# RIVER RED GUMS AS A BIOGEOCHEMICAL SAMPLING MEDIUM IN MINERAL EXPLORATION AND ENVIRONMENTAL CHEMISTRY PROGRAMS IN THE CURNAMONA CRATON AND ADJACENT REGIONS OF NSW AND SA

K.A. Hulme & S.M. Hill

CRC LEME, School of Earth & Environmental Sciences, University of Adelaide, SA, 5005.

## INTRODUCTION

River red gums (*Eucalyptus camaldulensis*) are one of the most widely distributed tree species within Australia and in particular the Curnamona Craton and adjacent regions (Figure 1), where they mostly occur along riparian zones of large alluvial channel systems. In these regolith-landform settings, regional mineral exploration and environmental chemistry sampling programs have traditionally focussed on sampling either: stream sediments, groundwater, soils, or else drilling to the underlying bedrock. This study investigates developing the use of river red gum organs in these sampling programs and considers some of the advantages of this over the use of more traditional sampling media. If river red gums can be developed as a mineral exploration and environmental chemistry sampling medium they may have many varied applications in regolith-dominated terrains including: mineral exploration along sedimentary basin margins; as an expression of shallow aquifer hydrogeochemistry in areas with potential salinity hazards; and, in regional biogeochemical baseline surveys.

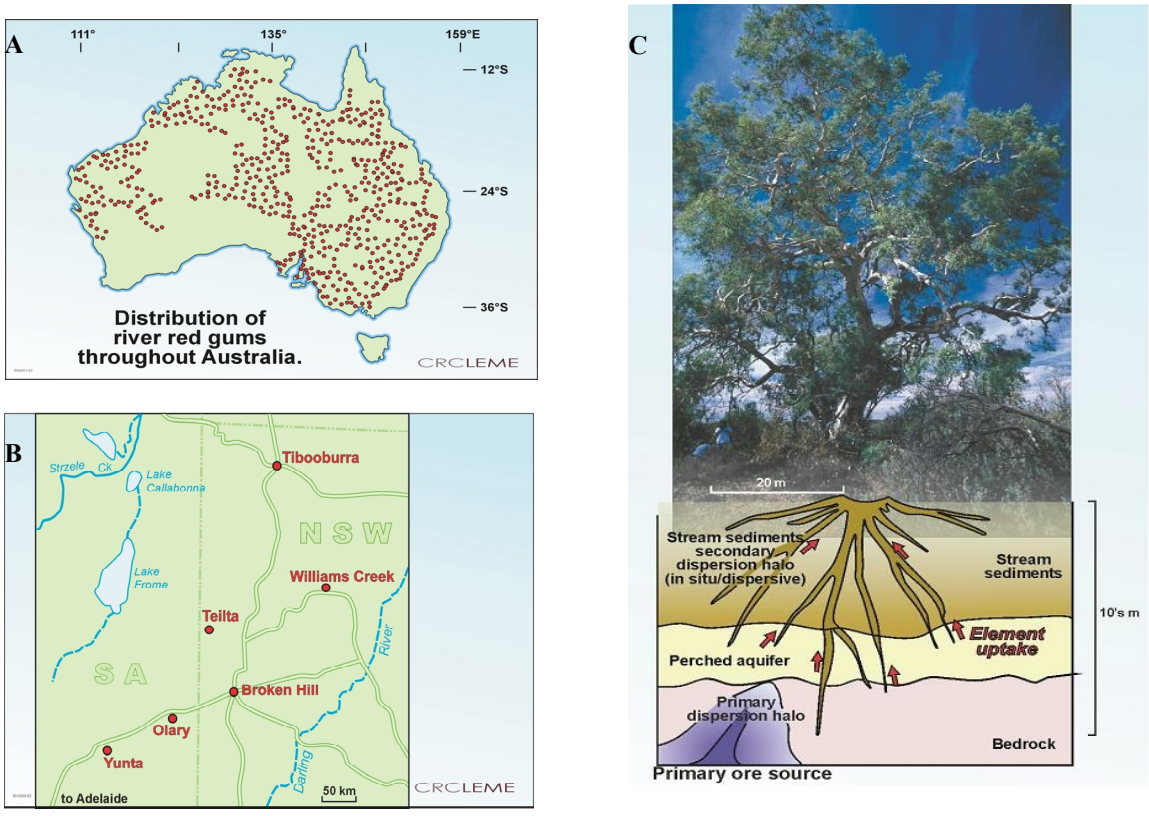


**Figure 1: A.** Distribution of river red gums throughout Australia with the study area enclosed by the rectangle. **B.** Regional map of northwest New South Wales and central east South Australia with the locations of the six orientation sites for this study. **C.** A cartoon depiction of the uptake of metal complexes by the root system from different regolith substrates.

## BACKGROUND

Biogeochemical studies, such as those undertaken by Warren & Delavault (1952, 1970), Cole (1970, 1991), Brooks (1972), Lintern (1996), and Arne (1999) have demonstrated the effectiveness of biogeochemistry at detecting local and regional geochemical dispersion patterns in regions either densely vegetated and/or dominated by regolith. As shown in Table 1, the use of biogeochemical media, such as river red gum organs,

has the potential for many advantages over other more traditionally used sampling media (low sampling cost; regional and local dispersion pathways depending on elements assayed; a relatively homogeneous sampling media for a given site; an easily obtained media across a wide area; and, negligible remediation costs following sampling). A major limitation however is the low background knowledge base of river red gum biogeochemistry.

**Table 1:** Some features of selected sample media for regolith-dominated terrains.

| | **Stream Sediments** | **Hydrogeochemistry** | **Soils** | **Bedrock Drilling** | **River Red Gum Biogeochemistry** |
|---|---|---|---|---|---|
| Relative Sampling Cost | Moderate | Very Expensive | Moderate | Expensive | Low to moderate |
| Dispersion pathways | Local - Regional | Variable | Local | Very Local | Variable |
| Chemical heterogeneity | Large | Low | Large | Large | Low |
| Accessibility - Availability | Good | Poor to variable | Good | Variable | Good to Variable |
| Remediation Costs | Negligible | Variable | Variable | High | Negligible |
| Knowledge Base | Good | Variable to Good | Good | Very Good | Low |

The Curnamona Craton and adjacent regions is an ideal location to examine the biogeochemistry of river red gums because not only are these trees widespread across the region, but it is highly prospective for a range of mineralisation styles in a wide range of regolith and landform settings. The bedrock and regolith-landforms of this region have been extensively studied (Peljo 2003). There are also rainfall chemistry (Hill & de Caritat 2002) and hydrogeochemistry (Kirste & de Caritat 2003) data sets being produced through CRC LEME that should provide a further context for many of the sampled trees. CRC LEME has been recently investigating the use of biogeochemistry within this region and a wide range of plants is being tested (Hill 2003, Hill & Hill 2003). A small, preliminary biogeochemistry survey of river red gums along Stephens Creek (Dann 2001), provided some encouraging results yet this study raised more questions than providing answers, suggesting that there is a need for greater knowledge and the refinement of the use of these trees as a biogeochemical sampling medium.

## BIOGEOCHEMICAL CONSIDERATIONS

All plants require macro- and micro-nutrients for their existence (Salisbury & Ross 1992). However the bioavailability of some metals can be restricted due to constraints relating to solubility, binding properties to soil particles, and antagonistic and synergistic interactions (Dunn *et al.* 1992). The majority of element uptake is via the root systems. This is made possible due to the characteristics of most root tips, in that they are weakly charged and slightly acidic, resulting in the exchange of $H^+$ for metals such as Cu, Zn, and Ni at the colloidal interface (Keller & Fredrickson 1952), or else they accommodate passive integration via simple diffusion. Incorporated elements will then translocate to various plant organs (e.g., leaves, twigs, fruit, bark and roots) due to their different physiological roles in the plant (Brooks 1972). This induces a chemical heterogeneity within the plant, which needs to be considered in the preliminary stages of a biogeochemistry survey when a suitable sampling medium is selected.

Additional factors that need to be considered are seasonal and spatial variations in plant chemistry. The former appears to be well documented but only in regions of temperate climates. Studies undertaken by (Cohen *et al*. 1987, Ashton & Riese 1988), for example show seasonal variation of Au and As in plant organs within temperate environments. Seasonal variation in plant chemistry appears to be less documented for arid and semi-arid regions. This could be because of the unpredictability of seasons in these climate zones, however biogeochemical variations due to proximity to rainfall events for example, are important to understand. Spatial variations in plant chemistry on the local scale are typically reflections of the underlying geology and groundwaters (Dunn *et al*. 1992), as well as the plant's regolith substrate and landform setting. To outline the spatial variations in river red gum biogeochemistry, trees will be sampled along two catchments. This will greatly refine the knowledge of spatial variations in river red gum biogeochemistry, helping to constrain suitable sampling spacings, dispersion pathway dimensions and the interactions between the spatial variations in environmental factors and river red gum biogeochemistry.

## CHARACTERISTICS OF THE RIVER RED GUMS

River red gums (*Eucalyptus camaldulensis*) are typically gnarled trees with a spreading evergreen canopy that extends from ground level up to heights between 15-30 m. There are two main taxonomic variations within the river red gums species: *Eucalyptus camaldulensis* Dehnh. Var. *obtusa* Blakely; and, *Eucalyptus*

*camaldulensis* Dehnh. var. *camaldulensis*. Flowering periods for the latter are variable in arid to semi-arid regions due to variable water availability. Generally, flowering takes place in late spring and summer, producing numerous creamy white flowers followed by fruiting (Holliday 1926). River red gums mostly form belts or stands with minimal woody understorey along the fringes and within watercourses throughout much of arid and semi-arid Australia (Beadle 1981 and Figure 1). Regolith types hosting river red gums include alluvial sediments ranging from poorly-sorted, gravels, to well-sorted, fine-grained sands, to organic-rich silts and fine sands. Landform assemblages include alluvial channels, swamps and depositional plains.

A characteristic of river red gums is the rapid development of an extensive and deep taproot system. The dense surface root system of a mature river red gum extends at least 20 m in the horizontal direction (Dexter 1967) and greater than 10 m vertically (Davies 1953). Field observations from western NSW suggest that even these figures are conservative. River red gums can therefore have a biogeochemical sampling area of >4000 $m^3$ , with potential for element uptake via their roots from: the adjacent stream sediments; the shallow ground water aquifers within the alluvial sediments; and, buried bedrock or saprolite.

Many of the characteristics of river red gums are consistent with the criteria required of a biogeochemical sampling media as outlined by (Dunn *et al*. 1992, Hill 2002). These include:

- an easy to identify plant species;
- a locally dominant and widespread distribution;
- a tendency to colonise areas of regolith cover (where bedrock related information is less readily available);
- an extensive root system that may penetrate transported cover and possibly also provide a homogenised expression of heterogeneous transported cover;
- an ability to retain many plant organs throughout the year; and,
- large, smooth and waxy leaves that may tend to shed detrital surface contaminants.

**SAMPLING AND ANALYTICAL APPROACH**

Six individual river red gums were chosen for detailed study across the Curnamona Craton and adjacent areas (central E of SA and far NW of NSW). The sites of individual trees for detailed study were selected to include a range of geological settings and proximity to different mineralisation styles, and the availability of an existing regolith-landform framework including regional mapping and geochemistry. Plants chosen were also of similar size, age and health. Sampling procedures were equivalent to those described by (Dunn *et al.* 1992, Hill 2002). Where possible, the river red gums were sampled from around the circumference of the lower canopy, at compass bearings of every 45$^o$. In most cases less than eight samples were taken from around the tree using this method because the canopy height put some sampling points out of reach. This sampling strategy helps to constrain any biogeochemical variation within the tree due to aspect (such as detrital contamination or preferential elemental translocation to particular sides of the tree). Individual samples were of approximately 300 g and specifically targeted different organs (leaves, twigs, bark and roots) from the six selected river red gums. The results from this stage of the study will be valuable in determining the sampling methods employed in later stages of the study.

The analytical techniques used in this study are INAA; ICP-OES and ICP-MS conducted at Becquerel Laboratories, Lucas Heights, NSW. Sample preparation, including drying times and temperatures followed that described by (Hill 2002).

**PROJECT DESIGN SUMMARY**

This project is designed in three main phases. These include:

- Phase 1: biogeochemical sample orientation, targeting six individual trees from different settings across the region. This will particularly examine temporal and organ biogeochemistry variation within individual trees, as well as temporal variations of the biogeochemistry of selected organs (trees sampled every three months over two years);
- Phase 2: spatial variation in biogeochemistry of a selected plant organ along two catchment systems in the region. This will involve detailed regolith-landform mapping and vegetation mapping of the selected catchments and the integration of the spatial distribution of other environmental components; and,
- Phase 3: testing results from the first two phases to applications in other areas.

**PRELIMINARY RESULTS**

Some of the features at each of the selected orientation study sites are shown in Table 2, while selected biogeochemical characteristics of some river red gum organs (leaves, twigs and bark) at each sample site are outlined in Table 3.

**Table 2:** Some characteristics of the sample sites for six individual trees across the study area.

| Site | Location | Geology | Regolith-Landform Map | Landscape Setting | Mineralisation Potential |
|---|---|---|---|---|---|
| Tibooburra Inlier | Racecourse Creek | Devonian Granodiorite and Palaeozoic metasediments | 1:25 k (Chamberlain & Hill 2002) | Margins of bedrock inlier – basin cover | Au in sediments |
| Williams Peak | Williams Creek | Koonenberry Belt | 1:500 k (Gibson & Wilford 1996) | Covered bedrock | Au and diamonds |
| Teilta | Teilta Creek | Poorly known. Possible Adelaidean and Willyama Supergroup | 1:500 k (Gibson & Wilford 1996)<br>1:100 k (Hill in prep) | Covered bedrock in basin and dune field | Unknown.<br>Cu-Au?<br>Ag-Pb-Zn? |
| Flying Doctor | Willawillyong Creek | Willyama Supergroup | 1:10 k - part (Earl *et al.* 2002)<br>1:25k (Lewis *et al.* 2002)<br>1:100 k (Hill 2001)<br>1:500 k (Gibson & Wilford 1996) | Covered bedrock | Ag-Pb-Zn |
| Bindarah | Cutana Creek | Willyama Supergroup | 1:500 k (Gibson 1996) | Covered bedrock | Ag-Pb-Zn<br>Unknown |
| Yunta | Winnininnie | Adelaidean & Cambrian Sediments | 1:500 k (Gibson 1996) | Covered bedrock | Cu-Au |

The analysis revealed that Sb, Cs, Hf, Ir, Se, Ta, In, Te, TI, Th, V, U, Zr, Be, Bi, Pb, Mo, Eu, La, Yb, and Ga for all sampling media at all locations were below detection limits. Although Pb contents were below detection limit in all of the samples from this study, recent results from another study in the region obtained several hundred ppm Pb contents in leaves near the Pinnacles Mine (Hill & Hill 2003). This could be because the results from the Pinnacles Mine area reflect some detrital contamination, or else the environmental Pb levels are expected to be higher near the Pinnacles Mine than from the six sample sites reported here. Further sampling is planned to test these possibilities.

**Table 3:** Variations of metal concentration within different oven dried tissues of individual river red gums at six study sites. Initial value represents the mean value; values in brackets () are the range of values; and, * signifies values below detection limit. To calculate means, below detection limit values were taken as half the detection limit value. Values with a mean but no range recorded represent only one sample in that data set. n= the number of samples recovered for each organ at each site.

| Site/organs | Au (ppb) | As (ppm) | Pb (ppm) | Zn (ppm) | Cu (ppm) |
|---|---|---|---|---|---|
| **Tibooburra:** | | | | | |
| **Leaves** (n=5) | 0.39 (*- 0.68) | 0.14(*-.24) | * | 28.6 (24-32) | 6.8 (6-8) |
| **Twigs** (n=5) | 1.4 (*-6.41) | 0.04(*-.062) | * | 15.4 (11-19) | 5.2 (4-8) |
| **Bark** (n=1) | * | * | * | 12.3 (10-17) | 2 |
| **Flying Doctor:** | | | | | |
| **Leaves** (n=5) | * | 0.051 (*-.081) | * | 28 (23-37) | 7.6 (6-9) |
| **Twigs** (n=5) | * | * | * | 29.2 (15-44) | 8.2 (6-11) |
| **Bark** (n=1) | * | * | * | 22 | 2 |
| **Telita:** | | | | | |
| **Leaves** (n=5) | 0.25 (*- 0.65) | 0.092 (0.059-0.16) | * | 19.40 (17-22) | 9 (8-11) |
| **Twigs** (n=5) | 0.62 (0.38-1.03) | 0.04 (*-.061) | * | 19 (17-23) | 12 (10-14) |
| **Bark** (n=1) | 0.39 | * | * | 5 | 2 |
| **Williams Creek:** | | | | | |
| **Leaves** (n=8) | 0.17 (*- 0.32) | 0.07 (*- 0.142) | * | 18 (16-22) | 7.9 (7-9) |
| **Twigs** (n=8) | 0.64 (*-1.31) | 0.03 (*- 0.07) | * | 21.8 (17-26) | 18.6 (15-22) |
| **Bark** (n=1) | 1.15 | * | * | 11 | 2 |
| **Bindarah:** | | | | | |
| **Leaves** (n=4) | * | 0.05 (*- 0.106) | * | 28.3 (24-37) | 8 (7-9) |
| **Twigs** (n=4) | * | 0.03 (*- 0.059) | * | 32.3 (19-49) | 10 (9-11) |
| **Bark** (n=1) | * | * | * | 15 | 2 |
| **Yunta:** | | | | | |
| **Leaves** (n=4) | * | 0.04 (*- 0.08) | * | 19.8 (16-27) | 6.5 (6-7) |
| **Twigs** (n=4) | * | * | * | 25.8 (22-31) | 18.3 (13-21) |
| **Bark** (n=1) | * | * | * | 7 | 1 |

Many of the other elements showed some detectable chemical heterogeneity between river red gum organs and the different sample sites. The small analytical data set at this stage of the project however, means that the discussion of these results is only at a preliminary level. The Au contents in the major organs are extremely variable both within individual trees and between sample sites. It is encouraging that two of the sites closely associated with Au mineralisation (Tibooburra and Williams Creek) had detectable Au contents in the trees. The detectable Au content at Teilta could also offer some encouragement for further exploration in that area. Au contents tended to be higher in twigs than in leaves, but the high variability of results suggest that obtaining representative results is a major challenge for interpretations associated with this element. The As contents tend to be higher in the leaves and also at the more Au-rich sites (Tibooburra, Teilta and Williams Creek). The Zn contents appear to be less variable than some of the other elements and are generally highest in twigs at all sites except Tibooburra where they are highest in leaves. The Cu contents are also generally higher in twigs than leaves at all sites except Tibooburra, however the Cu content in twigs is slightly more variable than in the leaves.

An assessment of the ease of sampling of the different media suggests that the leaves were a more convenient sampling medium to obtain than other organs. Leaves could be generally pulled straight from their branches. Twigs were reasonably simple to sample, however it required some effort to obtain twigs of consistent diameter (and therefore consistent bark to wood ratio) for sampling. Bark sampling created more visible damage to the tree, plus the samples were more difficult to grind during sample preparation, and the results were not as strong as for leaves and twigs in most elements. Fruit took a longer amount of time to collect an adequate sampling weight as they could only picked in small clusters, while root samples often required considerable digging to obtain, and the roots were typically covered (and therefore contaminated) by the surrounding regolith substrate.

## CONCLUSION

A continuing research program is aiming to further refine the knowledge for the use of river red gums as a sampling medium. So far the results and the ease of sampling suggest that firstly leaves and probably then twigs would make the best sampling media from the trees. The small set of results shown here suggests that some discrimination between the regional mineralisation styles is reflected in the biogeochemistry. More conclusive results and the influence of temporal and spatial variations in river red gum biogeochemistry are planned for the near future.

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