

Regional geochemical surveys: News from Australia

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Introduction

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

To date, we have conducted—or are conducting—pilot geochemical surveys in four regions of south-eastern Australia: the Riverina, Curnamona, Gawler and Thomson regions (Figure 1). The main focus of the surveys is to sample fine-grained transported regolith (sediments). In all but the Curnamona cases, the sampling strategy adopted consisted of collecting sediment samples at two depths from floodplains near the outlet of (mostly large) large catchments. In the Curnamona, only surface fine-grained soil was collected mostly from depositional plains (Caritat & Reimann 2003). Other sampling media are also being tried in these surveys, including groundwater, plant tissues, and lag. Various sampling densities are being tested (Table 1), and modelling is planned to test what minimum sampling density would be required for a national coverage. The most recent survey, which is still in a preliminary stage, is in the Thomson region, for which only reconnaissance sampling has taken

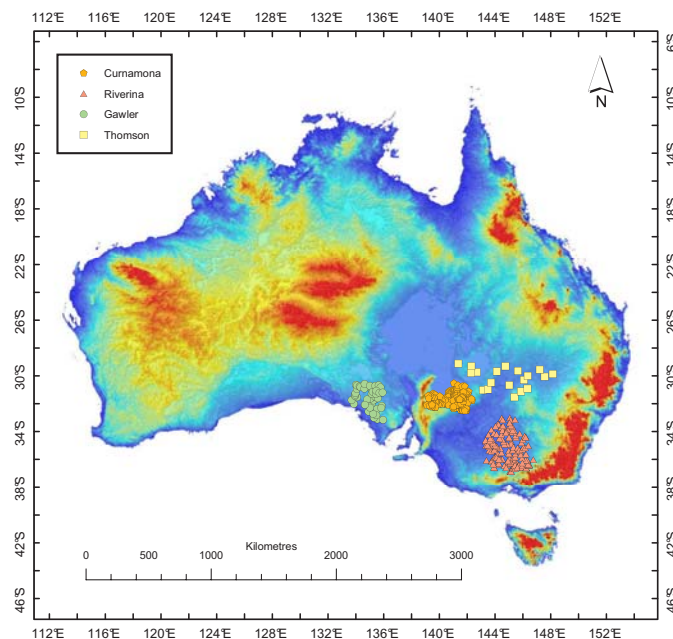


Figure 1. Location of sampling points for existing pilot regional geochemical surveys in Australia, over digital elevation model.

place so far. The most advanced pilot project is the one from the Riverina region, the subject of the remainder of this article.

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

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Table 1. Overview of sizes and sampling densities of pilot geochemical surveys.

Pilot survey	Distance east-west (km)	Distance north-south (km)	Approximate area (km ²)	Number of sampling sites	Average sampling density (1 sample per X km ²)
Riverina	288	427	122,976	142	866
Curnamona	305	203	61,915	199	311
Gawler	212	253	53,636	48	1117
Thomson	664	316	209,824	19 (preliminary) ~200 (target)	11,043 (preliminary) 1049 (target)

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 multi-media 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 (natural or man-made) can be quantified,
- new mineral potential can be recognised and areas for mineral exploration can be selected,
- appropriate and responsible land-use policies and decisions can be formulated,
- localised contamination can be identified and better remediated,
- local salinity stress can be detected and better understood, and
- potential geohealth risks can be identified.

Low-density geochemical mapping

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 & Wu 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).

Based on experience elsewhere (e.g., Reimann *et al.* 1998), a multi-media 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 (or floodplain) sediments near outlets from

large drainage basins or catchments. As this material is mixed and accumulated during 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 this sampling medium is well-suited to 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 future reports.

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 2; see Lambert *et al.* 1995 for bioregion concept).

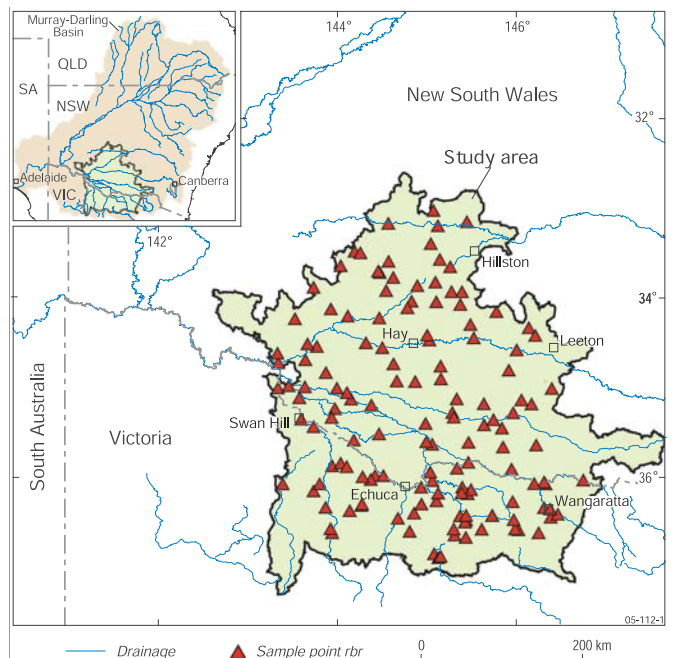


Figure 2. Location of the Riverina study area and sampling sites.

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,

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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, and
- is home to nearly two million people, or 11% of the total Australian population.

The Riverina pilot project

Undertaken collaboratively by the Cooperative Research Centre for Landscape Environments and Mineral Exploration (CRC LEME) and Geoscience Australia, the first pilot project to be completed is in the Riverina region, a prime agricultural district in southern New South Wales and northern Victoria (Figure 2). 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. 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.

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 low to modest relief and temperate to semi-arid climate:

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 (DEM), airborne gamma-ray and total magnetic intensity data coverages (Hallett *et al.* 2005).

Theoretical sample sites were located by conducting a hydrological analysis of the DEM to determine the lowest point in (mostly large) river catchments (see Caritat *et al.* 2004). The catchments were derived from a combination of DEM and drainage analysis. The 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.

Two sediment samples were taken at each site:

- a top overbank sediment (TOS) sample from 0-10 cm below the root zone, and
- a bottom overbank sediment (BOS) sample 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 μm then analysed by X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), instrumental neutron activation analysis (INAA) and Ion Specific Electrode (ISE) (see Caritat *et al.* 2004).

The concentrations of 62 elements were determined, providing data for maps showing the spatial and statistical distributions in the TOS and BOS samples and of the TOS/BOS ratios (Caritat *et al.* in prep.).

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. TOS samples are susceptible to the influence of human activity (e.g., fertiliser use), while BOS samples from well below tilling depth reflect more closely natural background levels. Median concentrations of most elements were higher in BOS samples, reflecting progressive mineral breakdown during weathering and ensuing mobilisation of soluble products. However, median concentrations of Ag, Pb, Sb, S, Y and most rare earth elements were similar at both depths, while median concentrations of Br, Hf, Mn, P, Si, Zr and organic matter were higher in TOS samples. These variations reflect relative upconcentration of more resistive minerals (quartz, zircon), precipitation of secondary weathering products (Mn 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 Th in TOS samples with airborne gamma-ray spectrometry patterns for the same element (Figure 3). The patterns from these two independent datasets coincide well, clearly indicating that

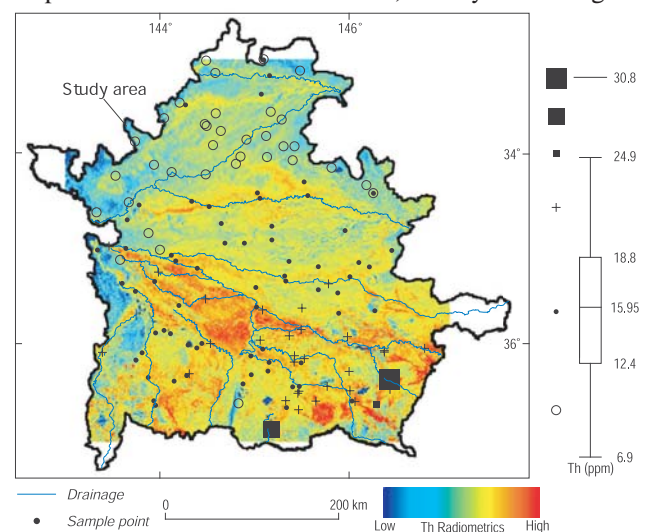


Figure 3. Geochemical map of total Th (ppm) in top overbank sediment Riverina overbank sediment samples (analysed by INAA), compared to airborne gamma-ray distribution of Th (background image, courtesy of the Department of Primary Industries of New South Wales and Victoria).

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the geochemical patterns that we obtained from the sediments are real. Results for K and U are similarly corroborated by the airborne gamma-ray spectrometry patterns.

Acidity and salinity

The survey found obvious patterns of Ca and Cl distribution in overbank sediments which have implications for soil pH and salinity management in agriculture. Ca in BOS samples increased from south to north, reflecting the increasing occurrence of carbonate material observed (Figure 4). Interestingly, the TOS Ca 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

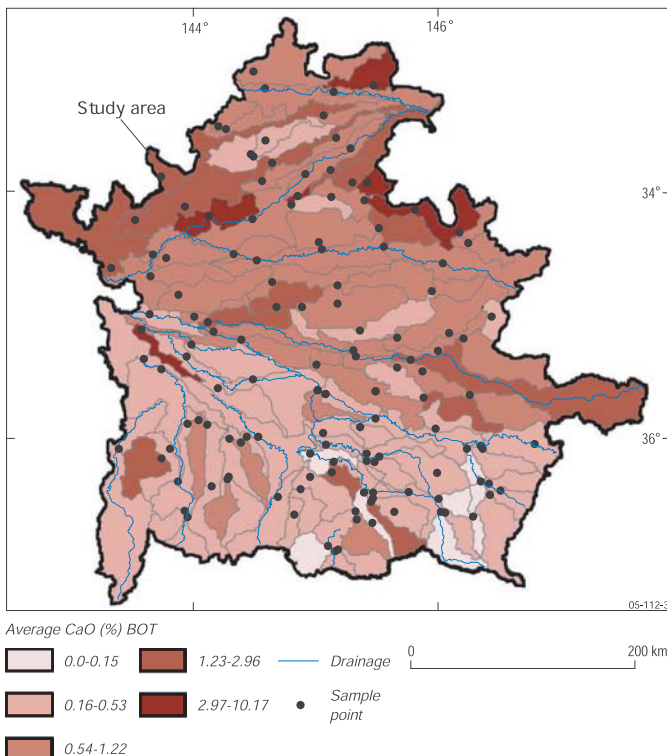


Figure 4. Geochemical map of total CaO (ppm) in bottom overbank sediment Riverina overbank sediment samples (analysed by XRF).

As and Sb are well-known pathfinder elements for gold mineralisation. The Victorian goldfields are located immediately to the south of the study area, and the As and Sb distribution maps clearly show a progressive decrease from the southern edge of the area towards the north (Figure 5). 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.

Sb 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 indus-

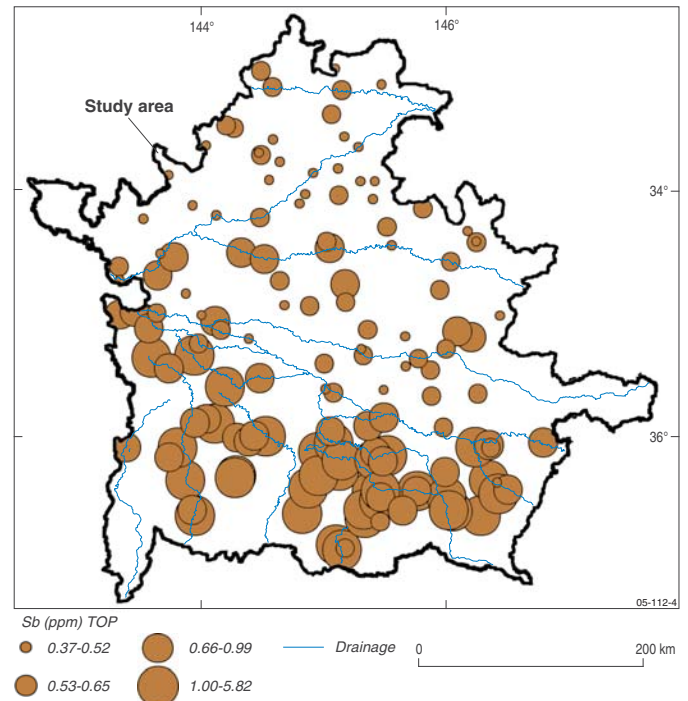


Figure 5. Geochemical map of total Sb (ppm) in top overbank sediment Riverina overbank sediment samples (analysed by INAA).

try to use such surveys for regional orientation purposes.

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. Total concentrations of As (0.8-159.8 mg/kg), Ba (189-1263 mg/kg), Br (<1-89.5 mg/kg), Cd (<0.1-2.33 mg/kg), Cr (29-200 mg/kg), F (150-610 mg/kg), Ga (6.3-26.1 mg/kg), Sb (0.37-10.8 mg/kg), U (1.26-8.49 mg/kg) and V (31-145 mg/kg) were locally elevated above these guidelines. Co (2.96-34.2 mg/kg) and Mo (0.5-1.9 mg/kg) were found to be potentially deficient in parts of the region.

Concentrations of Cr increase smoothly towards the southwest with sites in the central southern region amongst the most elevated (Figure 6). 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). Ten samples (max = 200 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 TOS and BOS 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. Whereas high Cr 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

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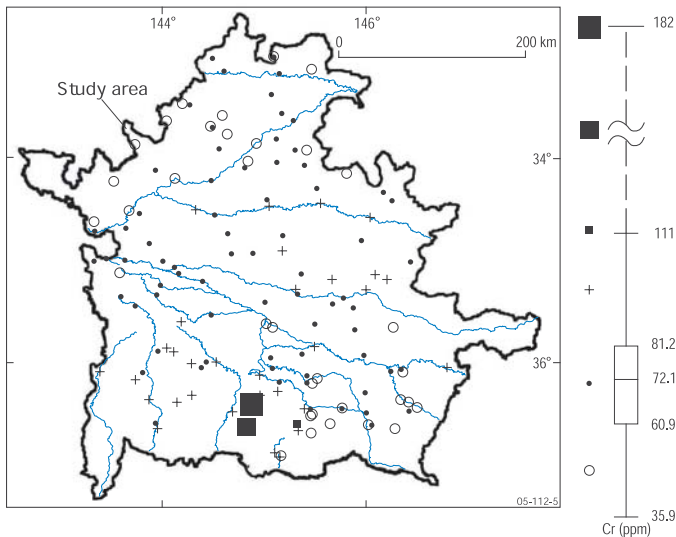


Figure 6. Geochemical map of total Cr (ppm) in bottom overbank sediment Riverina overbank sediment samples (analysed by INAA).

Italy, which found that <0.1% of total Cr was bioavailable (Maisto *et al.* 2004). Cr³⁺ is also likely to be the dominant oxidation state and is relatively non toxic and is normally tightly bound in soil (McLaughlin *et al.* 2000).

Mo is an essential nutrient to many crops. The global average concentration of Mo 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 Mo deficiencies (Adriano 2001). Six samples from the Riverina survey contained Mo concentrations of 0.5 mg/kg amongst 37 samples with concentrations of 0.6 mg/kg or below. Low Mo concentrations occur mostly in the north and are more common in the TOS samples (Figure 7). Mo 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 Mo deficient and that fertiliser applications reversed this problem (C. Simpson, pers. comm., December 2004).

Geohealth implications of the Riverina geochemical survey will be discussed in further detail in an upcoming publication (Lech & Caritat, in prep).

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 environmental and 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

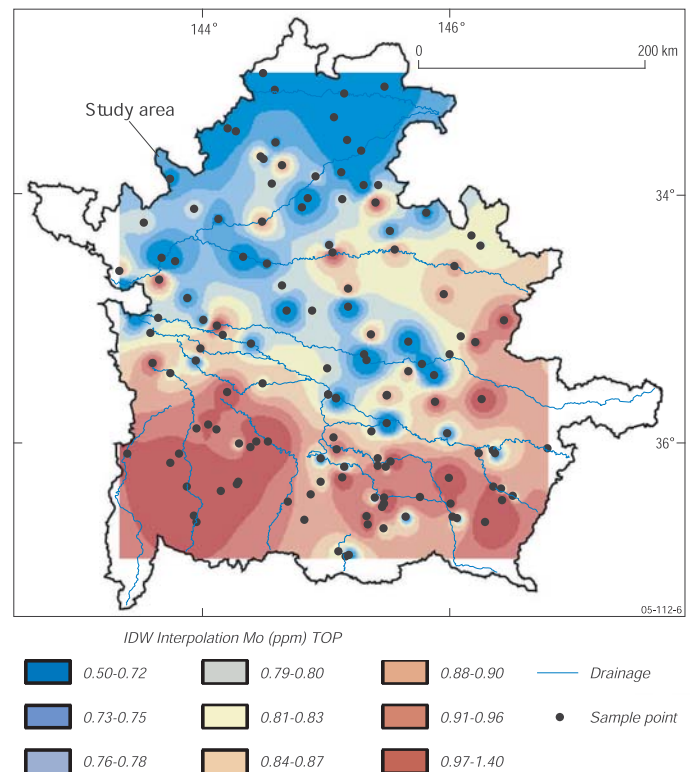


Figure 7. Geochemical map of total Mo (ppm) in top overbank sediment Riverina overbank sediment samples (analysed by ICP-MS).

are contributing to establishing and fine-tuning sampling and analytical protocols that can ultimately be applied at the national scale.

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References

- Adriano DC. 2001. Trace Elements in Terrestrial Environments—Biogeochemistry, Bioavailability, and Risks of Metals. Second edition, Springer-Verlag, New York, 867 pp.
- Caritat P de, Jaireth S, Lech M & Pyke J. 2004. Regional geochemical surveys: Riverina pilot project—methodology and preliminary results. Cooperative Research Centre for Landscape Environments and Mineral Exploration, Open File Report, 160, 156 pp. + CD-ROM. Available from: <http://www.crcleme.org.au/>
- Caritat P de *et al.* In preparation. Geochemical atlas of the Riverina region.
- Caritat P de, Reimann C. 2003. Baseline geochemistry of surficial regolith, Broken Hill region, Australia. In: Roach IC (Ed), Advances in Regolith (Canberra, ACT, 19-21 November 2003). CRC LEME: 53-54.
- Darnley AG, Björklund A, Bølviken B, Gustavsson N, Koval PV,

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- Plant JA, Steenfelt A, Tauchid M, Xuejing X, Garrett RG & Hall GEM. 1995. A Global Geochemical Database for Environmental and Resource Management. Recommendations for International Geochemical Mapping, Final Report of IGCP Project 259. UNESCO Publishing, 122 pp.
- Garrett RG & Nichol I. 1967. Regional geochemical reconnaissance in eastern Sierra Leone. Transactions of the Institution of Mining and Metallurgy, B76:97-112.
- Gustavsson N, Bølviken B, Smith DB & Severson RC. 2001. Geochemical landscapes of the conterminous United States—new map presentations for 22 elements. U.S. Geological Survey Professional Paper 1648, 38 pp.
- Hallett M, Vassallo J, Glen R & Webster S. 2005. Murray-Riverina region: An interpretation of bedrock Palaeozoic geology based on geophysical data. Quarterly Notes, Geological Survey of New South Wales, April 2005, 118, 16 pp.
- Lambert JA, Elix JK, Chenoweth A & Cole S. 1995. Bioregional planning for biodiversity conservation. Approaches to Bioregional Planning, Part 2. Background Papers to the Conference, 30 October - 1 November 1995, Melbourne. Available from: <http://www.deh.gov.au/biodiversity/publications/series/paper10/pubs/elix.pdf>
- Lech ME & Caritat P de. In preparation. Baseline geochemical survey of the Riverina region of New South Wales and Victoria, Australia: Geohealth implications.
- Li J & Wu G (Chief Compilers). 1999. Atlas of the Ecological Environmental Geochemistry of China. Geological Publishing House, Beijing, China, 209 pp.
- Maisto G, Alfani A, Baldantoni D, De Marco A & Virzo De Santo A. 2004. Trace metals in the soil and in *Quercus ilex* L. leaves at anthropic and remote sites of the Campania Region of Italy. *Geoderma*, 122:269-279.
- McLaughlin MJ, Hamon RE, McLaren G, Speir TW & Rogers SL. 2000. Review: A bioavailability-based rationale for controlling metal and metalloid contamination of agricultural land in Australia and New Zealand. *Australian Journal of Soil Research*, 38:1037-1086.
- Nichol I, Garrett RG & Webb JS. 1966. Studies in regional geochemistry. Transactions of the Institute of Mining and Metallurgy, B75:106-107.
- NSW EPA. 1997. Environmental Management Guidelines—Use and Disposal of Biosolids Products. New South Wales Environment Protection Agency (NSW EPA), 107 pp.
- Ottesen RT, Bogen J, Bølviken B & Volden T. 1989. Overbank sediment: a representative sample medium for regional geochemical sampling. *Journal of Geochemical Exploration*, 32:257-277.
- Plant JA, Reeder S, Salminen R, Smith DB, Tarvainen T, De Vivo B & Petterson MG. 2003. The distribution of uranium over Europe: geological and environmental significance. *Applied Earth Science*, 112:221-238.
- Reedman AJ & Gould D. 1970. Low sample-density stream sediment surveys in geochemical prospecting: an example from northeast Uganda. Transactions of the Institution of Mining and Metallurgy, B79:246.
- Reimann C & Caritat P de. 1998. Chemical Elements in the Environment—Factsheets for the Geochemist and Environmental Scientist. ISBN 3-540-63670-6. Springer-Verlag, Berlin, Germany, 398 pp.
- Reimann C, Äyräs M, Chekushin V, Bogatyrev I, Boyd R, Caritat P de, Dutter R, Finne TE, Halleraker JH, Jæger Ø, Kashulina G, Lehto O, Niskavaara H, Pavlov V, Räisänen ML, Strand T & Volden T. 1998. Environmental Geochemical Atlas of the Central Barents Region. ISBN 82-7385-176-1. NGU-GTK-CKE Special Publication, Geological Survey of Norway, Trondheim, Norway, 745 pp.
- Reimann C, Siewers U, Tarvainen T, Bityukova L, Eriksson J, Gilucis A, Gregorauskiene V, Lukashev VK, Matinian NN & Pasieczna A. 2003. Agricultural Soils in Northern Europe: A Geochemical Atlas. *Geologisches Jahrbuch Sonderhefte, Reihe D, Heft SD5*, 279 pp.
- Thalmann F, Schermann O, Schroll E & Hausberger G. 1989. Geochemischer Atlas der Republik Österreich (Textteil und kartenteil). Geologische Bundesanstalt, Rasumofskygasse 23, A-1031 Wien, Österreich.
- Velleman PF & Hoaglin DC. 1981. Applications, Basics and Computing of Exploratory Data Analysis. Duxbury Press, Boston, Mass, USA.
- WA DOE. 2003. Western Australian Department of the Environment Assessment Levels for Soil, Sediment and Water—Draft for Public Comment. In: Contaminated Sites Management Series, 31 pp. Available at: http://portal.environment.wa.gov.au/pls/portal/docs/PAGE/DOE_ADMIN/GUIDELINE_REPOSITORY/ASSESSMENT_LEVELS_FOR_SOIL%2C_SEDIMENT_AND_WATER.PDF

Several map types are shown here to illustrate various presentation styles, each with advantages and drawbacks. The simplest and most factual maps are the dot-maps (Figures 3, 6), 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 5).

The catchment or ‘mosaic’ maps (Figure 4) 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 7) 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, but they reflect a significant, and perhaps unacceptably high, degree of interpolation for these low-density surveys.

