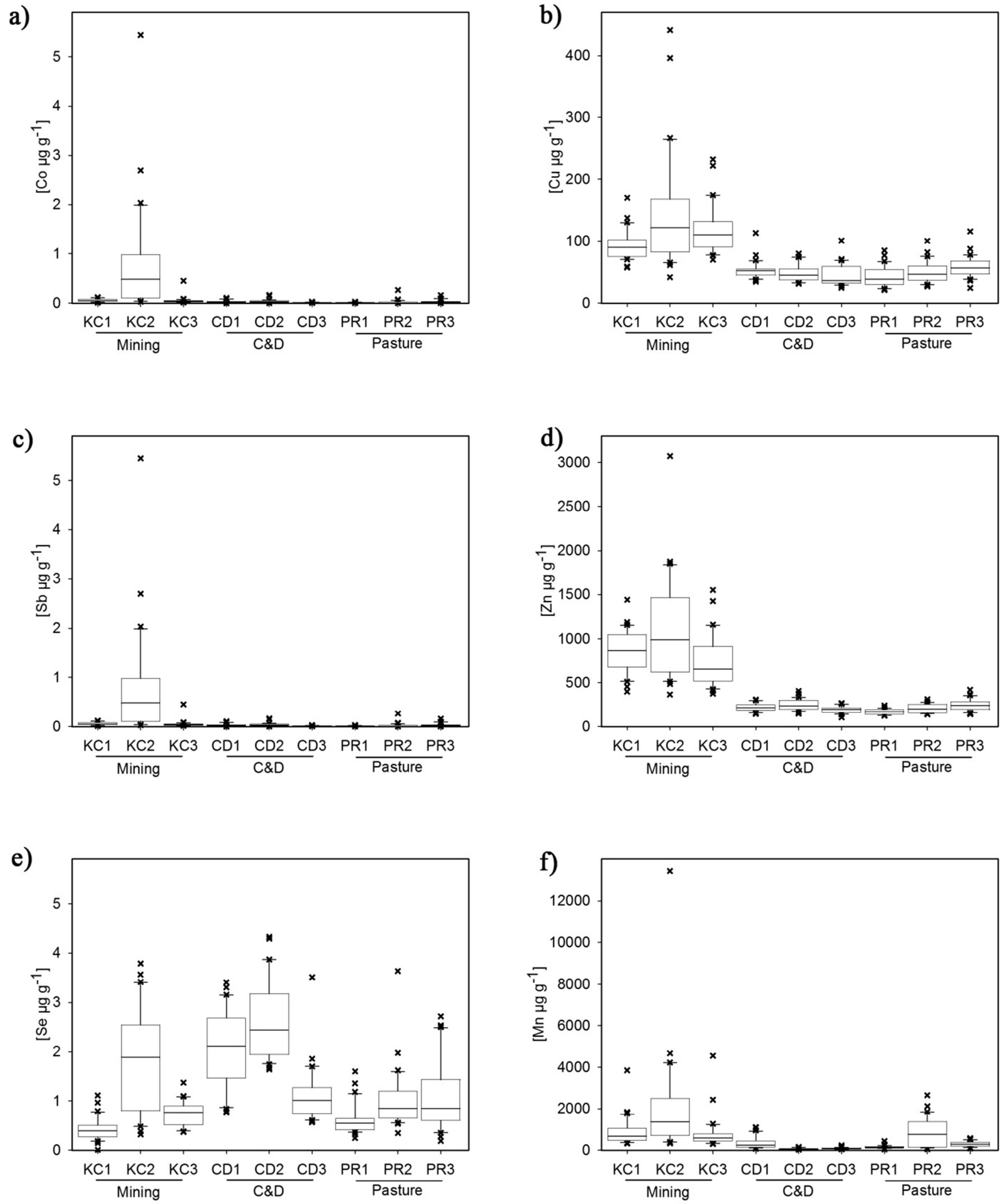

Fig. 4 (a-f) Boxplots showing median metal concentrations and outliers for Co, Cu, Sb, Zn, Se and Mn (data separated by site and sites grouped by category; n = 30 for each site).

have similarly shown control samples (unpolluted canal and remote hilltops respectively) to have elevated concentrations of Mn, Sr and Ti,[22,23] with no known reasons for the increased metal concentrations. Soil geochemical profiles[46] show background Mn, Ni and Ti levels to be similar for the C&D waste and unimproved pasture sites, while Mo, Sr and V are thought to be higher around the pasture sites than KC1 and KC2, although some localised variability is possible. In addition, Mn can occur naturally at elevated concentrations in limestone[54], which is the dominant lithology at all of the study sites. The uptake of Sr is thought to be reduced in *A. ater* with increasing concentrations of Pb,[22] so the low levels of Pb on the pasture (compared to mines; Table 4) may contribute to more efficient Sr accumulation. Nickel is thought to share a common poorly regulated uptake pathway with Co in the aquatic snail, *L. Stagnalis,*[24] so the elevated concentrations of Co at the C&D waste (Table 4) sites may compete directly with Ni, thereby reducing uptake of the latter.

The significantly elevated concentrations of Ag found in slugs from the pasture (compared to those from C&D waste), may be exaggerated by the slow excretion rates of Ag in gastropods.[55] It is worth noting that Ag (Fig 2) was found to be below the limit of detection for many samples on both C&D waste and unimproved pasture, and so this difference may be limited in it significance.

The concentrations of Zn and Cu observed in this study for mine sites concur with previous studies that used *D. reticulatum* (Table 5) collected on contaminated sites.[20,30,41] The concentrations of Cd found during the present study are slightly lower than the concentrations recorded in other field studies from contaminated sites.[20,30,31,41] Sphalerite (a Zn containing mineral mined at Silvermines[52] and Tynagh[51]) is associated with low Cd concentrations,[56] as evident from Cd concentrations close to the limit of detection in groundwater from KC2 (even when other elements were present in high concentrations).[53] For one site in this study (KC2), Pb concentrations were found to be similar to previous field studies (on mines). [20,30,31,41,42]

Although there is still some between-site variability, it is likely that slug metal content is a true reflection of the actual soil metal content across all sites. In the case of KC2, which shows significantly ($P < 0.05$) elevated concentrations for Ba, Co, Mn, Pb, Sb, Tl and V relative to the other mine sites, these increased soil metal concentrations are likely associated with the onsite smelting plant[52] (as seen near smelting plants on other mines[57]).

Concentration factors (ratio of metal concentration in slugs compared to the vegetation) have been shown to decrease as the metal concentrations increase, with the exception of Pb.[37] This suggests that care must be taken when attempting to determine precise metal concentrations in soil and vegetation based on *D. reticulatum* metal concentrations. However, metal concentrations (Cd, Pb, Zn) in *D. reticulatum* increase as concentrations increase in their food source.[37] This would suggest that slug metal concentrations should reflect ambient metal concentration trends in the surrounding vegetation, and also that metal accumulation in these plants impacts on slug metal concentrations. Although sub-lethal concentrations of some metals (such as Cd and Zn) are known to cause sub-cellular damage (e.g. nucleolus alteration, mitochondrial swelling and microvilli shortening) in gastropods,[58] including *D. Reticulatum,*[28] detoxification is utilised as a survival strategy.[33] This detoxification can involve either immobilisation (e.g. activation of metal-binding proteins such as metallothionein for Cd and Zn[59]) within cell lysosomes or precipitation into granules[60] (Pb) which can be excreted via faeces.[28] Detoxification is metal specific, with essential metals, needed for biological functions, having the most efficient rates.[61]

The non-essential Cd and Pb have no known function in biological systems and tend to be more poorly regulated.[59] Growth rates of molluscs are also known to be reduced by elevated concentrations of some metals (Cd, Cu, Ni),[24] which in turn may increase overall metal concentrations, because the potential dilution effect of newly generated tissue is reduced.[62,13] This may, therefore, compound slug metal content in contaminated sites. The uptake rate of metals by invertebrates is species specific, and dependant on a number of biotic (e.g. feeding behaviour and physiology[36]) and abiotic factors (e.g. metal speciation,[27] temperature[63] and pH[36]). In addition, the interactions of such biotic and abiotic factors with site specific characteristics could influence metal uptake.

The results of the one-way ANOVA Power Analysis (Table 4) suggest that the concentration of most of the target metals in this study could be accurately calculated using a smaller number of samples, i.e. n < 20. Therefore, future studies and site assessments could potentially involve even more cost-effective sampling.

Although the variable nature of C&D waste means that assumptions should not be made about which metals may be elevated at any single site, the present study highlights the bioaccumulation of priority metal pollutants (As, Ba, Cd, Co, Mo, Sb, Se, Sr and Tl) in slugs at C&D waste sites. While slugs from C&D waste sites should not have the same apparent degree of exposure to hazardous metals as slugs from mine sites, it is important to note that potential mobilisation of metals is not a criterion considered when waste licenses are issued for the disposal of such waste in the EU and elsewhere. Leachate from C&D waste is known[8,14,15,17] to contain elevated concentrations of metals (Al, As, Cd, Cu, Fe, Mn, Pb). One of the most important and useful aspects of utilising biomonitors in environmental monitoring and assessment is that their tissues provide quantitative information on the bioavailable fraction of contaminants, which also have the potential for biomagnification in the food chain. Many of the difficulties associated with obtaining representative soil and groundwater samples from a heterogeneous matrix (such as C&D waste) are also avoided. This study has identified that certain metals known to attain high concentrations in C&D leachate, including As and Cd, are bioavailable, and therefore ecotoxicologically relevant. This can result in significantly elevated concentrations in gastropods on C&D waste, compared to the baseline unimproved pasture. The potential risks of metal contamination in the biota at higher trophic levels or adjacent to such waste are not yet known, although terrestrial biomagnification is known to occur.[64] Insectivores such as *Erinaceus europaeus* L.,[65] are known to be sensitive to diet-borne metal accumulation. Any potential contamination threat to adjacent areas would likely be site-dependent, with variables such as waste contents,[8,15] geology,[54], soil[36] recharge, aspect (direction of surface runoff) and groundwater flow likely to be influential factors. The elevated metal concentrations in the leachate (as evident from previous

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Table 5 Comparison of available published metal data (µg g^{-1} dry weight) in *Deroceras reticulatum* . Concentrations expressed as mean ± standard deviation

Reference	Location	Pb	Cd	Zn	Cu	Fe (and Fe compounds)	Comment
Greville and Morgan, 1989[31,41]	UK (Rhondda Cynon Taf)	130 ± 15	65 ± 10	900 ± 100	70 ± 15	-	Contaminated site (mine) (September data)
Greville and Morgan, 1990[30]	UK (Rhondda Cynon Taf)	130 ± 15.2	64.2 ± 10.4	874.9 ± 122.1	68.8 ± 16	-	Contaminated site (mine)
Greville and Morgan, 1991[20]	UK (Rhondda Cynon Taf)	162.4 ± 21.6	65.1 ± 17.5	735.2 ± 119.6	-	-	Contaminated site (mine)
	UK (Vale of Glamorgan)	3.2 ± 0.3	9.3 ± 0.8	205.2 ± 32.1	-	-	Control site
Bullock et al., 1992[27]	Laboratory	-	-	-	-	2554 ± 140.5	Exposed to Contamination
	UK (Hertfordshire)	-	-	-	-	103 ± 5.2	Irrigated field
Greville and Morgan, 1993[42]	UK (Rhondda Cynon Taf)	62.5 ± 10	-	-	-	-	Contaminated site (mine)
	UK (Vale of Glamorgan)	4.7 ± 1.9	-	-	-	-	Control site
Graff et al., 1996[37]	Laboratory	1168.6 ± 1532.3	245.9 ± 135	4252.4 ± 2785			Contaminated
	Laboratory	7.6 ± 9.3	7.8 ± 8.9	92.8 ± 69.1	-	-	Control
Köhler et al., 1996[70]; Triebskorn and Köhler, 1996[28]; Köhler and Triebskorn, 1998[71]	Laboratory	1168.6 ± 1532.3	245.9 ± 135	4252.4 ± 2785	-	-	Contaminated
	Laboratory	178.7 ± 115.2	121.8 ± 7.6	393.1 ± 192.0	-	-	Medium contamination
	Laboratory	4.4 ± 7.2	2.9 ± 1.4	76.1 ± 26.5	-	-	Control
This study	Ireland (Galway)	0.47 ± 0.35	4.86 ± 2.81	220.7 ± 47.2	53.3 ± 14.6	91.9 ± 25.8	C&D (CD1)
	Ireland (Galway)	0.65 ± 0.38	8.65 ± 2.88	246.4 ± 64.4	48.4 ± 13.8	82.2 ± 20.3	C&D (CD2)
	Ireland (Galway)	0.22 ± 0.17	8.63 ± 5.35	193.6 ± 39.3	43.9 ± 17.4	100.2 ± 69.6	C&D (CD3)
	Ireland (Galway)	0.42 ± 0.14	2.35 ± 1.22	170.0 ± 31.9	43.2 ± 16.1	110.8 ± 30.5	Unimproved pasture (PR1)
	Ireland (Galway)	0.41 ± 0.32	5.04 ± 3.05	206.8 ± 50.1	49.6 ± 17.2	90.5 ± 16.9	Unimproved pasture (PR2)
	Ireland (Galway)	0.30 ± 0.14	4.89 ± 2.26	246.2 ± 66.7	58.7 ± 17.8	111.5 ± 36.0	Unimproved pasture (PR3)
	Ireland (Tipperary)	5.74 ± 3.62	42.9 ± 19.4	857.5 ± 249.3	92.9 ± 24.2	80.8 ± 34.5	Mine (KC1)
	Ireland (Tipperary)	274.2 ± 215.2	34.4 ± 18.5	1086.1 ± 573.2	144.7 ± 91.6	298.4 ± 338	Mine (KC2)
	Ireland (Galway)	8.29 ± 6.27	51.0 ± 45.7	742.6 ± 301.1	120.0 ± 40.0	90.8 ± 43.2	Mine (KC3)

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studies) and slugs from C&D waste indicate that action should be taken to minimise the risk of future contamination. By separating waste more efficiently (such as source/on-site separation)[66] and diverting more C&D waste to recycling,[67] the dependency on disposal would be reduced, meaning fewer infill sites would be required.[68] This improved separation would also be likely to reduce the amount of unpermitted items/substances that occur in C&D waste infill.

Conclusions and recommendations

This study demonstrates the potential usefulness of employing *D. reticulatum* as a biomonitor of metals on C&D waste sites and has, for the first time, shown that gastropods collected on C&D waste have significantly higher metal concentrations than those from the unimproved pasture (for As, Ba, Cd, Co, Sb, Se and Tl), and mines (for Mo, Se and Sr). The most likely source of these EU priority pollutants is the C&D waste itself, although the exact sources of contamination within the waste are difficult to isolate due to the varied nature of the materials within each site (and even between regions or countries). Improved waste separation and recycling rates would be likely to reduce the number of infill sites and the volume of unpermitted items mixed through the waste. Unlike soil or water analyses, these biomonitors reflect only the bioavailable (and so ecotoxicologically important) forms of metal, indicating the importance of such monitoring. This study is a first, from which other studies around the world can be compared. It has highlighted the need for further investigation into the bioaccumulation (and potential biomagnification) of metals in the biota from such C&D waste infill sites (and the toxicity thresholds of those metals), which are common and often unregulated throughout the world. Developing Ecological Investigation Levels[69] for molluscs to assess site contamination would increase their usefulness as future biomonitors. Small sample sizes (n < 20) should be sufficient for most metals, making the use of *D. reticulatum* a cost-effective biomonitor choice. Where metals are found to be bioaccumulating in organisms to dangerous concentrations, there is a need for better enforcement of existing environmental protection policies and possibly implementing policy changes to reduce the impact of such sites on other environmental compartments and to encourage more sustainable development in the future.

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Notes and references

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1 W.J. Mitsch and J.G. Gosselink, *Wetlands* 3[rd] ed. John Wiley and Sons Inc., New York, 2000, pp. 571-638.
2 P.A. Keddy, *Wetland Ecology: Principles and Conservation*, Cambridge University Press, England, 2000, pp. 3-80.
3 Statutory Instrument No. 821 of 2007, *Waste Management (Facility Permit and Registration) Regulations 2007*, Government of Ireland, 2007.
4 Environmental Protection Agency, *National Waste Report, 2010*, Environmental Protection Agency, Ireland, 2012, pp. 45-48.
5 Franklin Accociates, *Characterization of Building-Related Construction and Demolition Debris in the United States*, Report prepared for U.S. Environmental Protection Agency, Washington, 1998.
6 C. Clarke, J. Jambeck and T. Townsend, *Crit. Rev. Environ. Sci. Technol.*, 2006, **36**(2), 141-186.
7 European Commission DG ENV, *Service contract on management of construction and demolition waste - SR1. Final Report Task 2*, European Commission, Brussels, 2011.
8 W.J. Weber, Y.C. Jang, T. G Townsend and S. Laux, *J. Environ. Eng.*, 2002, **128**(3), 237-245.
9 P.T. Williams, *Waste Treatment and Disposal*, John Wiley & Sons Ltd., England, 1998, pp.114-115.
10 Eurostat, *Eurostat Yearbook 2011: Environment*, The Publications Office of the European Union, Luxembourg, 2011, pp. 480-489.
11 Symonds Group, ARGUS, COWI, PRC Bouwcentrum, *Construction and demolition waste management practices and their economic impacts*, 1999, Available via: http://ec.europa.eu/environment/waste/studies/cdw/cdw_report.htm Accessed 9th March, 2014.
12 ICF Incorporated, *Construction and Demolition Waste Landfills*, Report prepared for U.S. Environmental Protection Agency Office of Solid Waste, 1995.
13 J.L. Metcalfe-Smith, R.H. Green, L.C. Grapentine, *Can. J. Fish. Aquat. Sci.*, 1996, **53**, 205-219.
14 N. Roussat, J. Mehu, M. Abdelghafour, P. Brula, *Waste Manage.*, 2008, **28**, 2032-2040.
15 B.A. Melendez, *A study of leachate generated from construction and demolition landfills*, Florida Univ Gainsville Dept of Environmental Engineering Sciences, 1996, pp.1-51.
16 USEPA (United States Environmental Protection Agency), Priority Pollutants, http://water.epa.gov/scitech/methods/cwa/pollutants.cfm, accessed 10th February, 2014.

17 A. López, A. Lobo, *Waste Manage.*, 2014. DOI: http://dx.doi.org/10.1016/j.wasman.2014.04.004.

18 B. Faeiza, A.K. Mohamad Syarizal, M.D. Fairus, *e-Proceeding of 17th Analysis Chemistry Malaysia Symposium. 24 – 26 August 2004. Swiss-Garden Resort & Spa, Kuantan, Pahang*, 2004, pp. 699-708.

19 L. Leita, G. Petruzzelli, F. Pedron, M. Alja, R. Mena, M. Valentini, *E3S Web of Conferences*, 2013, **1**, 13008.

20 R.W. Greville and A.J. Morgan, *Environ. Pollut.*, 1991, **74**, 115-127.

21 M. Boshoff, K. Jordaens, T. Blackeljau, S. Lettens, F. Tack, B. Vandecasteele, M. De Jonge, L. Bervoets, *Sci. Total Environ.*, 2013, **449**, 470-481.

22 J.D. Popham, J.M. D'Auria, *Water Air Soil Poll.*, 1980, **14**, 115-124.

23 F.B. Pyatt, A.J. Pyatt, V.W. Pentreath, *Environ. Toxicol. Chem.*, 1997, **16**, 1393-1395.

24 S. Niyogi, K.V. Brix, M. Grosell, *Aquat Toxicol*, 2014, DOI: http://dx.doi.org/10.1016/j.aquatox.2014.02.012.

25 J. Staunton, C.D. Williams, R.J. McDonnell, G.T.A. Fleming, T. Henry, M.J. Gormally, *Appl. Ecol. Environ. Res.*, 2014, **12**, 457-479.

26 B. Berger, R. Dallinger, *Environ Monit. Assess.*, 1993, **25**, 65-84.

27 J.I. Bullock, N.P. Coward, G.W. Dawson, I.F. Henderson, L.F. Larkworthy, A.P. Martin and S.P. McGrath, *Crop Prot.*, 1992, **11**, 329-334.

28 R. Triebskorn and H.R. Köhler, *Environ. Pollut.*, 1996, **93**(3), 327-343.

29 I. Marigómez, M. Kortabitarte, G.B.J. Dussart, *Arch. Environ. Contam. Toxicol.*, 1998, **34**, 167-176.

30 R.W. Greville and A.J. Morgan, *J. Moll. Stud.*, 1990, **56**, 355-362.

31 R.W. Greville and A.J. Morgan, *J. Moll. Stud.*, 1989, **55**, 31-36.

32 P. Jones and P.L. Kaly, In *Detecting Ecological Impacts: Concepts and Applications in Coastal Habitats*, eds. R.J. Schmitt and P.J. Osenberg, Academic Press, UK, (1996). Ch 3 29-48.

33 A. Wiktor, *Annales Zoologici*, 1999, **49**(4), 348-590.

34 S. Aubry, C. Labaune, F. Magnin, P. Roche, L. Kiss, *J. Anim. Ecol.*, 2006, **75**, 802-813.

35 B. Baur, *Ann. Naturhist. Mus. Wien*, 1993, **94-95**, 307-321.

36 W.J.G.M. Peijnenburg, In *Bioavailability of Metals in Terrestrial Ecosystems*, ed. H.E. Allen, Society of Environmental Toxicology and Chemistry, Florida, (2002) Ch 5 89-112.

37 S. Gräff, M. Berkus, G. Alberti and H.R. Köhler, *Biometals*, 1997, **10**, 45-53.

38 R. Dallinger, B. Berger, R. Triebskorn-Köhler and H. Köhler, In *Soil Biology and Ecotoxicology*, ed. G.M. Barker, CAB International, UK, (2001). Ch 14 489-525.

39 M.J.M. Notten, A.J.P. Oosthoek, J. Rozema, R. Aerts, *Environ. Poll.*, 2005, **138**, 178-190.

40 M.N. Croteau, S.N. Luoma, *Environ. Sci. Technol.*, 2008, **42**, 1801-1806.

41 R.W. Greville and A.J. Morgan, *J. Moll. Stud.*, 1989, **59**, 287-303.

42 R.W. Greville and A.J. Morgan, *Environ. Pollut.*, 1993, **81**, 213-216.

43 D.C. Adriano, *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals 2nd ed.*, Springer-Verlag, New York, 2001, pp 1-28.

44 USEPA, *The Micronutrient Fertilizer industry: From Industrial By-product to Beneficial Use*, Office of Enforcement and Compliance Assurance, USEPA, Washington, DC, 2001.

45 R. Laskowski, S.P. Hopkin, *Environ. Poll.*, 1996, **91**, 289-297.

46 D. Fay, G. Kramers, C. Zhang, D. McGrath, E. Grennan, *Soil Geochemical Atlas of Ireland*, Teaagasc and Environmental Protection Agency, Wexford, 2007, pp 19-111.

47 H. Heuwinkel, E.A. Kirkby, J. Le Bot, H. Marschner, *J. Plant Nutr.*, 1992, **15**, 5, 549-568.

48 T.G. Sors, D.R. Ellis, D.E. Salt, *Photosynth. Res.*, 2005, **86**, 3, 373-389.

49 Council Directive 2006/11/EC of the European Parliament and of the Council, European Commission, Brussels, 2006.

50 G. Stanley, V. Gallagher, F. Ní Mhairtín, J. Brogan, P. Lally, E. Doyle and L. Farrell, *Historic Mine Sites – Inventory and Classification. Volume 1*, EPA and GSI, Ireland, 2009.

51 J. Brogan. Report of the investigation into the presence of lead and other heavy metals in the Tynagh Mines Area, County Galway. Report prepared for Office of Environmental Enforcement, Environmental Protection Agency, Ireland, 2003.

52 Office of Environmental Enforcement, *Final report of expert group for Silvermines, Co. Tipperary*. Environmental Protection Agency, Ireland, 2004.

53 T. Henry, *An Integrated Approach to Characterising the Hydrogeology of the Tynagh Mine Catchment, County Galway, Ireland*, PhD Thesis, National University of Ireland, Galway, 2014.

54 S.C. Homoncik, A.M. MacDonald, K.V. Heal, B.E. Ó Dochartaigh, B.T. Ngwenya, *Sci. Total Environ.*, 2010, **408**, 2467-2473.

55 P.B. Lobel, C.D. Bajdik, S.P. Belkhode, S.E. Jackson, H.P. Longrich, *Arch. Environ. Contam. Toxicol.*, 1991, **21**, 409-421.

56 M.N. Croteau, S.K. Misra, S.N. Luoma, E. Valsami-Jones, *Environ. Sci. Technol.*, 2011, **45**, 6600-6607.

57 J.D. Hem, *Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd ed. United States Geological Survey Water-supply Paper 2254*, USGS, Washington, DC, 1989.

58 B.J. Alloway, *Heavy Metal in Soils*, Springer Dordrecht, London, 2013, pp.3-50.

59 E. Hödl, E. Felder, M. Chabicovsky, R. Dallinger, *Cell Tissue Res.*, 2010, **341**, 159-171.

60 M.G. Vijver, C.A.M. Van Gestel, R.P. Lanno, N.M. Van Straalen, W.J.G.M. Peijnenburg, *Environ. Sci. Technol.*, 2004, **38**, 4705-4712.

61 I. Marigómez, M. Soto, M.P. Cajaraville, E. Angulo, L. Giamberini, *Microsc. Res. Techniq.*, 2002, **56**, 358-392.

62 S.N. Luoma, P.S. Rainbow, *Environ. Sci. Technol.*, 2005, **39**, 1921-1931.

63 Å. Fritioff, L. Kautsky, M. Greger, *Environ. Poll.*, 2005, **133**, 265-274.

64 N.M. Van Straalen, W.H.O. Ernst, *Oikos*, 1991, **62**, 255-256.

65 A. Rautio, M. Kunnasranta, A. Valtonen, M. Ikonen, H. Hyvärinen, I.J. Holopainen, J.V.K. Kukkonen, *Arch. Environ. Contam. Toxicol.*, 2010, **59**, 642-651.

66 V.W.Y. Tam, C.M. Tam, *Build. Res. Inf.*, 2008, **36**, 37-43.

67 X. Duran, H. Lenihan, B. O'Regan, *Resour. Conserv. Recy.*, 2006, **46**, 302-320.

68 Symonds Group Ltd., *Construction and demolition waste management practices, and their economic impacts. Final report to DGXI*. European Commission, Brussels, 1999.

69 D. Heemsbergen, M. Warne, M. McLaughlin, R. Kookana, *The Australian methodology to derive Ecological Investigation Levels in contaminated soils*. CSIRO, Australia, 2009.

70 H.R. Köhler and R. Triebskorn, *Biomarkers*, 1998, **2**, 109-127.

71 H.R. Köhler, B. Rahman, S. Gräff, M. Berkus and R. Triebskorn, *Chemosphere*, 1996, **33**, 1327-1340.