BLACK BLUEBUSH AND OLD MAN SALTBUSH BIOGEOCHEMISTRY ON A CONTAMINATED SITE: BROKEN HILL, NEW SOUTH WALES, AUSTRALIA

Christina Low[1], Damian Gore[1], Mark Patrick Taylor[1] & Honway Louie[2]

[1]Department of Physical Geography, Macquarie University, North Ryde, Sydney, NSW, 2109
[2]National Measurement Institute, Pymble, Sydney, NSW, 2073

INTRODUCTION

The mobilisation of heavy metals from soil into the trophic chain can pose a significant environmental and health risk if they accumulate in living organisms to toxic levels or levels that trigger illnesses. One important pathway by which soil-based heavy metals are mobilised into the trophic chain is through uptake by plants growing in metal-rich, often anthropogenically-contaminated soils. While many studies have focused on the soil to plant metal uptake pathway, these have been largely based in temperate areas and comparatively few similar studies have been conducted in arid locations, where a soil's mineral chemistry and environmental conditions are likely to be different those of more humid areas. Understanding how arid zone plants take up, store or alternatively reject metal contaminants has important implications, especially if the plant species are subject to grazing by animals.

This paper presents the findings of a study investigating Zn, Cd and Pb phytoavailability trends in two xeromorphic halophyte shrub species (*Atriplex nummularia* and *Maireana pyramidata*) growing on a contaminated site at Broken Hill in far western New South Wales, Australia. Particular focus is given to the distribution of selected heavy metal analytes in plant tissue and plant soil, with implications for environmental health. The full results of this study are currently being compiled into a Masters thesis at Macquarie University.

STUDY AREA

The study sites are located in the urban area of Broken Hill city (31° 56’ 00" S, 141° 28’14"E), a regional hub and Pb-Zn-Ag mining centre in far western arid New South Wales, Australia (Figure 1). The sites are vacant lots situated near large ‘skimp’ or mine waste piles, which indisputably contribute to local pollution input. Local heavy metal contamination is also attenuated by inputs from the continual mining of the Pb-Zn-Ag ore deposit, natural weathering and dispersion of the metalliferous bedrocks (Coggins 1977, Coggins *et al.* 1979, Woodward-Clyde P/L 1993, Gulson *et al.* 1994, 1996, Lyle 2001). Particularly high Pb and Zn values in local soils of up to 13,000 mg/kg Zn and 7,500 mg/kg Pb (Coggins 1977, unpublished) have been reported by Coggins *et al*. (1979).

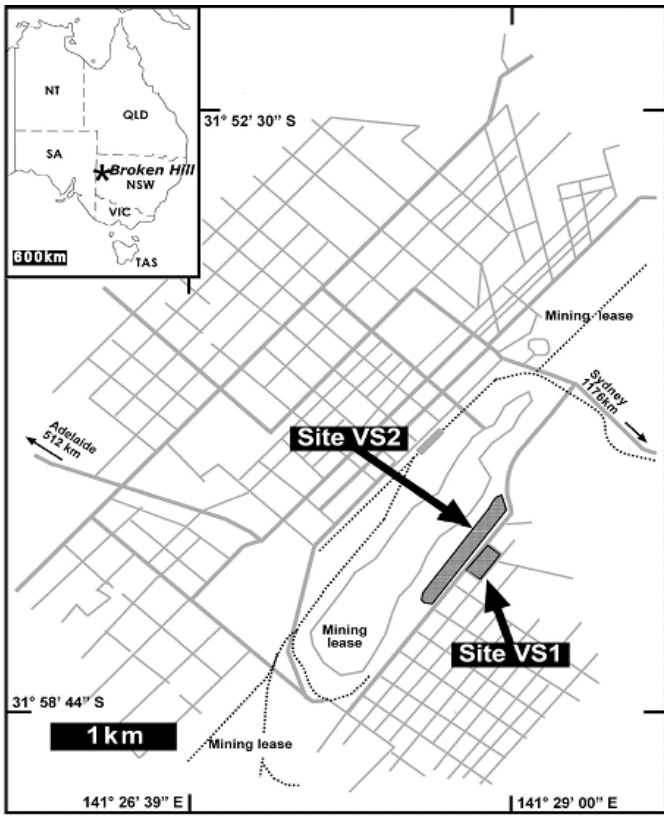

Figure 1: Location map of site VS1 and VS2 in Broken Hill.

Principle plant species growing on the sites are the Chenopods old man saltbush (*Atriplex nummularia*) and black bluebush (*Maireana pyramidata*). Both species are halophytes that are contaminant- and drought-tolerant (Merry & Tiller 1978, Osborne 1996, Brooke & McGarva 1998). Many Chenopodiaceae species have also been used as indicators of regional metal trends (i.e., Merry & Tiller 1978, Lintern *et al.* 1997; Hill & Hill 2003, Senior & Hill 2002, Thomas *et al*. 2002). Contaminants that may be stored in these plants have the potential to move up the food chain through

a variety of pathways, as both species are palatable to kangaroos, cattle and sheep, particularly during drought (Cowling 1995, Brook & McGarva 1998). Mulga parrots are also known to eat bluebush seeds.

METHODS AND MATERIALS

Sampling at study sites VS1 and VS2 (Figure 1) was carried out over the period of one day in October 2001. 60 plants were whole-harvested in random order from both sites. 40 plants were harvested from site VS1 (20 bluebush and 20 saltbush) while 20 plants were sampled from site VS1 (20 saltbush only). Plant samples were collected in 60 L plastic bin bags. Two hundred grams of soil from around the root area or rhizosphere of each plant was also collected. Using methods adapted from Azcue & Murdroch (1999), plant samples were cleaned rigorously with ALCONOX™ solution and deionised water, cut using Teflon® coated stainless steel secateurs into sub-samples of root, woody stem, twig and leaf, then washed again and dried for 3 hours at 100°C. Soils were air dried for 24 hours before sieving at 2 mm to exclude gravels. The 2 mm fraction was used because this was the predominant soil grain size diameter and it is the fraction used by for soil contaminant assessment in the NEPM soil quality guidelines (NEPC 1999). All soils and plant samples were homogenised and pulverised in a tungsten carbide ring mill for 30 seconds prior to metals analysis.

Total Pb and Zn in soil and plant tissue was determined by a non destructive analysis of loose compacted powders on a Philips PW4051 MiniPal™ Energy Dispersive X-Ray Fluorescence Spectrometer (EDXRFS). For soil, the EDXRFS was calibrated by measurement of certified base metal reference materials consisting of crushed ore and rock material (Geostats P/L). Typical limits of detection for the elements analysed were Zn (0.8 mg/kg) and Pb (4 mg/kg). Plant samples were analysed as pressed powder pellets, made by die-pressing 6 g of powdered plant material on 2 g of HBO_3 (boric acid) backing at 13 tonnes for 90 seconds. The EDXRFS was calibrated using a range of natural plant materials that had been analysed using ICPMS following nitric acid digestion. The limits of detection for the elements analysed were Fe (0.001 wt. %), Cu (5.3 mg/kg), Zn (2.3 mg/kg) and Pb (1.8 mg/kg). The EDXRFS QA/QC program comprised 17 % of the analytical program, whereby each carousel of 12 samples contained two pellets that were either certified reference materials or whose composition was known using INAA analysis or aqua regia (1:1 HNO_3:HCl) digestion followed by ICPMS analysis. All standards and known sample concentrations were within 10 % of their accepted values. Instrumental precision, assessed by analysing 12 replicates on a single analysis run, was better than 10 % for all analytes.

Cadmium in soil samples was measured using Inductively Coupled Plasma-Mass Spectrometry (Elan 6100 DRC Perkin Elmer ICP-MS) after digestion with aqua regia. Limits of quantitation for Cd were 50 µg/kg. Cd in plant material was also analysed with ICP-MS after digestion with HNO_3, with the same limits of quantitation as described for the soils analysis. The ICP-MS QA/QC program comprised more than 10 % of the analytical program. These consisted of reagent blanks, sample duplicates for every tenth sample analysed, reference materials of sediment and soil and matrix spikes. Blanks were used to monitor contamination during the digestion process and to test reagent purity. For soil analysis a river sediment (AGAL-10) and a biosoil (a mixture of soil and dried sewage sludge, AGAL-12) were analysed in the same batch of analyses with samples to monitor metal recovery by the extraction method. For plant analyses, a spiked plant sample (AGAL-6 cabbage leaf powder) was analysed in the same batch to monitor the efficacy of metal recovery by the extraction method. Matrix spikes consisted of the sample extracts spiked with a concentration of the relevant metal equivalent to 1 mg/kg metal in the sample. For plant analysis, the metal recovery rates were used to monitor matrix-influenced bias and to correct for results if necessary. Additionally, 400 µL of 125 ug/L In and Ir standard solution was added to each diluted solution prior to analysis as part of the internal standard protocol to monitor the efficiency of sample transfer during ICP-MS analysis and correct for drift.

RESULTS AND DISCUSSION

Zinc, Cd and Pb trends in plant soil

Zinc, Cd and Pb concentrations in soils from both sites were present at levels which exceeded NEPM interim soil quality guidelines for ecological (EIL) and health (HIL) considerations (Table 1). Heavy metal concentrations in soil from site VS2 were significantly greater than those from site VS1. This was most likely because site VS2 was adjacent to the skimp pile and closer to local mining leases than site VS1 (Figure 1). It was debatable whether these guidelines were appropriate or not as the NEPM guidelines are average values based on phytotoxicity studies from mainly North American studies. The propensity of the plant species analysed here to flourish under highly metalliferous soils suggests that the real EILs for these species should be much higher.

Zinc, Cd and Pb concentrations in saltbush soil were significantly greater those from bluebush soil at site

VS2 (Log10-transformed One-Way ANOVA result for Zn where $F_{1,38}$ = 12.20, P <0.01, 95% confidence interval (CI). For Pb, $F_{1,38}$ = 5.35, P = 0.025, 95% CI. Median Ranked Wilcoxon-Mann-Whitney Test for Cd, where P = 0.01, 95% CI). The significant differences between soil metal concentrations between species could indicate that heavy metals favoured pooling under saltbush stands in 'contaminant islands', but without inter-shrub soil concentrations, this is trend is inferred only. However, it is clear that there are distinct differences in Zn, Cd and Pb soil concentrations between the two plant species (Table 1).

Table 1: Average concentrations of Pb, Zn and Cd in leaves and soil from study sites VS1 and VS2. All values are expressed in mg/kg concentration.

		saltbush		bluebush	
Analyte	**Sample material**	**Site VS1**	**Site VS2**	**Site VS2**	**Background concentration ranges and environmental thresholds**
Pb	leaves	**379** n = 19	**261** n = 19	**253** n = 20	2.1-2.5 (*forage plants*)[4]
	soil	**9,245** n = 20	**4,966** n = 20	**2,865** n = 20	2 - 100 (*background range*)[3] 600 (*NEPM EIL*)[2] 1,500 (*NEPM HIL*)[1]
Zn	leaves	**567** n = 18	**335** n = 19	**403** n = 19	22-33 (*wheat*)[4] 12-47 (*grass*)[4] 24-45 (*clover*)[4]
	soil	**6,664** n = 20	**4,146** n = 20	**2,155** n = 20	10 -300 (*NEPM background range*)[3] 200 (*NEPM EIL*)[2] 35,000 (*NEPM HIL*)[1]
Cd	leaves	**14.23** n = 4	**27.30** n = 4	**28.63** n = 8	0.66 (*plant foodstuffs*)[4]
	soil	**20.25** n = 4	**11.90** n = 4	**5.88** n = 8	1 (*NEPM background range*)[3] 3 (*NEPM EIL*)[2] 100 (*NEPM HIL*)[1]

[1] Health Investigation Levels (HILs) for type F land use commercial/industrial sites, with premises such as shops and offices, factories and industrial complexes; NEPM Interim Soil Quality Guidelines (NEPC 1999).
[2] based investigation levels (EILs) - Interim Urban. Based on considerations of phytotoxicity (toxicity of metals in soil to plants); NEPM Interim Soil Quality Guidelines (NEPC 1999).
[3] Background Range Values: Based on collection of survey data on Australian soils; NEPM Interim Soil Quality Guidelines (NEPC 1999).
[4] From Kabata-Pendias & Pendias (1994) and references therein. n = number of samples

Zn, Cd and Pb concentrations in plant material

Metal concentrations in the leaf tissue were many orders of magnitude higher than average levels found in various crop species from non-contaminated areas (Table 1). Theoretically, the plant metal concentrations measured are more than enough to pose a risk to the health of grazing animals. However, as the study site was located in an urban industrial area, the environmental risk of significant uptake through grazing is minimal.

High concentrations of Pb and Zn were found in leaf tissue from both species, though these were not as high as concentrations in the associated soil. Cadmium, however, accumulated in both shrub species at higher concentrations than in the associated soil. This was particularly obvious in bluebush, which returned values of up to 100 mg/kg Cd in leaf tissue for one sample (Figure 3). Leaf Cd for both species showed no significant relationship to soil pH and EC variables, though it is likely that an alkaline soil environment (our soils had a pH of 7.4 to 9.6) could stimulate Cd phytoavailability (e.g., Greger *et al*. 1995, McLaughlin *et al.* 1996). Thus, a better correlation could be expected between root Cd and soil pH. This requires further investigation.

Although saltbush and bluebush communities growing on our study sites showed a high tolerance to selected heavy metals in the rhizosphere soil (Figures 2, 3 and 4), these generally yielded poor or insignificant correlations. This infers that at high concentrations, the plants are most probably operating an exclusion mechanism to avoid potentially toxic accumulation of metals in their tissue. This is most obvious for Zn in bluebush leaves, where concentrations tend to plateau around 600 mg/kg (Figure 2). At lower soil metal concentrations, a stronger correlation could be expected (i.e., Merry & Tiller 1978). Significant metal concentrations were accumulated in both species reinforcing their value as a heavy metal indicator.

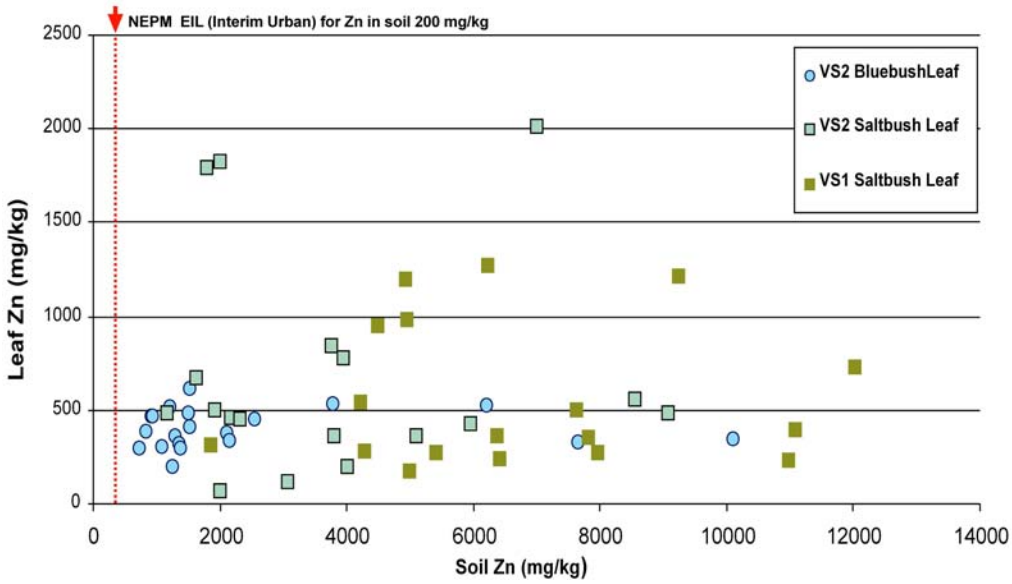

Figure 2: Zinc concentrations in soil and corresponding leaf samples. All values are expressed in mg/kg concentration. The red vertical line indicates the NEPM EIL (Interim Urban) value of 200 mg/kg Zn in soil, above which there may be phytotoxic effects.

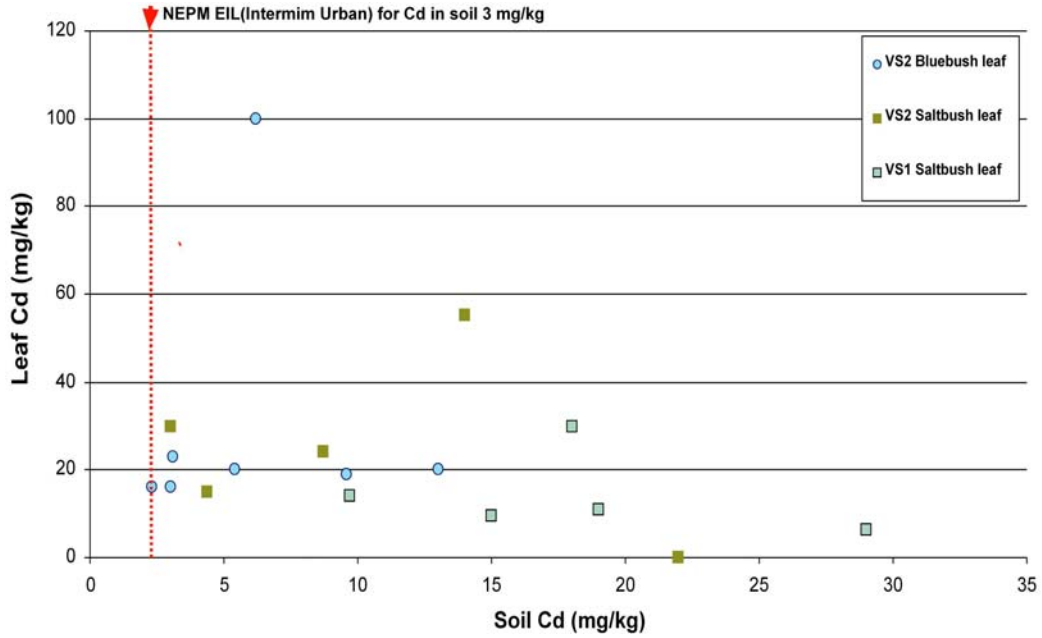

Figure 3: Cadmium concentrations in soil and corresponding leaf samples. Values are expressed in mg/kg concentration. The red vertical line indicates the NEPM EIL (Interim Urban) value of 3 mg/kg Cd in soil, above which there may be phytotoxic effects.

The results presented in this study indicate that the two plant species process and then accumulate metal contaminants differently. This may be due to differences in plant species physiology. Many dryland species manage to survive in saline soils with very low water potential by remaining largely inactive or by transpiring very slowly (Winter *et al*. 1982). Through low transpiration, metals could accumulate in leaf tissue at rates that do not immediately reflect soil trends. Low transpiration rates could also protect these plants from potentially toxic soil substrates. Saltbush was observed to grow much larger than the bluebush plants, with a far more extensive root mass and greater rate of leaf turnover or senescence. It is plausible that the bluebush accumulates Pb and Zn in its leaf vacuoles, up to toxicity limits, above which it activates a metal exclusion mechanism.

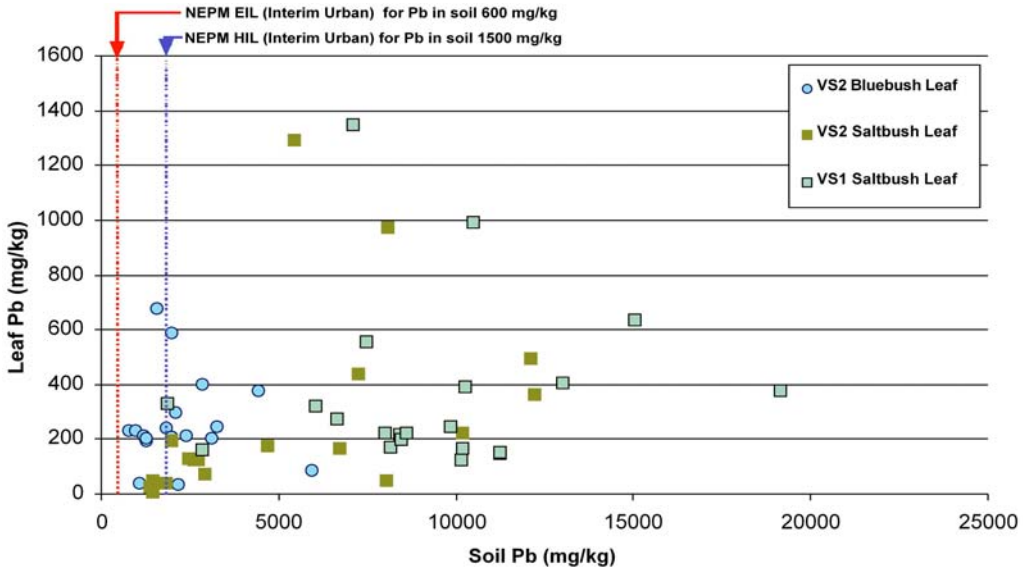

Figure 4: Lead concentrations in soil and corresponding leaf samples. All values are expressed in mg/kg concentration. The red vertical line indicates the NEPM EIL (Interim Urban) value of 600 mg/kg Pb in soil, above which there may be phytotoxic effects and necessitate investigation. The blue vertical line indicates the NEPM HIL (Industrial sites) value of 1,500 mg/kg Pb in soil, above which there may be significant effects on public health and necessitate investigation.

Saltbush also appears to use a metal exclusion mechanism but accumulates much higher levels of Pb and Zn in its leaves (Figures 2 and 4) compared to bluebush. It is possible that saltbush plants excrete metals in their leaf salt bladders, effectively rendering them safe by placing them outside the plant again while remaining part of the plant tissue. Metals stored this way may be released back into the soil through senescence, which may cause additional soil metal concentrations in a positive feedback loop. Once excreted, salts have the potential to be taken up again into the plant, in concentrations greater than that of the soil, so as to maintain a gradient of water potential that will ensure water uptake (Suttcliffe & Baker 1981). By this process, metals could accumulate in halophyte tissue also. Increased soil moisture however could result in decreased salt levels in halophyte tissue (Ungar 1984). Increased soil moisture could also generate acidic soil conditions, under which loosely sorbed metal contaminants could be ionised from soil ligands, effectively increasing the fraction of metals that are available for plant uptake. This illustrates the potentially dynamic processes that control metal phytoavailability in arid soil environments. Apart from abiotic considerations, there are also many other factors that control metal phytoavailability in arid soils. These may include effects of root exudate (Jalliard *et al*. 1996), symbiotic mycorrhizal fungi (Plenchette & Duponnois 2003) and interactions with soil micro-organisms (Whitford *et al.* 1982).

CONCLUSIONS

The heavy contaminants at sites VS1 and VS2 have been mobilised from soil sources into the plant material. This finding is not unexpected given the elevated soil metal concentrations. While only Pb-metal concentrations may pose a risk to public health (Table 1), Cd, Zn and Pb levels appear to be present at levels that may be phytotoxic to plants according to NEPM guidelines (Table 1). However, our test species (old man saltbush and black bluebush) were resilient to the high metal concentrations in the soil. Thus, considerations of phytotoxicity should be species-specific, which suggests that the current NEPM EILS are not necessarily ideal for these particular soils and plant species. In this study metal uptake was species-specific and the results to date indicate that different species can have real effects on rhizosphere metal concentrations. The ability of the two plant species to accumulate heavy metals is probably a function of halophyte and dryland plant physiology. Data regarding the metal concentrations in twig root and wood samples from site VS1 and VS2 are being currently evaluated. The dataset will provide greater insight into the specific mechanisms by which these species accumulate, reject or store heavy metals from associated soil sources.

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