PRELIMINARY GEOHEALTH IMPLICATIONS OF THE RIVERINA GEOCHEMICAL SURVEY

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INTRODUCTION

Low-density geochemical baseline surveys have been conducted in many countries for applications in resource evaluation, landuse management or health and well-being of humans and animals. The Riverina geochemical survey (Caritat *et al.* 2004), however, is one of very few of this kind in Australia (e.g., Subramanya *et al.* 1995). It will provide vital information on the natural concentration of chemical elements and compounds in the regolith suitable for a multitude of applications. These natural concentrations vary greatly due to local influences such as geology, biological processes and other factors (Reimann & Caritat 1998).

It is widely recognised that geological factors can impact on the health of humans and animals (geohealth). Well-known examples are Se toxicity and deficiencies in China, As poisoning from groundwater in Bangladesh and enrichment of U and other heavy metals in the "sickness country" of Kakadu, Australia (Selinus 2000, Lech *et al.* 2003). Trace elements essential for human health include: Co, Cr, Cu, Mn, Mo, Se and Zn (Selinus 2000, Adriano 2001). Excessive or deficient abundance of many (if not all) elements in living organisms can have adverse impacts on plant and animal health.

Apart from providing potential targets for mineral exploration (e.g., Xie & Ren 1993), geochemical baselines help determine the natural state of the environment (e.g., Reimann *et al.* 1998) from which future changes can be assessed. They can also contribute valuable information to help develop more informed environmental policies, and knowledge of anomalies, contaminations or deficiencies can provide information for geohealth studies. In order to establish reliable geochemical baselines it is important to sample "normal" (background) sites, rather than sites near known mineralisation (e.g., Lech *et al.* 2003) or pollution (e.g., Reimann *et al.* 1998).

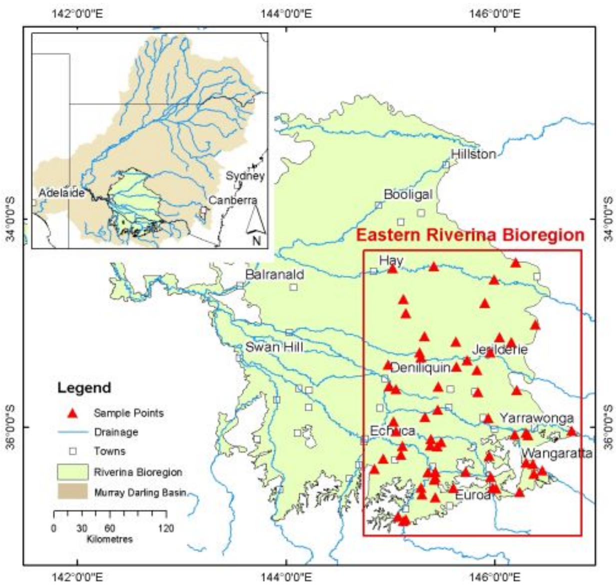

Figure 1: Location of the eastern Riverina study area (red rectangle in main figure) as part of the Riverina bioregion (light green) within the Murray-Darling Basin (inset).

The Murray-Darling Basin was selected as the focus for this survey, being a vital region in terms of social, agricultural and mineral importance. The first geochemical survey was undertaken in the Riverina bioregion at the centre of the Basin. This paper will only present results from the eastern Riverina subregion (Figure 1) as geochemical analyses are yet to be completed for the other Riverina samples.

Geologically, the study area is predominantly composed of Cainozoic alluvial sediments. Silurian-Devonian granites and volcanics and associated Ordovician-Carboniferous siltstones, sandstones and metasediments are located to the south with minor occurrences in the south-east of the study area.

AIM

The baseline geochemical project intends to:

1. Provide internally consistent background geochemical data and suitable maps for the Riverina region; and,
2. Help develop a suitable geochemical sampling methodology that can be adapted for other baseline geochemical studies across Australia.

The objective of this paper is to discuss, in a geohealth context, the deficiencies and excesses of elements within the eastern Riverina dataset.

METHODS

129 overbank sediment samples were collected in the eastern Riverina bioregion. Overbank sediments were the chosen sampling media as it is believed that they can be used across the entire Riverina region and beyond, enabling comparison between this and future datasets. The merits of overbank sediments for low-density baseline geochemical surveys in Australia are borne out by previous studies (Ottesen *et al*. 1989, Murrell 1991, Edén & Björklund 1994, Ridgway *et al*. 1995, Volden *et al*. 1997, Xie & Cheng 1997).

Theoretical sample sites were determined by conducting a hydrological analysis using Geoscience Australia's 9-second Digital Elevation Model and nested catchment coverage of Australia produced in 2000 by the Centre for Resource and Environmental Studies (CRES), Australian National University. This analysis was carried out using the ArcHydro extension of ESRI's ArcGIS™ (Whiteaker & Maidment 2004), which determines the lowest point in each catchment. These sample sites were then carefully adjusted using drainage and road coverages and field considerations such as land accessibility, landscape position and possible anthropogenic inferences at the site.

Top samples (O horizon, 0-10 cm depth) and bottom samples (B/C horizon, generally ca. 70-90 cm depth) were collected at each site to detect the residence and mobility of chemical elements in natural environments. Further, the sample pairs will allow impact of pollutants and land-use changes since European settlement to be quantified chemically. Soil texture, Munsell colour and field pH, as well as pH and EC in 1:5 (soil:water) solutions, were determined for each sample. Major and trace element compositions were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), X-Ray Fluorescence (XRF) and Instrumental Neutron Activation Analysis (INAA). Detection limits of these elements are shown in the first column of Table 1. A small number of samples were subjected to laser particle size analysis to determine relationships between geochemistry and grain-size distribution. The methodologies adopted in this study are detailed in Caritat *et al.* (2004). Selective extractions are currently being carried out on the Riverina samples.

RESULTS AND DISCUSSION

Several trace elements were deemed of interest when an assessment was made on possible deficiencies and excesses (Table 1).

Deficiencies

Cobalt deficiencies can cause anaemia and "white liver disease" in humans (Centeno 2003). Kabata-Pendias & Pendias (2001) reported an affinity between Fe and Co, which does appear to be present in the eastern Riverina. Levels below 5 mg/kg total Co have been reported as deficient and can occur in calcareous or coarse-textured soils (Sillanpää 1972). Thus, there is potential that the seven samples in the eastern Riverina below 5 mg/kg are deficient in Co. Although soils developed on sandstones and acid rocks are more prone to deficiencies (Adriano 2001), this does not appear to influence the distribution of Co within the study area as low Co is coincident with a range of geological types within a catchment including those catchments entirely composed of Tertiary sediments, or those that are a mixture of sediments, felsic and mafic volcanics. There is no clear correlation between concentration of Co and pH. As Co is quite soluble, Co^{2+} is probably long gone.

Copper deficiencies may cause anaemia, poor growth, degeneration of the nervous system and bone demineralisation leading to osteoporosis and bone fractures (Centeno 2003) and can be related to high Zn or Mo concentrations. Copper deficiencies occur below 5 mg/kg in soils (Reimann & Caritat 1998) and the five samples from the eastern Riverina below this limit are located in the south-eastern part of the study area. Low Cu in the eastern Riverina does not correlate with high Zn and Mo (in fact, Cu is weakly but positively correlated with both Zn and Mo (Sillanpää 1972), and Maisto *et al.* (2004) found that about 8-12 % of total Cu was bioavailable in their study in Italy. If this relationship is verified for the Riverina study, all the samples could have a Cu deficiency (max = 38 mg/kg). Indeed, Bertrand (2003) stated that alkaline soils in southern Australia are often deficient in Cu.

Molybdenum deficiencies have not been reported in humans. The average concentration of Mo in soil ranges from 0.2 to 5 mg/kg (Adriano 2001) and the median value in the study area is 0.9 mg/kg. 3 % of the samples from the eastern Riverina have Mo concentrations below 0.6 mg/kg. These appear to be broadly coincident with channel and flood plain alluvium, particularly in the central-north of the region along Billabong Creek. Molybdenum is more mobile at higher pH and hence can be leached from the more alkaline soils. This higher mobility can also facilitate uptake by plants (Adriano 2001). Low Mo levels are often, but not always, associated with high pH soils in the eastern Riverina.

Selenium is non-essential for plants and Se deficiencies in humans can cause muscular dystrophy and liver necrosis (Centeno 2003). Average concentrations of Se in non-contaminated soils are 0.03-2.0 mg/kg (Adriano 2001). Soils are deemed deficient in Se if the total concentration is below 0.04 mg/kg. The detection limit for Se in the Riverina samples was 5 mg/kg, and all samples were below this. Selected samples will be reanalysed with a lower detection limit.

Table 1: Trace elements with potential excesses and deficiencies in the Eastern Riverina Survey. All values in mg/kg.

Element (Detection limit, ppm)	Eastern Riverina Survey			WA Interim Ecol. Investig. Level (WAEIL)[5]	Max tolerable conc in Agric Soil (Germany)[1]	Remediation level (Netherlands)[6]	Lower critical values[#]
	Min	Med	Max				
Ba (2)	249	**476**	1263	400		625	
Br (1)	<1	6.97	36		10		
Co (1)	*2.96*	11.1	34.2	50	50	240	<2-5[3];0.02-0.3 AA[2]
Cr (4)	14	**56**	150	50	100	380	
Cu (2)	*<2*	17	38	60	100	190	<5 [1]; 0.8-3 (NA)[2]
F (50)	<50	277	668		200		
Hg (5)	<5	<5	<5	1	10	530	
Mo (0.01)	*0.5*	0.9	1.9	40[4]	5	200	<0.1 (HW); 0.01-0.6 (AO)[@2]
Ni (2)	<2	20	**81**	60		210	
Sb (0.01)	0.42	0.82	5.35	20	5	15	
Se (5)	*<5*	*<5*	*<5*		10		<0.04 (T)[%2]
U (0.07)	1.52	3.55	8.49		5		
V (6)	31	78	145		50		

[Boxed] Exceeds Remediation level for contaminated sites (Netherlands) | [Light blue] Potentially deficient

[Grey] Exceeds max tolerable conc. for agricultural soil (Germany) | **Bold** Exceeds WAEIL

[1]Reimann and Caritat (1998), [2]Kabata-Penidas & Penidas (2001), [3]Sillanpää, M (1972), [4]Smucker, S. (2002), [5]WA Department of Environment (2003), [6]VROM (2000)

[@] Highly pH dependent, [%] Animal response
[#] Critical deficiency limits are highly dependent on external factors like soil type, texture and pH. As no sequential leaches are performed it can only be used to determine if our total concentration is below the deficiency level. Explanation of symbols used for extraction methods determining contents of soluble elements: AA - 2.5% acetic acid; NA - 1 N Nitric acid; HW - hot water; AO - ammonium oxalate; T - total.

Excesses

Most concentrations of Ba in rocks are as barite but since Ba has a similar atomic radius to K, it can substitute into the matrix of micas and feldspars (Kabata-Pendias & Pendias 2001). Barium concentrations increase toward the south, and appear to correlate with the presence of feldspar- and mica-rich granites. Alternatively, Ba has been found to be associated with gold mineralisation in China (Kabata-Pendias & Pendias 2001) and so the higher concentrations found could relate to the Victorian gold fields located in the southern part of, and to the south of, the study area. The median Ba concentration for this study (476 mg/kg) is similar to the median value in world soils (500 mg/kg; Adriano 2001), but exceeds the Western Australian interim Ecological Investigation Level (WAEIL) of 400 mg/kg (WA Department of Environment 2003). Further, 26 Riverina samples also exceed the soil remediation level for the Netherlands of 625 mg/kg (VROM 2000). If allowed to enter the food chain, Ba is unlikely to cause harm to animals and is thus considered have a low toxicity (Adriano 2001). Reimann & Caritat (1998) and Adriano (2001) suggested that Ba can be especially enriched in Mn-oxides in soils but this does not appear to be the case in this instance as Ba and Mn enrichments are poorly correlated.

Chromium in large quantities is a known carcinogen and has been related to increased incidences of lung cancer, skin irritations and kidney, liver and circulatory system damage (Reimann & Caritat 1998, Adriano 2001). Over half of the overbank samples collected contain more than 50 mg/kg Cr, which is the WAEIL. Chromium shows a weak trend of decreasing concentrations toward the south of the study area. One location in the south-west, however, shows elevated values above the German maximum tolerable limit for agricultural soil (GMTLAS) (Reimann & Caritat 1998) of 100 mg/kg in both the top and bottom samples (122 and 150 mg/kg). In a study in Italy, Maisto *et al.* (2004) found that only <0.1 % of total Cr was bioavailable, thus, if this relationship holds true here, even our maximum total value is unlikely to yield excessive available Cr.

Fluorine is commonly associated with apatite and, as such, can be added to agricultural land through fertilizer application. If F is present in the food chain in excessive concentrations, it can lead to fluorosis, a disease that causes dental and skeletal abnormalities (Selinus 2000). If deficient, F is added to drinking water to ensure the healthy development of teeth and bones. About 75 % of the Riverina samples have F concentrations above the GMTLAS value of 200 mg/kg. The ratio of F concentration in top relative to bottom sample increases toward the south-east of the study area. The four samples with the highest F above 400 mg/kg are not spatially correlated and do not appear to be related to fertilizer application as elevated levels of P, Mg are not coincident.

Gallium is associated with felspars and micas and excess Ga can lead to DNA damage (Reimann & Caritat 1998). 85 % of the samples analysed were above the GMTLAS value of 10 mg/kg, with increasing concentrations to the south-east. This probably reflects the presence of felsic rocks in the southern portion of the region.

The mobility of Sb into the food chain is minimal as there is minimal uptake of Sb by plants (Adriano 2001), but if taken up Sb could be carcinogenic (Reimann & Caritat 1998). About 20 % of the Riverina samples have Sb levels above the GMTLAS value of 5 mg/kg (max = 11 mg/kg). These values are slightly higher than the median world value of 1 mg/kg (Adriano 2001).

Elevated concentrations of U can be carcinogenic. 16 of the 129 samples have U levels above the GMTLAS value of 5 mg/kg. Uranium concentrations increase toward the south-east and are likely to be related to the Silurian-Devonian granites and volcanics in this part of the Riverina bioregion.

Vanadium is essential for some organisms, but can be toxic at high levels (Reimann & Caritat 1998). Elevated V in the environment can result from oil combustion (Reimann & Caritat 1998) and can be found close to high traffic routes. Although 80% of the samples are above the GMTLAS value of 50 mg/kg V, there is no evident correlation in this study with combustion; high V levels are associated with both top and bottom samples from localities near towns and highways but also in relatively remote localities away from high traffic corridors. There was also no obvious correlation of elevated V in recently ploughed paddocks indicating that no significant V is being added into the soil via tractor exhaust when the soil was ploughed or tilled.

CONCLUSIONS

There is a fine balance between excesses and deficiencies of trace elements in soil and this balance is essential for healthy growth of crops, plants and animals. The geochemical survey of the eastern Riverina bioregion found that Ba, Cr, F, Ga, Sb, U and V concentrations in overbank sediments are locally above the German maximum tolerable limit for agricultural soil. Conversely, Co, Cu, Mn, Mo, P and Se were found to be potentially deficient in parts of the region.

The total concentration of an element is not a reliable indication of its bioavailability as availability varies markedly with pH, electrical conductivity and many other environmental conditions. They may adsorb onto clay or be incorporated into oxides and silicates and may not be readily taken up by plants and animals. To determine element bioavailability sequential leach extractions will be conducted and be assessed in due course.

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