Do hyper accumulators act as vectors for soil based heavy metal contamination in grazing food chains in the Comeya de vega mining site, Covadonga, Spain?

Roles: Editor - Lewis Swadling; Introduction and Methods - James Sokolnicki; Results & Discussion - Lewis Swadling *

Participants - Stuart Farrington, Ewan Hitchcoe, Madison Errington, Miriam Treadway, Abby Pidgen, James Sokolnicki, Lewis Swadling, Katherine Lower, Hayley Dancer, Eleanor Carlton, Joshua Blaber. Keane Aroun-Maxwell, Melissa Stephens, Abigail Croker.*

*Ecology & Wildlife Conservation, Bournemouth University, Christchurch House, Talbot Campus, Poole, Dorset, BH12 5BB, UK

Introduction

Mining started in the Comeya de vega mining site at around 1850 and has had had several different owners during its heterogeneous life, until it finally closed for good in 1972. A large glacier eroded the rock to expose ore deposits; these were then smashed, washed, bagged and shipped. A cable car was used to transport the ore from the mine through the valley. The minerals extracted from the mine through its history were: cinnabar, mercury ore, goethite, hausmannite, hematite, pyrolusite, quartz, romanechite, nickel and cobalt. The result of this activity is a toxic habitat with little competition for plants that can cope with these elemental pollutants. Heavy metals cannot be broken down, thus they hyper accumulate in certain plant species. It is very expensive and destructive to clear contaminated land, and like many former aggregate sites, Covadonga has developed into an extremely diverse piece of montane grassland. The site is heavily grazed, with 500 cattle and 100 equines in the 1.2km valley. The beef from the cattle has shown high levels of heavy metals when tested, which are worryingly entering the human food chain. Initial soil surveys in 2013 found arsenic, mercury and manganese contamination in 5 separate points (figure 1.) across the site.

The plants that accumulate metals are known, so the aim of the survey on 20/07/16 was to assess the cattle's health by testing their potential exposure, by finding out where they are feeding and if they are consuming contaminated plants.

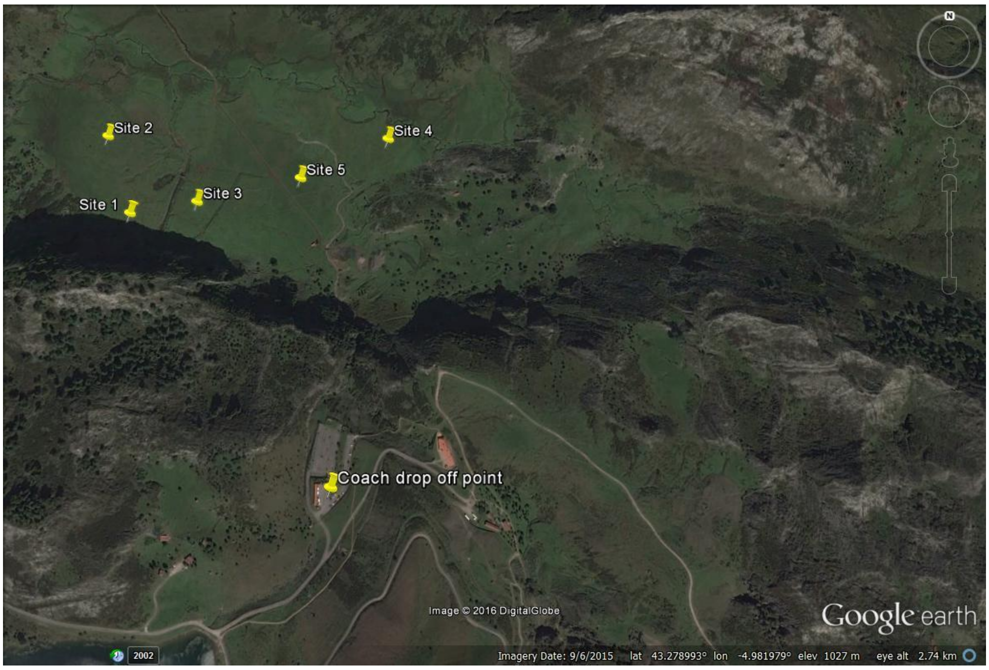

Figure 1: Aerial view of the Comeya de vega mining site and survey locations: provided by google maps.

Method

- ***Field Survey***

There were 2 surveys carried out to monitor the cattle's feeding habits at the 5 points shown in figure 1, and soil samples were taken to analyse the toxicity at these same points.

Two 10 metre pat transects were carried out at each point; a surveyor walked the 10m route, bisecting the centre of each point, whilst their partner recorded the number of pats seen up to a metre either side.

Five 1 x 1 metre quadrats were studied at each point; a species list of herbs within them was compiled, as well as their percentage cover, along with the percentage cover of bare ground, grasses and mosses. Then the vegetation structure was noted by recording the maximum, minimum and mean height in cm of the total vegetation cover and for the individual herbs. Soil samples were taken by pulling up two pieces of vegetation adjacent to the quadrat.

- ***Heavy Metal Analysis***

0.2g of each soil sample was air dried, ground gently and passed through a 2mm sieve to form fine-earth fraction soil. This was then heated at 60 C for 15 hours in 12ml of aqua regia (mixture of 9ml concentrated hydrochloric acid and 3ml concentrated nitric acid). The samples were then heated to 105 C for 1 hour and after at 150 C to facilitate digestion i.e. ripping apart non-silicate minerals and organic matter to release heavy metal contaminants. After the samples were then re-suspended in a 5% nitric acid solution and analysed using an ICP-OES instrument.

Results & Discussion

Table 1: Mean % cover and % nibbled for identified flora species at 5 site locations on the Comeya de vega mining site, Covadonga, Spain. Means were calculated from the data collected in five random 1m2 quadrats on each location.

	Site 1		Site 2		Site 3		Site 4		Site 5	
Species	**% Cover**	**% Nibbled**	**% Cover**	**% Nibbled**	**% Cover**	**% Nibbled**	**% Cover**	**% Nibbled**	**% Cover**	**% Nibbled**
Buttercup:	6.2	47	0.4	62	5.2	10	2	14	3	0
Daisy:	0	0	0	0	1	0	0	0	0	0
Dandelion:	0	0	0.2	0	1.4	0	0	0	0	0
Grass:	49.4	47	60	62	38	56	45.4	56	42.6	45
Heath speedwell:	0	0	0	0	1	0	0	0	0	0
Mouse ear:	1.6	1	0	0	4.8	0	7.4	0	0	0
Mountain eryngo:	0	0	12	0	5.2	2	0	0	0	0
Moss:	13	0	8.2	0	1	0	4.2	0	1.2	0
Plantain:	0.4	2	2	3	3.2	12	0.4	2	3.4	8
Ragwort:	4.2	2	7.4	0	4.8	18	8.2	3.6	31	13
Red clover:	0	0	0	0	0	0	1	0	0	0
Ribwort plantain:	0.4	0.2	0	0	1.4	3	0	0	1	0.6

Self-heal:	0.4	12	0.4	1	3.4	2	0.4	0	0.6	0
Stitchwort:	0	0	0.4	2	0	0	0	0	0	0
White clover:	28	12	31	10	59.4	10.4	39.8	12	31	6.4
Welted thistle:	0	0	0	0	0	0	8	0	0	0

Across all sites grass and white clover had the greatest mean coverage (see table 1). In regards to grass the coverage varied from 38 – 60%, the lowest of which was site 3 and the highest site 2. Conversely for clover site 3 had the highest coverage (=59.4%). Suggesting that this is likely to be caused my interspecific competition between species, rather than the effects of potential heavy metal toxicity. Grass was much more heavily nibbled than white clover (45-62%), in comparison to 6.4-12%, with no obvious trend in relation to coverage. Coverage and nibbling recordings for other flora species was consistently low in regards to quadrat size, and as such can be deemed insignificant in terms of the aims of the investigation.

Table 2: Number and mean cow pats recorded during 2x20m transects across 5 mine site locations on the Comeya de vega mining site, Covadonga, Spain.

	site 1		**site 2**		**site 3**		**site 4**		**site 5**	
	transect 1	***transect 2***	***transect 1***	***transect 2***	***transect 1***	***transect 2***	***transect 1***	***transect 2***	***transect 1***	***transect 2***
Pats recorded:	21	20	35	14	21	21	28	52	23	22
Mean:	20.5		24.5		21		40		22.5	

The mean result for pats recording during the transect surveys was highest in site 4 (=40 pats). The mean result for other the sites varied from 20.5 – 24.4 pats. Suggesting that the grazing animals are spending more time around the site 4 and thus potentially feeding as well. Although when analysing the mean results of the quadrat surveys in table 1, the data does not demonstrate a higher rate of grazing, nor a lower coverage of grass, white clover or other flora species suggesting heavier historic grazing. Therefore it is likely that grazing animals use the site a resting place, rather than to just feed.

Table 3: Concentrations of potentially toxic metals in soils from the Comeya de vega mining site, Covadonga, Spain. Elements were extracted from the soil by *aqua regia* digestion and concentrations in digests determined by Inductively Coupled Plasma – Optical Emission Spectroscopy. Values are mean for three replicates.

Site	**Concentration in soil (mg kg^{-1})**								
	As	**Cd**	**Co**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
1	127.1	8.09	27.3	15.0	97.5	24,446	103	80.1	147
2	142.5	7.04	27.9	13.3	88.9	21,938	113	73.9	178
3	90.7	5.63	23.9	18.1	319	12,181	87.9	33.5	155
4	55.0	0.49	6.00	20.0	11.1	1,246	14.4	34.2	51.6

5	62.8	1.08	7.02	17.2	11.1	2,317	13.4	34.6	49.8

The results of the analysis (see table 3) indicate that Mn and As concentrations are high in all sites when compared to ambient background concentrations (McGrath and Zhao, 2006). Though site 1, 2 and 3 had notably higher levels of both contaminants. Site 4 has the lowest contamination overall, and although these would be considered high compared to background concentrations for Mn and As, they do not exceed highest concentrations recorded for uncontaminated soils (Kabata-Pendias, 2010). Therefore the natural geology of the site could account for the concentrations noted; site 4 seems to have experienced minimal impact from the historic mining activities. With the exception of Cr all elements are elevated by the mining activities (Kabata-Pendias, 2010). This concentration increases in line with expected levels of contamination from the historic mining activity (site 1, most contaminated; site 2 less; site 3 moderately contaminated and site 5 mildly contaminated). The only exception is Cu on site 3, which is the highest concentration found; three times higher than the upper range for soils (Kabata-Pendias, 2010). In sites 1, 2 and 3 As, Cd and Mn are at levels which would be of concern for cattle. Mn concentrations were around 2.5 times above the normal maximum concentration in soil (Kabata-Pendias, 2010)..

The ability of numerous grass species to accumulate heavy metals, suggests the ability of this contamination to enter the food chain (Sarma, 2011). And it is highly probable that this has consequences for the health of grazing animals on the site. This is significant as a mix of miscellaneous grass species had generally the highest % coverage and nibbling % across the individual sites, although notably not site 3. Furthermore the presence of pats demonstrates that grazing/visits were uniform across the mostly affected areas. Other recorded species to have been nibbled may also be demonstrated to be hyper accumulators;, thus providing a further premise that the contamination could be affecting grazing animals, especially when considering the vastly elevated soil contamination identified during the lab analysis. Although it should be noted that the high coverage and consumption of white clover is insignificant in terms of the investigation, as it is not known to be a hyperaccumulator of heavy metals. Due to the results of this study, as a precaution it may be advisable to temporary cease grazing in the location, at least until further conclusive studies and/or remediation work is conducted.

Conclusion

Grass and white clover has the highest % cover across all sites. In comparison the coverage of other flora species was consistently low. The mean presence of cow pats recorded at each site indicates the use by grazing animals. For sites 1, 2, 3 & 5 this was similar, for site 4 this was considerably more suggesting higher usage. However the nibbling and grazing rates recorded for the site reflect the others, therefore not demonstrating increased historic grazing and suggesting that the site may be used for resting or other functions by the animals. The results of the lab analysis indicate that Mn and As concentrations are high across all of the sites. Though in site 4 these are likely to be caused by the natural geology of the site. All other elements are elevated by the historic mining activities. The concentration increases in line with expected levels of contamination (site 1, most contaminated; site 2 less; site 3 moderately contaminated and site 5 mildly contaminated). In sites 1, 2 and 3 As, Cd and Mn are at levels which would be of concern for cattle. The ability of grass species to accumulate Mn, Cd and As, suggests the implications of the contamination and its ability to enter the food chain. Furthermore other species recorded may be hyper accumulators, thus providing a further premise that the contamination may be affecting grazing animals. Due to these results as a precaution it may be advisable to temporary cease grazing in the location, at least until further conclusive studies and/or remediation work is conducted.

References

Kabata-Pendias, A. (2010) *Trace elements in soils and plants*. 4th edn. Boca Raton, FL: CRC Press.

McGrath, S. and Zhao, F. (2006) *Ambient background metal concentrations for soils*. Available at: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290474/scho1106blpv-e-e.pdf (Accessed: 22 August 2016).

Sarma, H. (2011) 'Metal Hyperaccumulation in plants: A review focusing on Phytoremediation technology',*Journal of Environmental Science and Technology*, 4(2), pp. 118–138. doi: 10.3923/jest.2011.118.138.