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RIVERINA GEOCHEMICAL SURVEY
a national first

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Baseline geochemical surveys have been conducted for most developed countries, but not yet for Australia. In a country as large and diverse as Australia, an initial step in the development of a national low-density geochemical map needs to be the pilot testing of geochemical survey methodologies in representative regions displaying contrasting topographic, drainage and climatic conditions.

Undertaken collaboratively by the Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME) and Geoscience Australia, the first such pilot project has been completed in the Riverina, a prime agricultural Riverina region in southern New South Wales and northern Victoria. A second pilot study has commenced in the remote, flat, dry Gawler Craton of South Australia, where there is very limited stream drainage.

The Riverina survey has delivered cost-effective, internally consistent and quality-controlled data on the inorganic chemical composition of surface and subsurface sediments of large catchments in the region

The resulting geochemical maps show concentrations of 62 elements. Independent data on the distribution of radioactive elements potassium, thorium and uranium corroborates the findings, clearly indicating that the methodology works.

This multi-element geochemical data layer will be made available to decision makers, catchment management authorities, farmers, mineral explorers and other stakeholders to guide activities and decisions in a multitude of land-use and resource management applications.

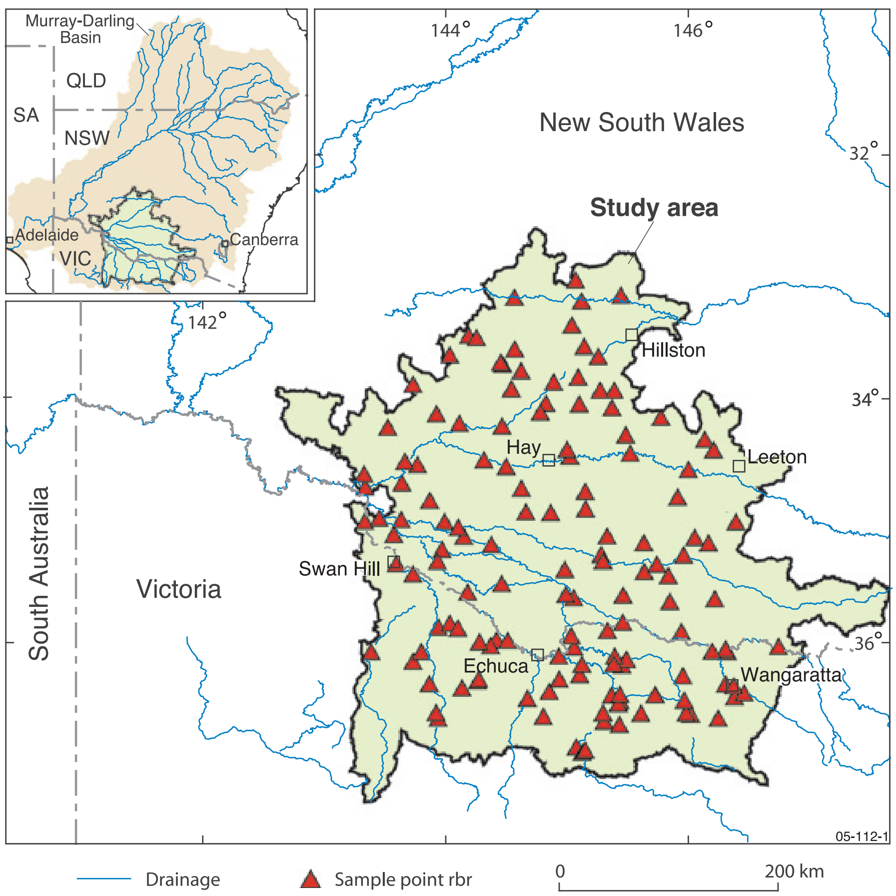


Figure 1. Location of the Riverina study area and sampling sites.

Among a range of findings, the survey identified:

- patterns of calcium and chlorine levels with implications for soil acidity and salinity
- patterns of arsenic and antimony dispersion from known gold mineralisation
- concentrations of some elements above or below national and international guidelines for agricultural soils.

The Riverina survey was designed to prove the value of geochemical mapping and to fine-tune sampling and analytical protocols for a well drained region with modest relief and temperate climate.

Why geochemical mapping?

Australia's regolith—the blanket of soils, sediments and weathered rocks covering fresh bedrock—is the natural resource upon which our multimillion dollar agricultural industry is based. It also hosts much of our precious groundwater resources and contains or covers ore bodies vital for our economic development.

Baseline geochemical surveys provide invaluable information about the natural concentrations of chemical elements in this substrate on which we live, grow crops and raise livestock, and from which we extract water, raw materials and mineral wealth.

Overseas data collated from multimedia and multi-element geochemical surveys carried out over large areas indicates that natural concentrations of chemical elements in water, sediment, soil and plants vary spatially by up to several orders of magnitude due to geological, climatic, biological and other factors (Reimann & Caritat 1998).

It is important to know the natural concentrations and distributions of elements in the near-surface environment so that:

- baselines can be established against which future changes can be quantified
- appropriate and responsible land-use policies can be formulated
- localised contamination can be identified and better remediated
- new mineral potential can be recognised
- local salinity stress can be detected and better understood
- areas for mineral exploration can be selected
- potential geohealth risks can be identified
- comparative suitability of particular land uses can be assessed.

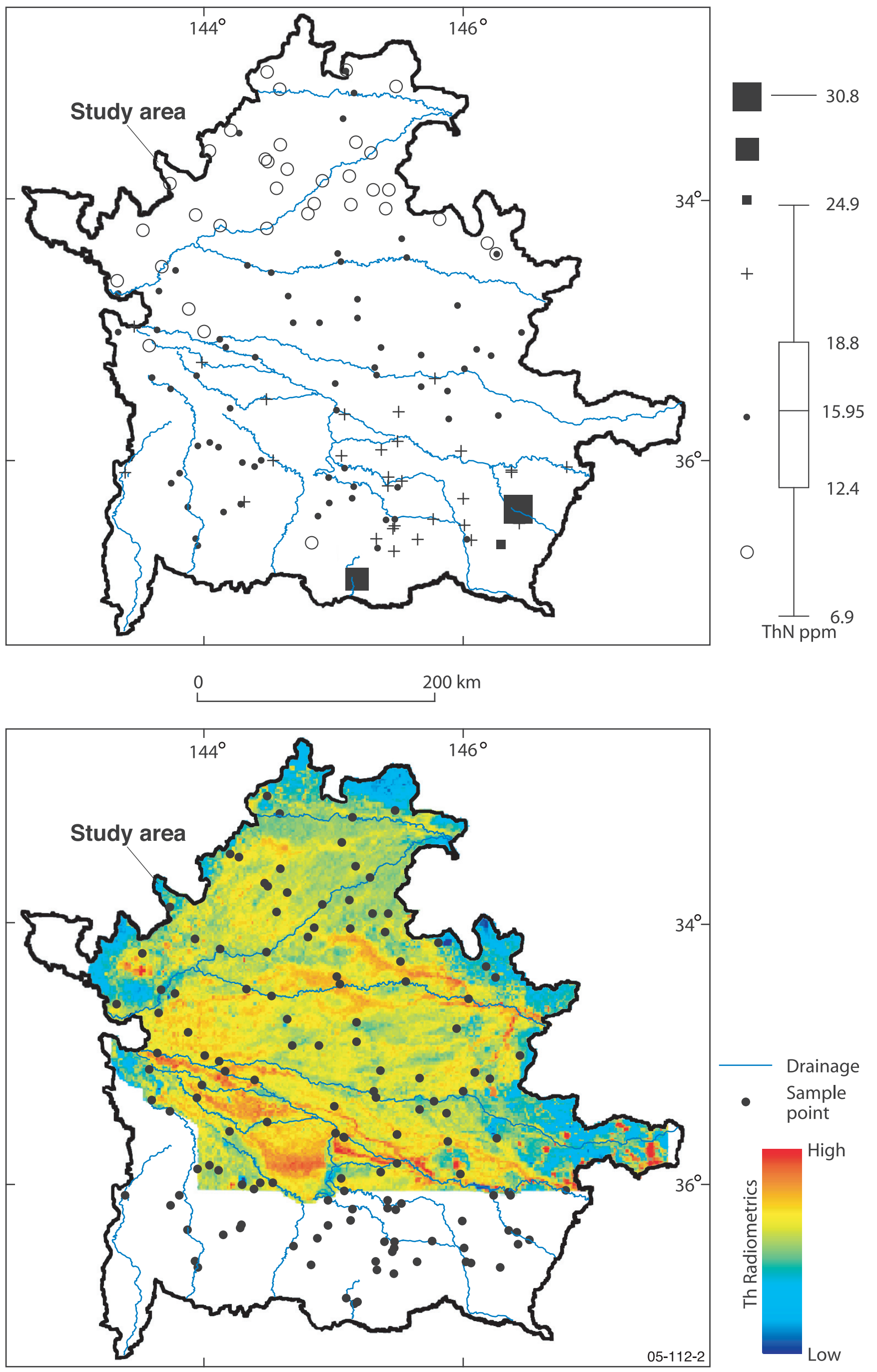


Figure 2. Geochemical map of total thorium (ppm) in TOP Riverina overbank sediment samples (analysed by INAA) (a), compared to airborne gamma-ray distribution of thorium (b).

Low-density geochemical mapping

Based on experience elsewhere (e.g. Reimann et al 1998), a multimedia sampling strategy cost-effectively yields information about sources, sinks and pathways of chemical elements in the near-surface environment.

The main sampling medium used for the Riverina survey was overbank (levee or floodplain) sediments near outlets from large drainage basins or catchments. As this material accumulates during active widespread erosion related to flooding episodes, it is judged to best represent the average lithological input of whole catchments (Ottesen et al 1989). Deposited outside main drainage channels onto floodplains, this fine-grained sediment has an enhanced propensity to host adsorbed and absorbed chemical species.

We believe that this sampling medium is ideal for Australia's low-relief, regolith-dominated landscapes in tropical to arid climates. It had not previously been used here for low-density geochemical mapping and needed to be tested under local conditions. Other sampling media trialled in the Riverina pilot project were plant leaves and groundwater, which will be discussed in forthcoming reports.

The concept of low-density sampling for geochemical mapping has been around for a long time (Nichol et al 1966, Garrett & Nichol 1967, Reedman & Gould 1970) and has recently experienced renewed interest in Europe (Reimann et al 1998, 2003), the United States (Gustavsson et al 2001) and China (Li Jiaxi & Wu Gongjian 1999), for instance. Darnley et al (1995) have suggested a framework for global geochemical mapping, and the sampling media selected include overbank sediments. Sampling densities used for geochemical surveys elsewhere range from high (~1 sample/1 km2) (e.g. Austria: Thalmann et al 1989) to 'ultra low' (~1 sample/1000 to 10,000 km2) (e.g. Europe: Plant et al 2003, Reimann et al 2003).

The Riverina region

For the purposes of the pilot project, the Riverina was defined as the 123,000 km2 area encompassing catchments that are wholly or partly contained within the Riverina Bioregion (figure 1; see Lambert et al 1995 for bioregion concept).

The Riverina is part of the Murray–Darling basin, a significant agricultural, social and mineral district in Australia, which:

- covers 1.06 million km2, or 14% of the country's total area
- contains 45% of the Australian crop area and 43% of the total number of farms
- is Australia's most important agricultural region, accounting for 41% of the nation's gross value of agricultural production
- is an important provider of resources such as wheat (34% of national production), cotton (96%), dairy products, rice and grapes
- is home to nearly two million people, or 11% of the total Australian population.

Sampling and analysis

The Riverina was the focus of a recent airborne geophysical data acquisition initiative led by the New South Wales Department of Primary Industries, which resulted in new digital elevation model, airborne gamma-ray and total magnetic intensity data coverages (NSW DPI 2005).

Theoretical sample sites were located by conducting a hydrological analysis of the digital elevation model to determine the lowest point in large river catchments (see Caritat et al 2004). These sample sites were carefully adjusted in the context of drainage and road/track coverages and field considerations such as land accessibility, landscape position and possible anthropogenic interferences. A total of 142 sample sites were selected near outlets or spill points of large catchments, yielding an average sampling density of one sample per 866 km2.

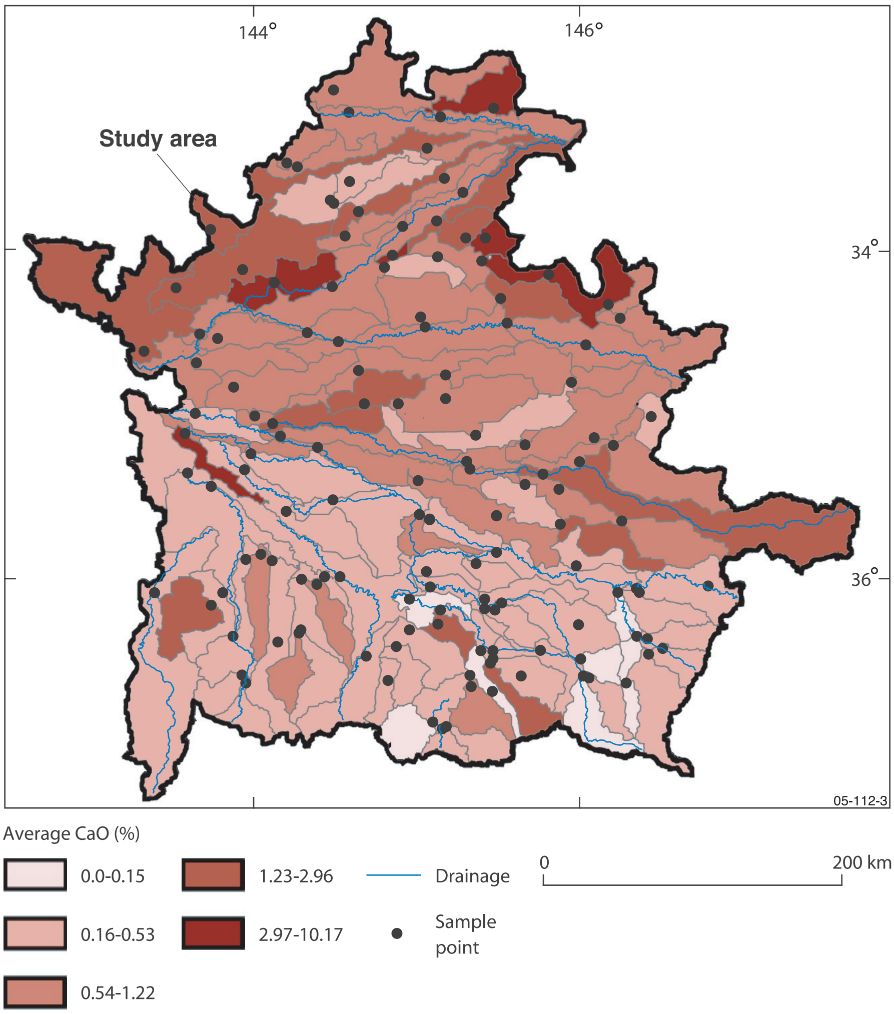


Figure 3. Geochemical map of total calcium (ppm) in BOT Riverina overbank sediment samples (analysed by XRF).

Two sediment samples were taken at each site:

- a near-surface overbank sediment sample (TOP) from 0–10 cm below the root zone
- a bottom overbank sediment sample (BOT) from a ~10 to 15 cm interval between ~65 cm and 95 cm below the root zone.

All samples were subjected to a detailed site description in the field, where measurements of pH, texture and moist and dry Munsell colours were also taken. In the laboratory, pH 1:5 (solid:water), EC 1:5, moisture content and laser particle size distribution were determined. Sediment splits were dried and sieved to <180 mm then analysed by X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS) and instrumental neutron activation analysis (INAA) (see Caritat et al 2004).

The concentrations of 62 elements were determined, providing data for maps showing the spatial and statistical distributions in the TOP and BOT samples and of the TOP/BOT ratios (report in preparation).

Results and potential applications

Sampling at upper and lower levels at each site allows for a more detailed understanding of the potential sources of chemical elements in the environment. TOP samples are susceptible to the influence of human activity (e.g. fertiliser use), while BOT samples from well below tilling depth reflect more closely natural background levels.

Median concentrations of most elements were higher in BOT samples, reflecting progressive mineral breakdown during weathering and ensuing mobilisation of soluble products. However, median concentrations of silver, lead, antimony, sulfur, yttrium and most rare earth elements were similar at both depths, while median concentrations of bromine, hafnium, manganese, phosphorus, silicon, zirconium and organic matter were higher in TOP samples.

These variations reflect relative concentration of more resistive minerals (quartz, zircon), precipitation of secondary weathering products (manganese oxyhydroxides), greater concentration of organic matter and perhaps fertilisers, and possibly evaporation of irrigation water near the surface.

As a means of independently evaluating the geochemical patterns obtained through this survey, we compared the geochemical map of thorium in TOP samples with airborne gamma-ray spectrometry patterns for the same element (figure 2). The coincidence of patterns is striking and the geochemical maps are faithful to a high degree of detail, clearly indicating that the patterns are real.

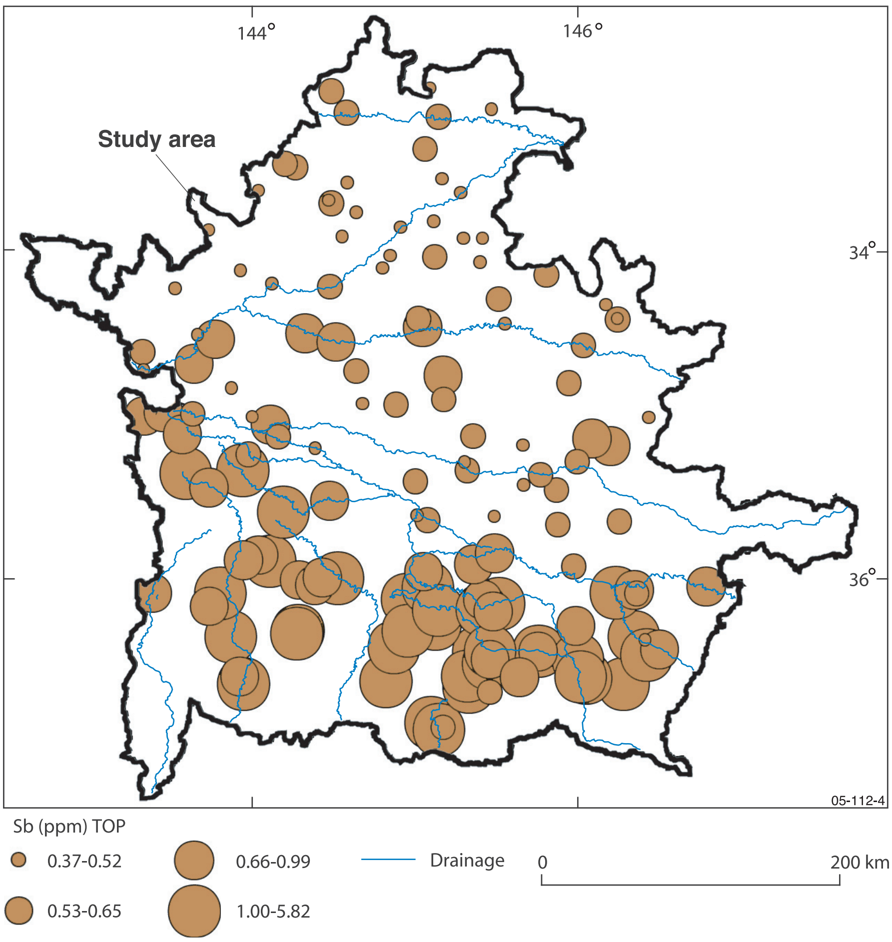
Acidity and salinity

The survey found obvious patterns of calcium and chlorine distribution in overbank sediments which have implications for soil pH and salinity management applications in agricultural soils. Calcium in BOT samples increased from south to north, reflecting the increasing occurrence of carbonate material observed (figure 3). Interestingly, the TOP calcium map shows an east–west ridge of values going through the middle of the study area, with lower values to both the south and the north.

Indicators of gold mineralisation

Arsenic and antimony are well-known pathfinder elements for gold mineralisation. The Victorian goldfields are located immediately to the south of the study area, and the arsenic and antimony distribution maps clearly show a progressive decrease from the southern edge of the area towards the north (figure 4). We interpret this as a representation of mechanical dispersion trains from the source regions to the south and perhaps also concealed sources below shallow basin sediments.

Antimony levels range up to nearly 11 mg/kg, over 20 times the median world soil concentration (Reimann & Caritat 1998). This confirms the anomalous nature of the sediments in the southern part of the study area and highlights the potential for the minerals exploration industry to use such surveys for regional orientation purposes.

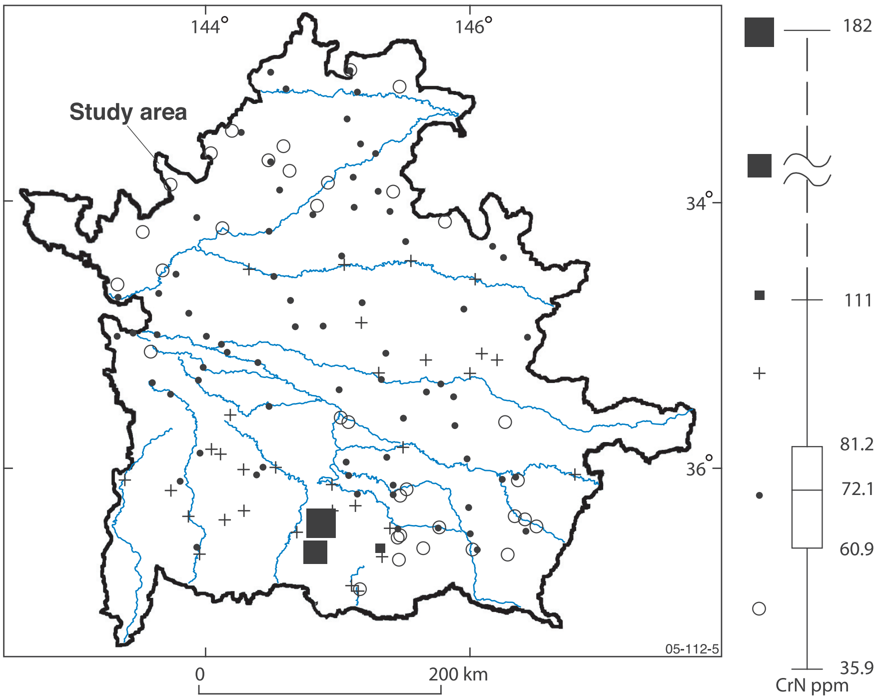


▲ **Figure 4.** Geochemical map of total antimony (ppm) in TOP Riverina overbank sediment samples (analysed by INAA).

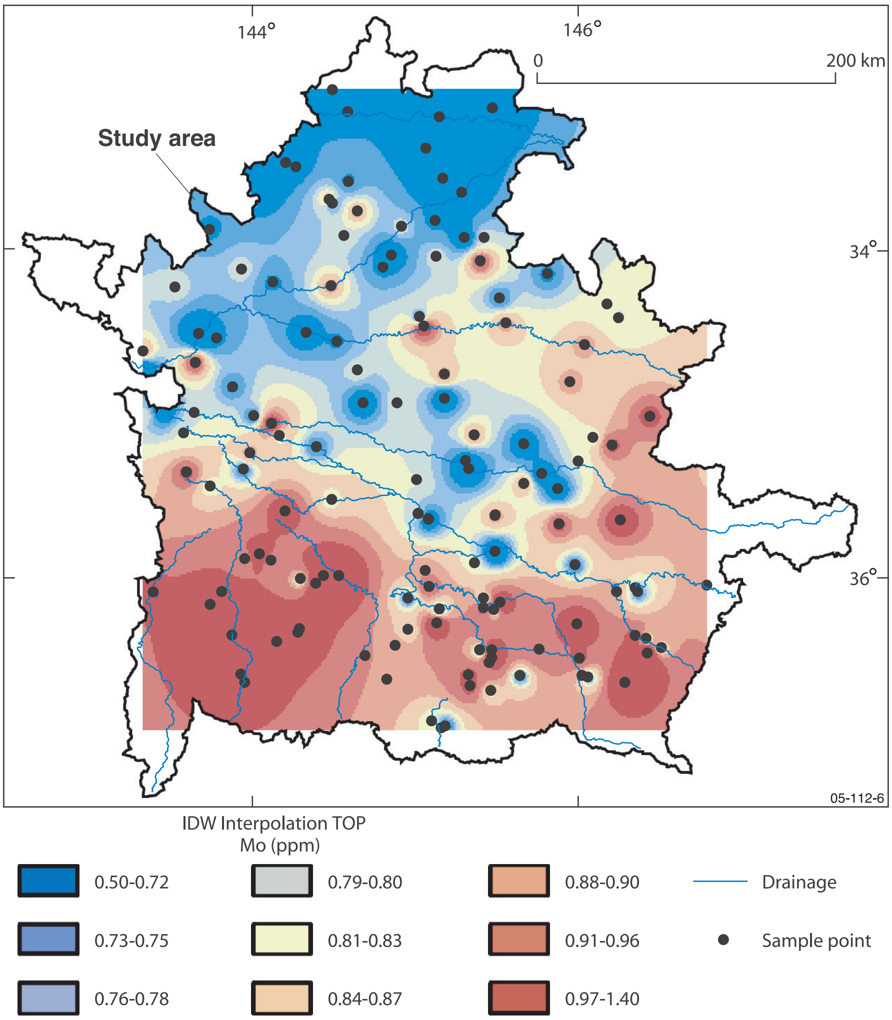
Trace element enrichments and deficiencies

Several trace elements were found to be above or below national and international guidelines for maximum allowable concentrations for agricultural soils, soil remediation and biosolids application. Concentrations of arsenic, barium, bromine, cadmium, chromium, copper, iron, gallium, nickel, antimony, uranium and vanadium were locally elevated above these guidelines. Cobalt, copper and molybdenum were found to be potentially deficient in parts of the region.

Concentrations of chromium increase smoothly towards the south (figure 5). Over half of the overbank samples collected contain more than 50 mg/kg Cr, which is the Western Australian 'ecological investigation limit' (WA DOE 2003). Five samples (max = 162 mg/kg) have elevated values above 100 mg/kg, which is the maximum allowable soil contaminant concentration for application of biosolids to agricultural land (NSW EPA 1997). Two of these samples were from the southern central portion of the study area and were elevated in both TOP and BOT samples. These catchments drain a ridge of Cambrian mafic volcanics. Another possible source of elevated Cr is the Quaternary tholeiitic basalts located near the edge of the Riverina region. While high chromium levels may have human health implications (Reimann & Caritat 1998, Adriano 2001), even the maximum total value in the Riverina is unlikely to yield excessive available Cr based on the results of a study in Italy, which found that <0.1% of total Cr was bioavailable (Maisto et al 2004).



▲ **Figure 5.** Geochemical map of total chromium (ppm) in BOT Riverina overbank sediment samples (analysed by INAA).



▲ **Figure 6.** Geochemical map of total molybdenum (ppm) in TOP Riverina overbank sediment samples (analysed by ICP-MS).

Molybdenum is an essential nutrient to many crops. While the global average concentration of molybdenum in soil ranges from 0.2–5 mg/kg (Adriano 2001), the median value in the study area was 0.8 mg/kg. Levels at or below 0.5 mg/kg can be considered low, and those with concentrations of 0.1–0.3 mg/kg can be expected to produce molybdenum deficiencies (Adriano 2001). Six samples from the Riverina survey contained molybdenum concentrations of 0.5 mg/kg amongst 37 samples with concentrations of 0.6 mg/kg or below. There is no obvious pattern to the location of low molybdenum concentrations (figure 6). Molybdenum has lower bioavailability in acid soils, so those in the southeast are more likely to be prone to deficiencies. This corresponds to observations by farmers that soils in the south of the study area were molybdenum deficient and that fertiliser applications reversed this problem (C. Simpson, pers. comm., December 2004).

Conclusions

Australia is one of few developed nations without nationwide baseline geochemical information at the disposal of government, industry, landholders and the general public.

The results of the Riverina survey illustrate how low-density geochemical surveys convey information about regional patterns in soil quality, mineral prospectivity and potential geohealth risk. Ongoing interpretation of this data will provide information on chemical element residence and mobility in the environment.

Pilot projects such as the Riverina geochemical survey contribute to establishing and fine-tuning sampling and analytical protocols that can ultimately be applied at the national scale.

The authors

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The maps illustrate a variety of presentation styles, each with advantages and drawbacks. The simplest and most factual maps are the dot-maps (figures 2a, 5), where real concentrations are shown at the exact points where they were obtained.

For easy interpretation, exploratory data analysis (EDA) principles instruct us that boxplot classification with symbology as used here works best (e.g. Velleman & Hoaglin 1981). The resulting maps represent an improvement in the interpretation capability over growing dots maps (figure 4).

The catchment or 'mosaic' maps (figure 3) assign the value obtained at the bottom of each catchment to the entire catchment. This is based on the assumption that the overbank sediments analysed are the best possible reflection of the average geochemical composition of near-surface materials in the catchment. Although this assumption is fundamentally valid and faithful to geological understanding, the resulting maps are somewhat difficult to read at first.

Inverse-distance weighted maps (figure 6) interpolate concentrations to fill in the gaps between real samples (the search radius used here is 50 km). Thus, they are based on mathematical models that may or may not match how the geochemical composition of sediments really varies around known points (i.e. no account is taken of lithology, erosion and transport processes, discontinuities etc.). These maps, when smooth and 'well behaved' are very easy to read and convey their message efficiently