LEAD ISOTOPES FOR CONSTRUCTING GEOCHEMICAL DISPERSION MODELS IN SULFIDIC WETLANDS

Andrew K.M. Baker[1] & Robert W. Fitzpatrick[1,2]

[1]CRC-LEME, University of Adelaide, PMB 2, Glen Osmond, Adelaide, South Australia, 5064
[2]CRC LEME, CSIRO Land and Water, PMB 2, Glen Osmond, Adelaide, South Australia, 5064

INTRODUCTION

Study sites consist of two typical, perched wetlands in a saline sulfidic discharge area at the Mount Torrens Prospect (45 km east of Adelaide - 139° 01' E; 34° 53' S; area about 2 km^2) where minor Pb-Zn-Ag mineralisation occurs in calc-silicate rocks at the base of the Talisker Calc-siltstone (Skwarnecki *et al.* 2002). Weathering of the sulfides and calc-silicate rocks has produced sulfate-rich groundwaters, which have led to the development of a range of acid sulfate soil materials such as sulfidic materials (secondary sulfides containing mainly pyrite) and sulfuric horizons (oxidised sulfidic materials containing a variety of oxyhydroxysulfate and oxide minerals). This contributes to degraded saline seepages and poor stream water quality. The wetlands are part of the 10% of strongly waterlogged landscape identified by GIS analysis of a larger 80 km^2 area (Davies *et al.* 2000). Approximately 40% of this area was identified as being poorly drained, but only a small proportion (less than 10%) supports wetland vegetation (Fitzpatrick *et al.* 1996). The undulating, hilly landscape of the Mt Lofty Ranges, with altitudes in the range 400 m to 500 m and local relief about 30 m to 50 m, supports agriculture varying from predominantly extensive grazing and minor viticulture with a variety of soil and groundwater processes. Climate of the area is Mediterranean, with a pronounced maximum of rainfall in winter (May to August) and hot, dry summers (December to February). The annual rainfall is 600-700 mm. Redox data and Pb isotopes were used to refine the 2, 3 and 4-D process models for wetlands devised by Fitzpatrick *et al.* (2003) and Fitzpatrick & Skwarnecki (2003). The refined model permits assessment of the environmental significance and mineral exploration potential of sulfidic wetlands in the Mt Lofty Ranges, S.A.

PHYSICAL SETTING

The lower wetland (wetland B) is circular, about 40 m in diameter, and has been the focus of previous studies (Fitzpatrick *et al.* 1996, Fitzpatrick & Skwarnecki 2003). The upper wetland (wetland A) is located 500 m southwest of wetland B and is circular, with an approximate diameter of 20 m (Figure 2 in Fitzpatrick *et al.* 1996). Both wetlands consist of a central marsh area surrounded by a seasonally variable seepage area. The wetland B is situated upslope from the confluence of two incised streams. As the existing vegetation is typical of marsh areas in the region, it is likely that the site has been wet for a long period. However, rising saline water tables have resulted from decreased water use efficiencies of the annual agricultural plant species that have replaced native, perennial plants. Increased local recharge has resulted in a significant increase in size of the surrounding saline seepage over the past decade or two (Merry *et al.* 2002). Elevated sodium concentrations have resulted in clay dispersion, together with iron oxide clogging of soil pores, thus reducing soil hydraulic conductivities. What was originally a valley floor wetland has migrated upslope of the two streams. Wetland A is constantly draining and lacks the large saline seepage area of wetland B but is likely to develop in time to a similar state due to the reducing hydraulic conductivities discussed above.

The current generic model (Fitzpatrick *et al.* 1996) for the formation of the sulfidic materials in these wetlands involves saline groundwaters, enriched in sulfate (with Pb, Zn, etc. sourced from the mineralised zone), seeping up through soils and concentrating by evaporation forming precipitates. The combination of rising sulfate-rich groundwater, anaerobic conditions associated with saturated carbon-rich soils yield pyrite-enriched material through anaerobic bacterial reduction of sulfate. Weak and/or incipient oxidation of the sulfidic materials has produced minerals such as jarosite and plumbojarosite in sulfuric horizons overlying mineralised zones.

MATERIAL AND METHODS

Soil samples were collected from wetlands A and B in summer and winter. Sample sites were characterised according to vegetation type and wetland morphology. Samples were analysed for soil chemistry including exchangeable cations, saturation index, pH, EC and soluble salts, and were geochemicaly analysed for 53 elements using ICP-MS and ICP-OES. Selected samples were analysed for Pb-isotope analysis along with some regional samples relevant to base metal exploration in the Mt Lofty Ranges.

Wetland B contained monitoring equipment (installed by CSIRO L & W in the late 1990s) that included a data logger, redox electrodes, thermistors and a tipping bucket rainfall collector. Wetland A had no existing

infrastructure. A fence was installed to prevent cattle from pugging the upper marsh. Two data loggers were also installed here along with 32 redox electrodes, thermistors, piezometers and rainfall collectors.

Aerial photography equipment was installed over wetland A to provide time-lapse images of seasonal changes and to record the rate of rehabilitation following the construction of the fence.

Logging of soil cores and pits combined with soil chemistry, geochemistry and Pb isotopic analysis identified areas within the wetlands worthy of closer investigation. Water samples were collected from wetlands, streams and local dams. Multi element analysis was carried out on soil-water samples using ICP. Water was also tested for pH and EC.

REVIEW
Investigations of different aged deposits, host rocks, ore types, depth of weathering and grade of metamorphism confirmed the stability of lead isotopes in the secondary environment (Gulson & Mizon 1979). This led to the development of a detailed method of exploration based on the Pb isotopes. The fundamental premise of the technique is that specific styles of mineralisation in any geologic province will have a unique isotopic composition based on the age and provenance of the Pb (Gulson 1986, Gulson & Mizon 1979). The often homogeneous Pb isotopic signatures in ore deposits are produced by large, long-acting hydrothermal systems during metal solution, transport and deposition. These homogeneous compositions are preserved in very Pb-rich systems but may be modified in low Pb systems due to *in situ* radiogenic growth (Carr *et al.* 1995, Gulson 1986). As these signatures are retained in the secondary environment, Pb isotopes can be used as an effective means of mineral exploration. Lead isotopes are useful in areas other than mineral exploration. For a number of years they have been used to identify sources of environmental pollution (Ketterer *et al.* 2001). The method used in that process is very similar to that used in mineral exploration described above. Lead from anthropogenic contaminants can be fingerprinted via isotopic ratios allowing differentiation between sources and vectors to pollution.

Giblin *et al.* (1994) used the Pb isotopic composition of surface and groundwater as a vector to mineralisation at the Mt Torrens Prospect. Follow up Pb isotopic work was warranted.
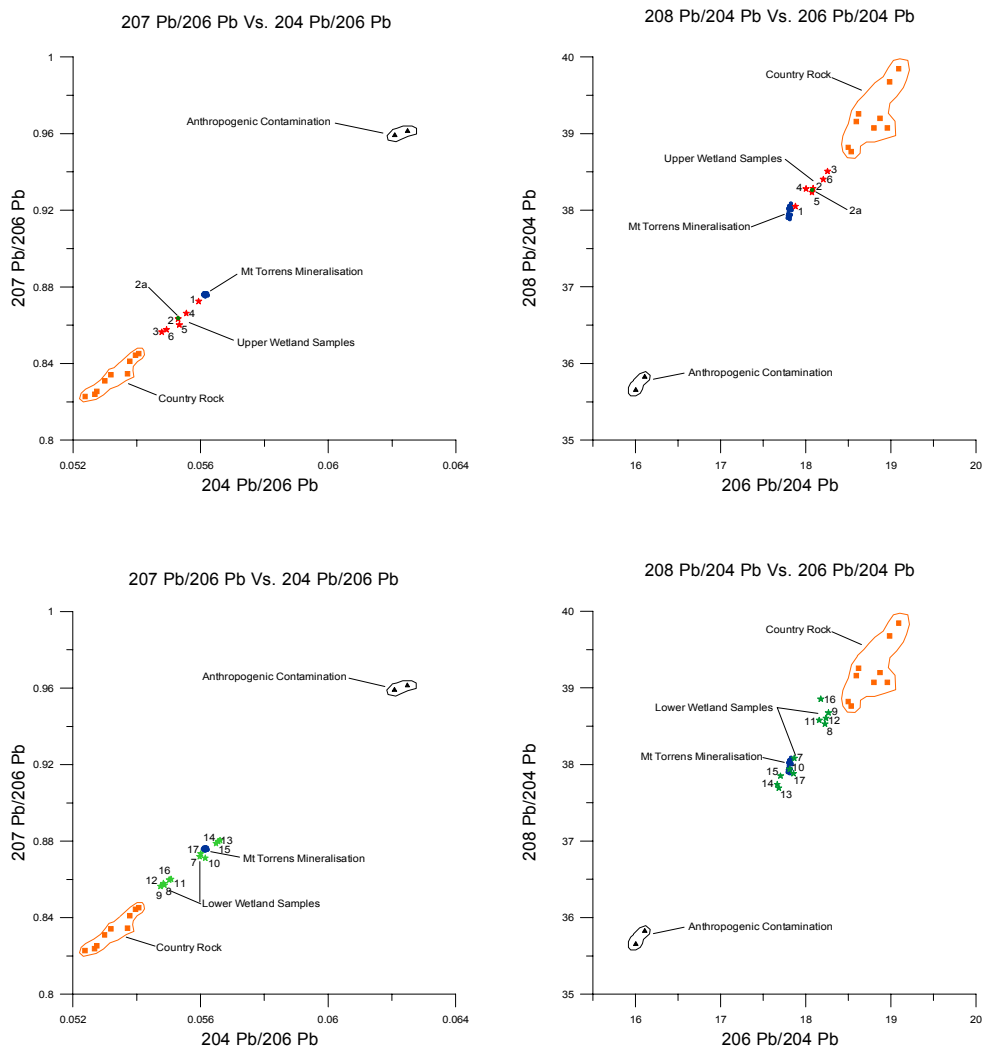
SELECTED RESULTS AND DISCUSSION
Samples were selected from wetlands A and B along with regional sediments for Pb isotope analysis. All were analysed for 55 elements using ICP-OES and ICP-MS. Samples analysed for Pb isotopes are described below (Table 1).

Previously collected data were used to establish Pb isotopic signatures for the: (i) Mt Torrens mineralisation (CSIRO 2003); (ii) country rock (CSIRO 2003); and, (iii) anthropogenic contamination (Gulson *et al.* 1981). Isotopic signatures are displayed in Figure 1. These three sources of Pb contribute to the Pb content of the sediment samples described above (Table 1). A linear mixing curve can be constructed to describe the Pb ratios in each sample. Gulson *et al.* (1981) established that there was little or no atmospheric heavy metal contamination in the Mt Torrens region. Thus any Mt Isa or Missouri Pb input in the Mt Torrens area may be considered anthropogenic contamination derived from fertilisers, fencing and other agricultural infrastructure. The majority of sediment samples collected for this study were influenced by Mt Torrens mineralisation and country rock Pb (Figure 1). Results were used to construct a preliminary geochemical dispersion model to explain the interaction of groundwater and surface water with the Pb reservoirs in the study area (Figure 2).

The mineralised zone at Mt Torrens lies beneath and to the west of wetland A (Figure 2a). Wetland B is located down slope to the northeast of wetland A (Figure 2a). There is a sandy recharge zone at the top of the catchment (Figure 2a). Hydro-geochemical analyses and piezometer data suggest groundwater is sourced from the sandy recharge zone and from fractured aquifers in the Kanmantoo basement. As the freshwater percolates through the regolith to the saline groundwater it acquires the Pb isotopic signature of the Kanmantoo rocks (country rock)(green arrows in Figure 2; Figure 1). Where groundwater comes into contact with mineralised zones and secondary dispersion haloes, it acquires the Pb isotopic signature of the Mt Torrens mineralisation (red arrows in Figure 2; Figure 1). As groundwater moves out of the mineralised zone through country rock, the Pb isotopic signature is diluted (orange and yellow arrows in Figure 2; Figure 1). Lead isotopic signatures return to background (country rock signatures) approximately one kilometre from the mineralised zone.

Table 1: Description of samples used for Pb isotopic analysis.

Sample	Code	Depth (m)	Description
Wetland A			
1	Gel	0.01	Fe oxide gel from seep
2	Crust	0.05	Fe crust
2a	Mottles	0.05	Mottles in Fe crust
3	SulfMud	0.09	mottled & Fe-rich with some black sulfidic mud
4	Sand	0.15	sandy jarositic layer
5	SulfMud	0.17	black sulfidic layer
6	BlkMud	0.23	grey to black clays with jarosite on roots
Wetland B			
7	Loam	0.05	Loamy A1 horizon. Soil at dry edge of discharge zone - tall wheat grass
8	Sandy loam	0.35	E-horizon. Soil at dry edge of discharge zone - tall wheat grass
9	Clay	0.45	Clay B2-horizon. Soil at dry edge of discharge zone - tall wheat grass
10	Loam	0.05	Salt-rich loam. Inner edge of discharge zone - Mimulus plants
11	Loam	0.15	Loamy soil. Inner edge of discharge zone - Mimulus plants
12	Clay	0.25	Clay B-horizon. Inner edge of discharge zone - Mimulus plants
13	Salt crust	0	Salt crust. Inner edge of discharge zone - Mimulus plants
14	Org/Mud	0.05	Iron/organic soil. Centre of wetland -sedge and rushes
15	SulfMud	0.15	Sulfidic material. Centre of wetland -sedge and rushes
16	SulfMud	0.25	Sulfidic material. Centre of wetland -sedge and rushes
17	Clay	0.35	Clay B horizon. Centre of wetland -sedge and rushes

Figure 1: Wetland sediment samples displayed on Pb isotope ratio plots.

A.K.M. Baker & R.W. Fitzpatrick.
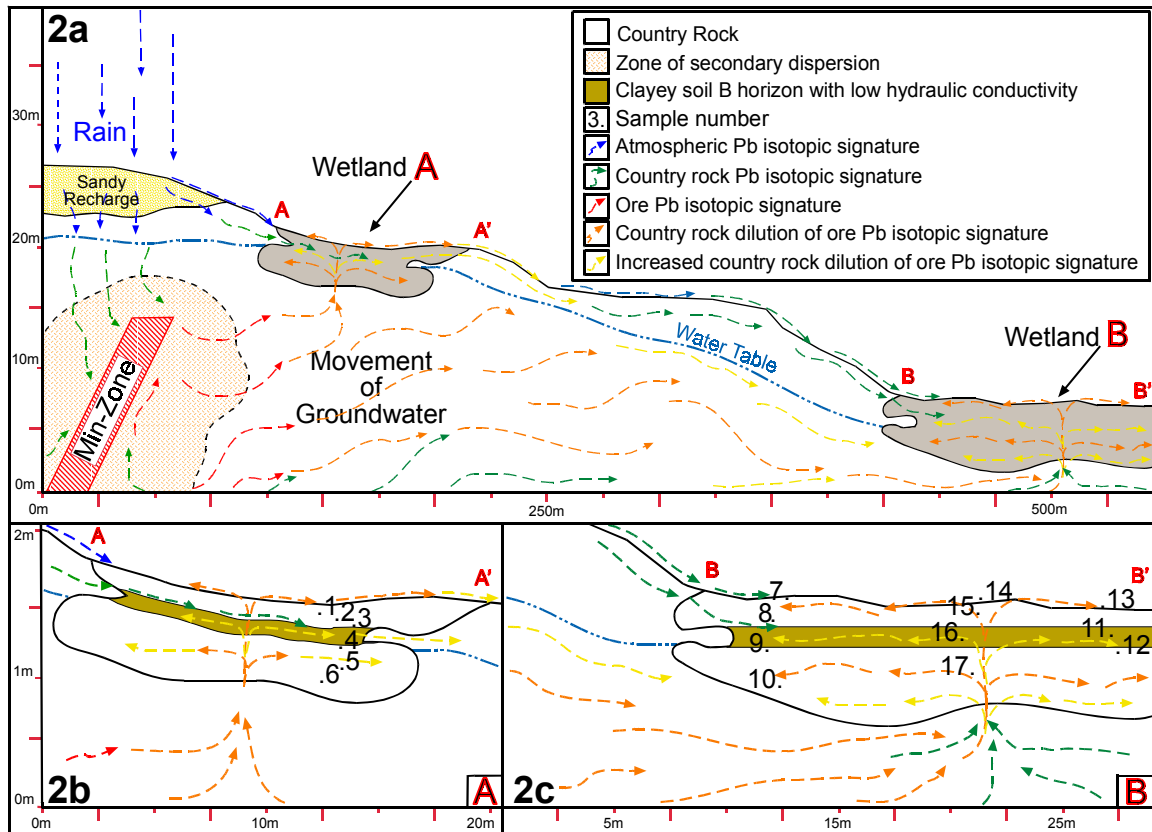*Lead isotopes for reconstructing geochemical dispersion models in sulfidic wetlands.*

Figure 2: Schematic cross-section through the Mt Torrens Prospect depicting the interaction between surface water and groundwater with Pb isotopic composition.

The mineralised zone at Mt Torrens lies beneath and to the west of wetland A (Figure 2a). Wetland B is located down slope to the northeast of wetland A (Figure 2a). There is a sandy recharge zone at the top of the catchment (Figure 2a). Hydro-geochemical analyses and piezometer data suggest groundwater is sourced from the sandy recharge zone and from fractured aquifers in the Kanmantoo basement. As the freshwater percolates through the regolith to the saline groundwater it acquires the Pb isotopic signature of the Kanmantoo rocks (country rock)(green arrows in Figure 2; Figure 1). Where groundwater comes into contact with mineralised zones and secondary dispersion haloes, it acquires the Pb isotopic signature of the Mt Torrens mineralisation (red arrows in Figure 2; Figure 1). As groundwater moves out of the mineralised zone through country rock, the Pb isotopic signature is diluted (orange and yellow arrows in Figure 2; Figure 1). Lead isotopic signatures return to background (country rock signatures) approximately one kilometre from the mineralised zone.

Confined aquifers beneath wetlands A and B are under positive hydraulic pressure (i.e. positive hydrostatic head). As the water moves to the surface it enters the wetland where organic carbon, combined with anaerobic conditions associated with saturated soils, produces a highly reducing environment (Figures 2a and b). Organic matter scavenges lead in solution as sulfate-rich groundwater passes into the wetland. Pyrite-enriched material is formed through anaerobic bacterial reduction of sulfate. Weak and/or incipient oxidation of the sulfidic materials produces minerals, e.g. jarosite and plumbojarosite (Pb sourced from groundwater).

From May to October, Mt Torrens receives approximately 70-80% of its, 600 mm, annual rainfall. Increased hydraulic pressure during this period produces a bulging-out effect in the two wetlands. Where the confined aquifer, below the clayey B horizon, is punctured (e.g. tree roots) groundwater can spread throughout the more porous A and E horizons (Figures 2a and b). Beneath the confines of the low hydraulically conductive B-horizon the wetland bulges out (Figures 2a and b). This results in the expansion of the hydro geochemical conditions expected in a sulfidic wetland. Anaerobic, reducing conditions bulge out above and below the B-horizon. Lead and other heavy metals associated with sulfate rich groundwater are deposited in halos that define the seasonal extent of the wetlands. Porous soil horizons are easily infused by the sulfate rich groundwater giving them Pb isotopic signatures similar to the Mt Torrens mineralisation. Soil horizons with

lower hydraulic conductivities are not as easily penetrated by groundwater and are thus dominated by the Pb isotopic signature of the country rocks.

CONCLUSIONS AND FUTURE WORK

A Pb isotopic analysis of wetland sediments has enabled the construction of a geochemical dispersion model that describes the interaction of base metal mineralisation and sulfidic wetlands at the Mt Torrens Prospect (Figure 2). This model provides an insight into the seasonal fluctuations observed in the wetlands and helps to explain the hydro-geochemistry and geochemistry of the area.

The model shows that heavy metals and other contaminants will tend to build up in soil horizons with high hydraulic conductivity. Thus indiscriminate sampling of wetland sediments for exploration and environmental purposes will produce mixed quality results at best. Targeted sampling is required away from soil horizons with low hydraulic conductivity to (i) identify true base metal signatures and (ii) pinpoint zones containing potentially hazardous concentrations of environmental contaminants.

Ongoing and future work in the area aims to refine the model discussed above. Redox probes measure the 3-D seasonal fluctuations of the wetlands to complement the isotopic data. Time-lapse photography is being employed to chart the surficial expression of the wetlands that are closely linked to seasonal changes and anthropogenic influences. Sulfur isotopes will be used to compliment the Pb work already undertaken. The refined geochemical dispersion model will be applied at a regional scale to improve land management practices and base metal exploration.

REFERENCES

CARR G.R., DEAN J.A., SUPPEL D.W. & HEITHERSAY P.S. 1995. Precise lead isotope fingerprinting of hydrothermal activity associated with Ordovician to Carboniferous metallogenic events in the Lachlan fold belt of New South Wales, pp. 1467-1505. *In:* WALSHE J.L., MCQUEEN K.G. & COX S.F. eds. *A special issue on the metallogeny of the Tasman fold belt system of eastern Australia.* Economic Geology Publishing Company, Lancaster, PA, United States.

CSIRO 2003. Unpublished Pb isotope data base, CSIRO Exploration and Mining, North Ryde, NSW, Australia.

DAVIES P.J., FITZPATRICK R.W., BRUCE D.A., SPOUNCER L.R. & MERRY R.H., 2000 Use of spatial analysis techniques to assess potential waterlogging in soil landscapes. *In:* ADAMS J.A. & METHERELL A.K. eds *Soil 2000: New Horizons for a New Century. Australian and New Zealand Second Joint Soils Conference*, Volume 3: Poster Papers, Lincoln University. New Zealand Society of Soil Science.

FITZPATRICK R.W., FRITSCH E. & SELF P.G. 1996. Interpretation of soil features produced by ancient and modern processes in degraded landscapes; V, Development of saline sulfidic features in non-tidal seepage areas. *Geoderma* **69,** 1-29.

FITZPATRICK R.W. & SKWARNECKI M. 2003 Mount Torrens, eastern Mount Lofty Ranges, South Australia: Regolith Models of Soil-Water Landscape Degradation. *In:* ANAND R. & DE BROEKERT P. eds. *Regolith-Landscape Evolution Across Australia: A compilation of regolith-landscape case studies and landscape evolution models*. CRC LEME, http://leme.anu.edu.au/, pp. 6.

GIBLIN A.M., CARR A.R., ANDREW A.S. & WHITFORD D.J. 1994 Exploration of concealed mineralization: Multi-isotopic studies of groundwaters. AMIRA Project 388. *Regional hydrogeochemistry of the Kanmantoo fold belt*, pp. 22. CSIRO Exploration and Mining.

GULSON B.L., 1986 *Lead isotopes in mineral exploration*. Elsevier, Amsterdam, Netherlands.

GULSON B.L. & MIZON K J. 1979. Lead isotopes as a tool for gossan assessment in base metal exploration. *Journal of Geochemical Exploration* **11,** 299-320.

GULSON L.B., TILLER K.G., MIZON K.J. & MERRY R.H. 1981. Use of Lead Isotopes in Soils To Identify the Source of Lead Contamination Near Adelaide, South Australia. *Environmental Science & Technology* **15,** 691-696.

KETTERER M.E., LOWRY J.H., SIMON J.JR, HUMPHRIES K. & NOVOTNAK M.P. 2001. Lead isotopic and chalcophile element compositions in the environment near a zinc smelting-secondary zinc recovery facility, Palmerton, Pennsylvania, USA. *Applied Geochemistry* **16,** 207-229.

MERRY R.H., FITZPATRICK R.W., BONIFACIO E., SPOUNCER R.L. & DAVIES P.J., 2002 Redox Changes in a Small Wetland with Potential Acid Sulfate, Saline and Sodic Soils. *Transactions of the 17th World Congress of Soil Science, International Union of Soil Science*, pp. 10.

SKWARNECKI M., FITZPATRICK R.W. & DAVIES P.J. 2002 *Geochemical dispersion at the Mount Torrens lead-zinc prospect, South Australia, with particular emphasis on acid sulfate soils*. CSIRO / CRC LEME, Adelaide, South Australia, pp. 67.