AN ENVIRONMENTAL ASSESSMENT OF ARSENIC IN SOILS FROM THE STAWELL GOLD MINE AREA, VICTORIA

Ryan R.P. Noble

CRC LEME, CSIRO Exploration and Mining and Curtin University of Technology, ARRC, 26 Dick Perry Ave., Kensington, WA, 6151

INTRODUCTION

Geochemical background characterization was conducted on numerous soil and sediment profiles in the Stawell region of NW Victoria. The Stawell Gold Mine (SGM) lies close (< 2 km) to the town of Stawell. The SGM operation mines Au-bearing sulphides with significant As (ca. 2700 mg kg^{-1}) and the potential exists to release As-rich tailings to the nearby environment. Since As can cause serious health problems it is important to understand the extent of As in the soil around the mine site, as well as investigating the soil properties and mineral phases with which the As is associated.

The aim of this research was to determine the regional geochemical background and the host mineralogical phases associated with elements that may pose a potential environmental hazard, such as As, Cd and Pb. Regional geochemical characterisation is essential for understanding potential anthropogenic influences, as general crustal averages of 2-3 mg kg^{-1} (Francesconi & Kuehnelt 2002, Mandal & Suzuki 2002) are not representative for most study sites, particularly those in mining areas. The soils associated with gold mining in north western Victoria are naturally higher in As than most soils, with reported values of between 6 and 40 mg kg^{-1} (Dowling *et al.* 2005, Noble & Watkins 2005, Pearce *et al*. 2005; Sultan *et al*. 2005).

METHOD

Surface soil samples were taken from the area immediately surrounding the Stawell Gold Mine following the derivation of background soil geochemical concentrations. Regional samples were treated using a sequential leach extraction adapted from Gray *et al*. (1999), total acid digestion and a bioavailable leach (Munksgaard & Parry, 2002) that is recommended by the ANZECC (2000). Local samples around SGM were treated using a total digestion and a bioavailable leach. All samples were analysed for pH, electrical conductivity (EC), total C and a field estimation of clay percentage.

RESULTS AND DISCUSSION

Regional Stawell soils are naturally enriched relative to world average soils, with mean and median values of 26.3 mg kg^{-1} and 11.4 mg kg^{-1} As, respectively (Table 1). However, background bioavailable As concentrations are low, with a mean of 0.004 mg kg^{-1} (Table 1). The ANZECC Ecological Investigation Limit (EIL) of 20 mg kg^{-1} bioavailable As is 5000 times greater than this (Department of Environment 2003).

Table 1: Background As concentration statistics for Stawell regional soils.*

	As Total	As Bioavailable	As Exchangeable	As Carbonate	As Mn oxide	As Fe oxide	As Organic
Mean	26,000	3.9	62	60	46	194	1,984
Median	11,000	<0.1	20	53	35	130	939
Max	189,000	30	357	178	291	1,179	14,030
Min	1,300	<0.1	<1.0	6	<1.0	13	70

* All values in µg kg^{-1}.

Total and organic bound As are highest in the clay-rich argillic horizons of the Stawell soils, while exchangeable As, Mn-oxide bound As, Fe-oxide bound As and bioavailable As are all greatest in the surface horizons, which often corresponds to highest cation exchange capacity (CEC) and organic C content (Table 2). In order of decreasing concentration, As is typically fractioned in the sequence Total>Organic>Fe-oxide>Exchangeable>Mn-oxide>Carbonate>Bioavailable in the Stawell regional soils (Tables 1 and 2).

There is little to no correlation between As and some of the commonly measured soil attributes, including clay content, pH, EC, total Fe, Al, Mn and S. The one exception is % C. The majority of correlations exist between various As phases (Table 3). High As in the organic fraction correlates with high As concentration in the Fe-oxide fraction and possibly in other phases, too. Bioavailable As is strongly associated with Fe-oxide phase As (Table 3). The relationship indicates that the phase being targeted by the bioavailable leach could be the very weak amorphous Fe-oxides and is not likely to be truly “bioavailable”. The bioavailable

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leach is a weak HCl extraction, however HCl is often used in stronger concentrations to dissolve Fe oxides. A true bioavailable fraction is more likely to be associated with the easily exchangeable fraction; raising the issue of the relevance and accuracy of this bioavailable technique. The sequential extraction revealed that As was predominantly in the organic phase, excluding total concentrations (Figure 1).

Table 2: Mean values of As fractions based on soil horizon types for Stawell regional soils.*

Soil Horizon Type	As $_{Exch}$	As $_{Carb}$	As $_{Mn-ox}$	As $_{Fe-ox}$	As $_{Org}$	As $_{Bio}$	As $_{Total}$
Surface	114	63	100	372	2,041	11.9	14,996
Transitional Leached	90	71	76	124	528	8.9	7,536
Argillic	78	49	46	162	3,122	6.2	44,500
Saprolite	84	66	40	107	1,268	7.4	23,220
All	93	60	67	194	1,984	8.6	26,282

* All values in µg kg^{-1}.

Table 3: Correlation coefficients of As in various fractions and %C. *

	As $_{Exch}$	As $_{Carb}$	As $_{Mn-ox}$	As $_{Fe-ox}$	As $_{Org}$	As $_{Bio}$	As $_{Total}$	% C
As $_{Exch}$		0.47	0.82	0.68	0.65	0.66	0.38	0.55
As $_{Carb}$	0.25		0.29	0.27	0.18	0.26	0.06	0.22
As $_{Mn-ox}$	0.65	0.10		0.91	0.78	0.89	0.31	0.76
As $_{Fe-ox}$	0.70	0.06	0.46		0.80	1.00	0.32	0.85
As $_{Org}$	0.71	0.00	0.27	0.77		0.78	0.80	0.75
As $_{Bio}$	0.67	0.10	0.56	0.80	0.64		0.22	0.85
As $_{Total}$	0.57	0.12	0.19	0.56	0.81	0.63		0.33
% C	0.24	-0.08	0.20	0.46	0.44	0.22	0.21	

* Pearson correlations are shown in the upper half of the diagonal and Spearman correlations shown in the lower half. Shaded values are strong to moderate correlations.

Arsenic is a potential problem in the soils surrounding the mine. Total metal concentrations ranged from 15.9 to 946 mg kg^{-1} (Table 4), and are significantly higher than regional background concentrations. The bioavailable As content surrounding the mine is higher than regional background, but still quite low, averaging 0.5% of total As (Table 4). The bioavailable leach revealed low quantities of As, as well as most other elements of environmental concern including Cd, Cr, Cu, Ni and Pb. Maximum bioavailable As is 5.6 mg kg^{-1} (Table 4), well below the EIL. All other potentially toxic metals had less than 1 mg kg^{-1} bioavailable concentrations and are well below ANZECC guidelines (Department of Environment 2003). Statistical analysis revealed that total soil Pb, Zn and Mn concentrations are highly correlated to bioavailable concentrations around the mine site, while As was not (Table 5). Total and bioavailable extractions for Cu and Mn were strongly correlated in regional soils (Table 5).

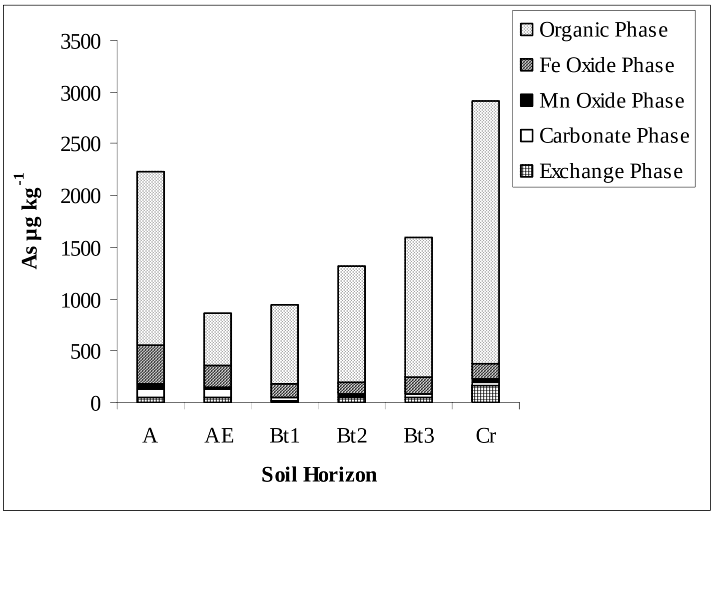

Figure 1: Concentrations of As in soil horizons for a typical Stawell regional soil profile. Soil horizons were determined using U.S. Soil Taxonomy (Soil Survey Staff 1999).

Table 4: Local Stawell Gold Mine soil sample As statistics.

	As Total*	As Bioavailable*	Bioavailable As as % of Total As
Mean	175	0.78	0.56
Median	118	0.46	0.36
Max	946	5.60	1.93
Min	16	0.15	0.07
SD	182	0.97	0.47

* Values are in mg kg^{-1}.

Table 5: Bioavailable leach and total digestion correlation coefficients for various elements from local and regional soil samples.

Element	Regional Background Soils	Local Stawell Gold Mine Soils
As	0.47	0.36
Cu	0.81	0.42
Mn	0.84	0.90
Pb	0.56	0.96
Zn	-0.12	0.86

Local SGM soil As bioavailability is similar to regional soils as they are not well correlated to total concentrations (Table 5). Total As, often used for baseline geochemical samples, is poorly associated with either the bioavailable or exchangeable As. Surveys for As using total and strong multi acid digestions cannot provide a clear indication of "hot spots" in regard to the bioavailability of As. Total As was distributed unevenly, with the highest value just west of the mine site, while bioavailable As was highest near the township (Figures 2 and 3). The highest concentrations of total As in the region were in the town centre and not related to modern mining at the SGM. The enriched soil As in the Stawell environment is attributed to two factors: natural, due to the high background and geochemical halo associated with the major ore body; and, anthropogenic. It would appear that modern mining practices are slightly increasing the total As in the area immediately around the site, probably due to dust from grinding of the sulphidic rocks, however, the total As surface soil concentration seems to be a projection of the natural geochemical halo associated with the NW strike of the mineralization (Figure 2). SGM operations are probably not responsible for the elevated bioavailable As near town (Figure 3).

Low bioavailable As concentrations, low rainfall, and significant vegetative cover in the Stawell region provide environmental conditions where soil As is unlikely to be hazardous to biota. Regional background and local soil geochemistry will prove more accurate and realistic than average crustal values for future mine closure and remediation requirements.

REFERENCES:

ANZECC 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality, 1*. Australian and New Zealand Environment and Conservation Council and Agriculture and Resources Management Council of Australia and New Zealand, Canberra, ACT.

DEPARTMENT OF ENVIRONMENT 2003. *Assessment levels for soil, sediment and water*. Version 3, Department of Environment, Perth.

DOWLING K., PEARCE D.C., HARVEY G., BEATTIE N., SULTAN K., SLADE G., SMITH E., NAIDU R., WALDRON H. & GARNETT D. 2005. Living in a mining environment: A case study of arsenic exposure pathways in the goldfields of Victoria, Australia. *In:* WATKINS R.T. ed. *4th Asia Pacific Symposium on Environmental Geochemistry*. Curtin University of Technology, Perth, pp. **O.4**.

GRAY D.J., WILDMAN J.E. & LONGMAN G.D. 1999. Selective and partial extraction analyses of transported overburden for gold exploration in the Yilgarn Craton, Western Australia. *Journal of Geochemical Exploration*, **67(1-3)**, 51-66.

FRANCESCONI K.A. & KUEHNELT D. 2002. Arsenic compounds in the environment. *In:* FRANKENBERGER W.T. ed. *Environmental chemistry of arsenic*. Marcel Dekker, New York, pp. 51-94.

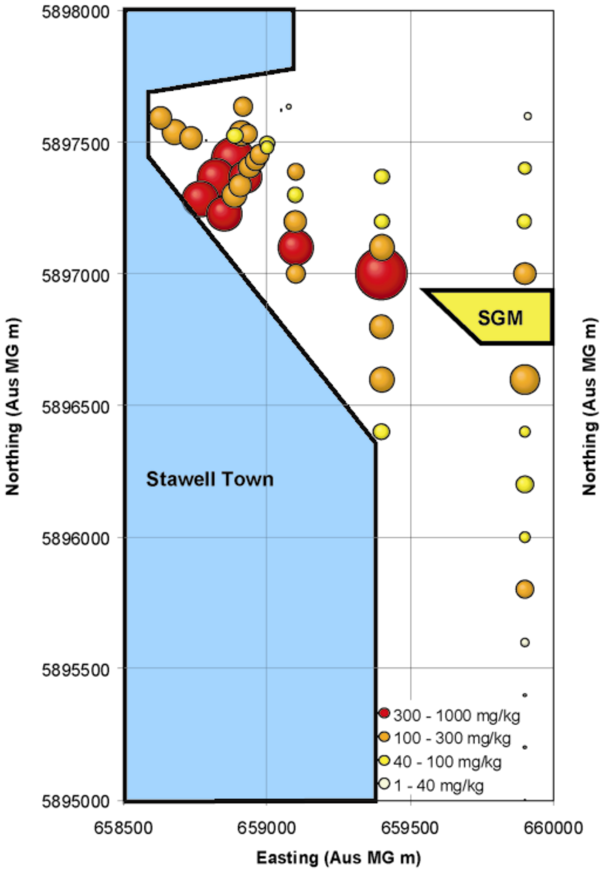

Figure 2: Local geochemical distribution of total As.

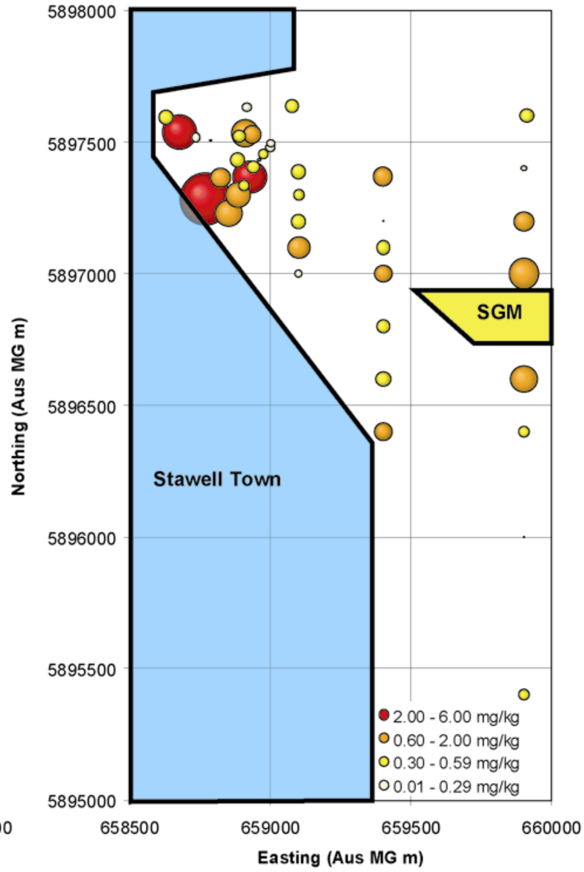

Figure 3: Local geochemical distribution of Bioavailable As.

MANDAL B.K. & SUZUKI K.T. 2002. Arsenic round the world: a review. *Talanta* **58(1)**, 201-235.

SOIL SURVEY STAFF 1999. *Keys to soil taxonomy*. Blacksburg, Virginia, Pocahontas Press.

NOBLE R.R.P & WATKINS R.T. 2005. Background characterization and exposure assessment of soils from the Stawell gold mine and surrounding areas. *In:* WATKINS R.T. ed. *4th Asia Pacific Symposium on Environmental Geochemistry*. Curtin University of Technology, Perth, pp. O.33.

PEARCE D.C., DOWLING K., WALDRON H. & GARNETT D. 2005. Child's play: Investigating exposure potential from arsenic in soil. *In:* WATKINS R.T. ed. *4th Asia Pacific Symposium on Environmental Geochemistry*. Curtin University of Technology, Perth, pp. O.23.

SULTAN K., DOWLING K. & MCKNIGHT S. 2005. Distribution of metals in soils of central Victoria (Creswick-Ballarat) with emphasis on arsenic in relation to geology and mining activities. *In:* WATKINS R.T. ed. *4th Asia Pacific Symposium on Environmental Geochemistry*. Curtin University of Technology, Perth, pp. O.10.

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