SEASONAL ELEMENT VARIATIONS OF *EUCALYPTUS CAMALDULENSIS* BIOGEOCHEMISTRY AND IMPLICATIONS FOR MINERAL EXPLORATION: AN EXAMPLE FROM TEILTA, CURNAMONA PROVINCE, WESTERN NSW

K.A. Hulme & S.M. Hill

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

INTRODUCTION

The chemical composition of living trees and shrubs can provide information for delineating local and regional geochemical dispersion patterns associated with mineralisation in regolith-dominated terrains. If these sampling media are to be successfully used, however, it is important that a rigorous and robust sampling procedure is developed, mostly to ensure that different samples are comparable both within individual sampling programs and between different sampling programs. One aspect of the biogeochemical characteristics of trees that is not widely understood is the temporal variations in biogeochemical characteristics, particularly within semi-arid and arid parts of Australia. Several researchers have noted pronounced seasonal variation in the element concentration in plants elsewhere in the world, especially for Au assays, with the largest trace metal concentrations generally occurring in the springtime (Ashton & Riese 1989, Stednick *et al.* 1987). This paper considers whether *E.camaldulensis* displays equivalent seasonal chemical trends.

The river red gum biogeochemistry results from the Teilta study site are shown here because this area is within a recently studied regolith-dominated terrain that overlies highly prospective Willyama Supergroup rocks (de Caritat & Kirste 2004, Ruperto 2004, Hill in press). As such, this area would be ideal for further use of *E. camaldulensis* biogeochemistry for regional sampling of major drainage courses within mineral exploration programs.

BACKGROUND

Teilta is located in southeastern central Australia, approximately 150 km north-northwest of Broken Hill. The Teilta 1:100,000 mapsheet (Hill in press) extends from the western margins of the Barrier Range, through to the Strzelecki Desert dunefields as far west as the NSW-SA border. The closest meteorological station in the region is Broken Hill. The average annual rainfall for Stephens Creek Reservoir is 221.3 mm with an average maximum 32.7°C and minimum 18.1°C in summer (January) and 15.5°C and 3.8°C in winter (July) (Bureau of Meteorology 2003).

The vegetation communities and dominant species are closely associated with the major landform settings for the region. River red gum riparian woodlands dominate major drainage channels and alluvial outwash plains, while smaller tributaries are colonised by prickly wattle (*Acacia victoriae)* shrubs and small trees. Understanding the biochemistry of river red gums within these landforms within prospective terrains potentially offers mineral explorers another means of sampling that can be employed, along with traditional methods (Hulme & Hill 2003a, b).

During the mid-1960s to the late 1980s and early 1990s companies such as Kennecott Exploration, CRAE and BHP minerals managed mineral exploration leases within the Teilta region, searching for base metal Cu-Au and Zn-Pb-Ag mineralisation within covered Palaeo-proterozoic Willyama Supergroup and Neo-proterozoic Adealaidean metasediments (Cameron 1993a & b). Table 1 summarises a small number of mineral exploration surveys undertaken across the Teilta region over the last 28 years and the exploration methods that were employed.

Table 1 shows that for the most part, previous exploration surveys returned inconclusive results. The area is within an encouraging geological setting and some geophysical and drilling targets were identified, but it was difficult to thoroughly follow these through because of the extensive regolith. The aim of recent biogeochemical research in the region by CRC LEME is to investigate the ability of this approach to express mineralisation that is otherwise concealed in regolith-dominated terrains. Studies undertaken by Warren & Delavault (1952, 1970), Cole (1970, 1991), Brooks (1972), Lintern (1996), Arne (1999), and Hill & Hill (2003) have demonstrated the effectiveness of biogeochemistry at detecting local and regional geochemical dispersion patterns in regions that are either densely vegetated and/or dominated by regolith. For the most part, however, this type of mineral exploration has previously been undertaken in cold to temperate climates,

In: Roach I.C. ed. 2004. *Regolith 2004*. CRC LEME, pp. 151-156.

which has demonstrated pronounced seasonal variations in the metal contents of plant samples (Dunn 1983, 1984, Stednick *et al.* 1987). Equivalent studies from semi-arid to arid terrains are more limited. To date the general understanding is that in semi-arid and arid regions of Australia there are no distinct and regular seasonal growing periods because of the irregular rainfall patterns that are a major control on plant growth (Hill 2002). One study undertaken by Huenneke *et al.* (2001) in the Chihuahuan Desert of North America, however, proposes that vegetation in semi-arid terrains displays highly variable temporal chemical changes. These may be associated with the following annual growth cycle:

(i) winter - most species are dormant;
(ii) spring - reproduction has begun;
(iii) summer - summer rains give rise to peak reproduction activity; and,
(iv) autumn - peak biomass.

Table 1: An overview of selected exploration surveys undertaken across Teilta.

Company	Exploration Lease	Year	Method	Mineralisation Target	Results
Kennecott Exploration	EL 24	1965	Stream Sediments, aeromagnetics and Bedrock Drilling	Base metal Co and Ag mineralisation	No significant results returned
CRAE	1449,1850-1851, 1879	1980-1983	Aeromagnetic and radiometric surveys Stream Sediments & geochemical surveys	Stratiform & stratabound base metals Sn-W and Au	Hindrance due to semi-consolidated sands, clays and gravel overlying the Willyama basement
BHP Minerals	EL 3952-3963, 4005-4009, and 4140	1993	Aeromagnetic and radiometric surveys and limited drilling	base metal Cu-Au and Zn-Pb-Ag mineralisation	Failed to identify prospective units of the Willyama Supergroup

The parameters established by Huenneke *et al.* (2001) may imply that the greatest concentration of trace metals is most likely to occur in summer for semi-arid arid terrains. During the summer period increases in temperature, available rainfall and daylight lengths will enhance plant growth and many reproductive processes. Theoretically these factors will contribute to an increase in evapotranspiration rates, resulting in a greater movement of elements being transported throughout the xylem and being allocated to specific sites given their physiological role and the increase in cellular activity during the peak period of reproduction (Garland 1981). A challenge for Australian semi-arid and arid areas, however is that rainfall patterns are irregular, especially near the summer-dominated to winter-dominated rainfall transition zone, such as occurs in western NSW (Hill 2004).

Investigations carried out by Markert & Weckert (1989) on the aerial foliage of *Polytrichum formosum* during 1985-1987, defined categories of seasonal variations in element concentrations, such as: high seasonal variation (> 80%); intermediate seasonal variation (ca. 50%); low seasonal variation (ca. 30%); and, slight variability (< 30%). The percentage variation here refers to the amount of fluctuation an element may experience over a season, and this approach is used later in this manuscript to describe the seasonal variation in biogeochemical characteristics.

Through recognising the physiological role that the essential elements play in plant growth, there is also potential to define periods corresponding to biogeochemical changes that are associated with either maximum and minimal growth development. Table 2 summarise the functions of some essential elements in plants.

Table 2: Some of the essential elements required by plants for growth, survival and reproduction (Dunn *et al.* 1995)

Element	Available form	Typical concentration ranges (ppm)	Physiological role
Calcium (Ca)	Ca^{2+}	500-3000	Cell wall and membrane stability
Magnesium (Mg)	Mg^{2+}	100-500	Central element in chlorophyll
Copper (Cu)	Cu+, Cu^{2+}	5-15	Promotion of e^- transfer during light reactions (photosynthesis)
Zinc (Zn)	Zn^{2+}, $Zn(OH)_2$	20-100	Chlorophyll synthesis

In order to investigate elemental seasonal variation of elements in *E. camaldulensis* a series of 6 test sites across the Curnamona Province and adjacent regions (Yunta, Bindarrah, Teilta, Tibooburra, Williams Creek and Flying Doctor) were selected (Hulme & Hill 2003b). Repeated sampling of *E. camaldulensis* leaves was carried out on a seasonal basis (autumn, winter, spring, and summer) for 2003. This paper outlines the temporal biogeochemical variations from an individual river red gum sampled at Teilta and from these results suggests when sampling should or should not be undertaken, and if there are any implications as to biogeochemical exploration within the area.

RESULTS

Temporal dimensions

Recent results from Teilta have revealed that As, Ba, Br, Ca, Fe, La, K, Rb, Sm, Na, Zn, Al, Cu, Mg, Mn, Nb, Nd, P, S, Sn, and Sr are detectable in the sampling media (leaves) across all seasons. While elements Au and Cr were only detected during the autumn.

Observations on the physical appearance of the *E. camaldulensis* sample tree were noted, and include:

- Autumn: abundant fruit, buds and leaf production;
- Winter: minor fruit and bud production.
- Spring: initiation of flower bud production; and,
- Summer: an increased bud, fruit and leaf production.

Preliminary results for six selected elements from the seasonal variation study from Teilta are shown in Figure 1. The elements chosen represent both essential elements (Ca, Mg, Cu and Zn) and non-essential elements (Au and As).

The highest assay results for the macro-elements Ca (16,700 ppm) and Mg (3,148 ppm) were obtained during spring, which corresponds to the period of initial bud and shoot production (Huenneke *et al.* 2001). Considering the physiological role of these elements (Table 2), the increase in assay results for these elements may relate to the initial preparation of the tree for maximum reproduction and activity that is suggested to take place during summer.

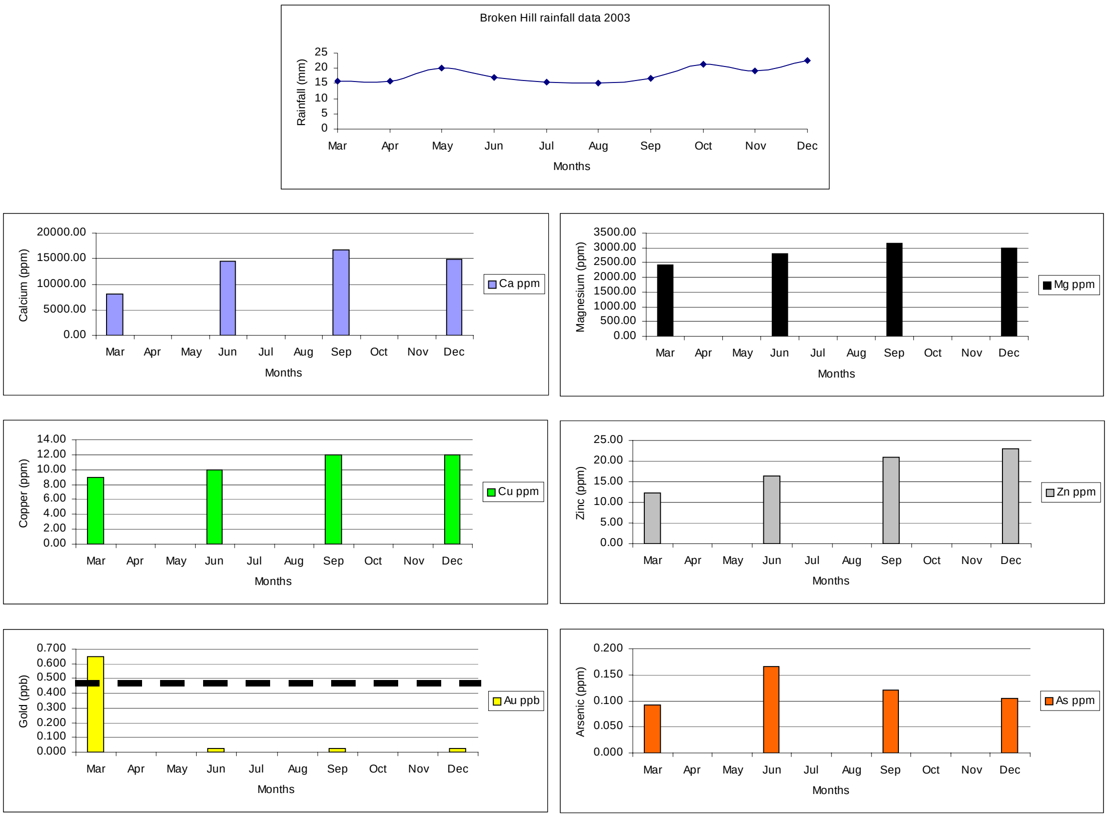

Figure 1: Seasonal rainfall variations for Broken Hill in 2003 and the corresponding fluctuations in the concentrations of Ca, Mg, Cu, Zn, Au and As in leaf samples taken during 2003. -------- denotes below detection limit.

The highest concentrations of Cu (12 ppm) and Zn (23 ppm) were obtained from the summer samples. Summer corresponds with an increase in temperature, rainfall and extended periods of daylight, and therefore the potential for peak photosynthetic activity. As shown in Table 2, Cu and Zn are important for chlorophyll production, so it is expected that the increase in these assay results may be associated with an increase photosynthetic activity. This increase during summer is also consistent with the suggestion of Garland *et al*. (1981) that the ultimate concentration of an element is related to the flux of transpiration through evaportranspiration which should peak during summer.

The lowest assay results for Ca (8,000 ppm), Mg (2,408 ppm), Cu (9 ppm) and Zn (12 ppm) are from autumn, which is suggested to be the period of peak biomass (Huenneke *et al.* 2001). The reduced concentration levels are possibly due to dilution where these elements are dispersed across a larger biomass within the tree.

The element As is shown here because of its Au and sulphide pathfinder properties, while Au is shown here because of its direct economic interest. The highest assays for As were from winter, when the plant could be considered less biologically active. An increase in As concentrations in the plant during periods of dormancy may be related to a substitution of one element for another. For example the element P is considered antagonistic towards As (O'Neill 1995). Given their chemical similarity and the reduced concentration of P during the winter period As maybe taken up. When the biological activity of the tree is less active, potentially harmful elements such as As may accumulate within the tree, and are less diluted by the reduced uptake and activity of other elements.

Gold shows distinct seasonal variations with the only detectable concentration obtained from the autumn sample, The relative decrease in Au concentration (below detection limit) during spring and summer may be related to dilution due to the increase in cellulose and starches created during the growing period, as for the winter season which is defined as a period of dormancy. This may indicate a reduction in activity of the *E. camaldulensis* and microorganisms residing in the surrounding sampling media (stream sediments) resulting in below detection levels for Au. In contrast, during the autumn the Au content of 0.65 ppb was detected within the leaves. All other elements show a decrease in concentration during the autumn period, suggesting that the available essential elements are possibly dispersed across the increased biomass produced at this time. This dilution of the elements may promote the expression of Au within the leaves, as Au does not appear to have any essential or beneficial requirements to vegetation.

Variability

The importance of understanding the influence of climatic seasons on the essential element concentration in the *E. camaldulensis* outlines periods of plant development, but it also delineates periods of minimal changes in elemental concentrations. Examination of the elemental concentration of *E.camaldulensis* leaves for 2003 across the Teilta site enables the definition of the degree of variability as described by (Markert & Weckert 1988). The degree of variability was estimated by ($max_{(conc)} – min_{(conc)} = X; X/max_{(conc)}$ (x) 100 = %). The results shown in Table 2, display the degree of element variability during period of plant growth and periods of reduced plant growth across Teilta during the 2003 seasons.

Table 3: Shows the degree of elemental variation between periods of plant growth and periods of reduced plant growth and defines the optimal sampling period that should utilised during one season (2003) for selected elements.

Parameters	Plant growth	Reduced plant growth	Plant growth	Reduced plant growth	Plant growth	Reduced plant growth	Plant growth	Reduced plant growth	Plant growth	Reduced plant growth	Plant growth	Reduced plant growth
	Ca ppm		Mg ppm		Cu ppm		Zn ppm		As ppm		Au ppb	
High seasonal variability > 80 %												96.6 %
Intermediate seasonal variability ~ 50 %		44.82 %								44.57 %		
Low seasonal variability ~ 30 %												
Slight seasonal variability < 30 %	10 %		5.18 %	14.29 %	0 %	10 %	8.70 %	25 %	12.5 %		Below detection	

The degree of variability is defined as slight for Mg, Cu and Zn, intermediate for Ca and As, and high for Au. The slight to intermediate variations suggest that seasonal variations are less important for many elements, with the exception of Au, which suggests that the most appropriate sampling period appears to be during autumn when plant growth is reduced but biomass is at its maximum.

Conclusion

The use of *E. camaldulensis* as an aid in detecting mineral occurrences requires an understanding of its biochemical composition with regards to essential and non-essential elements, and the fluctuation of these elements across the seasons. On the basis of the above results a number of preliminary conclusions maybe drawn:

1. Temporal variations in *E. camaldulensis* biogeochemical characteristics from semi-arid settings may not be extreme for most elements but they do exist;
2. The use of macro- and micro-elements (Ca, Mg Zn and Cu) possibly aids in outlining periods of growth development across the seasons;
3. Through understanding the periods of growth development and associated elemental variations, optimal sampling periods may be defined;
4. The slight seasonal variability expressed for Cu and Zn and the slight-intermediate seasonal variability for As suggests that in semi-arid terrains sampling for assays of these elements would be appropriate at any time of the year; and,
5. Large seasonal variations observed for Au content in leaves reveals that there is a restricted ideal sampling period of autumn, and that comparison of results between seasons is not advisable.

These results are preliminary and understanding seasonal biogeochemical variations is still being investigated for 2004. The additional information will provide greater assurance for determining if element variations are a function of growth development, and whether the understanding of the periods of growth development provided knowledge of the optimal sampling periods.

Acknowledgements: This research has been conducted with the assistance of a CRC LEME and University of Adelaide scholarship and CRC LEME operating funds. NSW DMR have also provided additional support. Becquerel Laboratories, in particular David Garnett, are greatly appreciated for their assistance with the biogeochemical analyses.

References

ARNE D.C. 1999. Biogeochemistry of the Ballarat east goldfield, Victoria, Australia. *J. Geochem. Explor.* **67**, 1-14.

ASHTON L.W & RIESE W.C. 1989. Seasonal variation of gold and arsenic in biogeochemical samples from a disseminated gold deposit in the Northern Cordillera. *J. Geochem. Explor.* **31**,171-184.

BUREAU OF METEOROLOGY 2003. Averages for Flying Doctor: Stephens Creek Reservoir. http://www.bom.gov.au/climate/averages/tables/cw_047031.shtml.

BROOKS R.R. 1972. *Geobotany and Biogeochemistry in Mineral Exploration*. Harper & Row, 231 pp.

CAMERON J. 1993a. *Exploration Licenses 3953 - 3963, 4005 - 4009 and 4140, North Broken Hill, NSW: First Annual Report*. BHP Minerals Exploration Department (**GS 1993/164**) 16 pp. plus appendices.

CAMERON J. 1993b. *Exploration Licenses 3953 - 3963, 4005 - 4006 and 4008 - 4009, North Broken Hill, NSW: Final Report*. BHP Minerals Exploration Department (**GS 1993/164**) 10 pp. plus appendices.

COLE M.M. 1970. The importance of environment in biogeographical/geobotanical and biogeochemical investigations. *Geochemical Exploration: proceedings of the 3rd International Symposium. Toronto*. Canadian Institute of Mining and Metallurgy, Montreal **Special Volume 11**, pp. 414 - 425.

COLE M.M. 1991. Remote sensing, geobotany and biogeochemistry in detection of Thalanga Zn-Pb-Cu deposit near Charters Towers, Queensland, Australia. *Trans. Instn. Min. Metall (Sect. B: Appl. Earth Sci.)* **100**, pp. B1-B8.

CARITAT P. DE. & KIRSTE D. 2004. Teilta Regolith Project: groundwater geochemistry. *CRC LEME* **Open File Report 158**.

DUNN C.E., HALL G.E., COHEN D.R., CATT P. & LINTERN M.J. 1995. Applied biogeochemistry in mineral exploration and environmental studies. *17th International Geochemical Exploration Symposium, Townsville, Australia*. The Association of Exploration Geochemists, p. 198.

GARLAND T.R., CATALDO A. & WILDUNG R.E. 1981. Absorption, transport, and chemical fate of plutonium in soyabean plants. *Journal Agricultural Food Chemistry* **29**, 915-920.

HILL L.J. 2002. Branching out into Biogeochemical surveys: A guide to vegetation sampling. *In*: ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia*. CRC LEME, pp. 50-53.

HILL L.J. 2004. *Geochemical and biogeochemical dispersion and residence in landscapes of western New South Wales*. CRC LEME, Australian National University, PhD thesis, unpublished.

HILL S.M. in press. Teilta, western NSW. *In:* ANAND R.R. & DE BROEKERT P. eds. *Regolith-Landscape Evolution Across Australia: a compilation of regolith-landscape case studies and landscape evolution models.* CRC LEME Monograph, Perth.

HILL S.M. & HILL L.J. 2003. Some important plant characteristics and assay overviews for biogeochemical surveys in western New South Wales. *In*: ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 187-192.

HULME K. & HILL S.M. 2003a. River red gum biogeochemistry: towards an innovative new tool for mineral exploration programs in the Curnamona Craton and adjacent regions. *In:* PELJO M. comp. *Broken Hill Exploration Initiative: abstracts from the July 2003 conference*. Geoscience Australia **Record 2003/13**, pp. 83-84.

HULME K.A., & HILL S.M. 2003b. 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. *In:* ROACH I.C. ed. *Advances in Regolith.* CRC LEME, pp. 205-210.

HUENNEKE L.F., CLASON D & MULDAVIN E. 2001. Spatial heterogeneity in Ciluahuan Desert vegetation: implications for sampling methods in semi-arid ecosystems. *Journal of Arid Environments* **47**, 257-270.

LINTERN M.J., BUTT C.R.M. & SCOTT K.M. 1996. Gold in vegetation and soil-three case studies from the gold fields of southern Western Australia. *J. Geochem. Explor*. **58**, 1-14.

MARKERT B. & WECKERT V. 1989. Fluctuations of element concentration during the growing season of Polytrichum formosum (hedw.). *Water, Air and soil Pollut.* **43**,177-189.

O'NEILL P. 1995. Arsenic. *In: Heavy metals in soils.* Blackie Academic and Professional; 2nd Edition, pp 363.

RUPERTO L. 2004. Teilta regolith project: basement modelling. *CRC LEME* **Open File Report 157**.

STEDNICK J.D., KLEM R.B & RIESE W.C. 1987. Temporal Variations of Metal Concentrations in Biogeochemical Samples over the Royal Tiger Mine, Colorado, Part 1: Within Year Variation. *Journal of Geochemical Exploration* **28**, 75-88.

WARREN H.V. & DELAVAULT R.E. 1952. Trace Elements in Goechemistry and Biogeochemistry. *American Association for the Advancement of Science* **5**, 26-30.