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

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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,

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 Hueneke 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.

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

The parameters established by Hueneke 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)

<table>
<thead>
<tr>
<th>Element</th>
<th>Available form</th>
<th>Typical concentration ranges (ppm)</th>
<th>Physiological role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium (Ca)</td>
<td>Ca²⁺</td>
<td>500-3000</td>
<td>Cell wall and membrane stability</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>Mg²⁺</td>
<td>100-500</td>
<td>Central element in chlorophyll</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>Cu⁺, Cu²⁺</td>
<td>5-15</td>
<td>Promotion of e⁻ transfer during light reactions (photosynthesis)</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>Zn²⁺, Zn(OH)₂</td>
<td>20-100</td>
<td>Chlorophyll synthesis</td>
</tr>
</tbody>
</table>

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, Tiboburra, 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, Rh, 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.

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

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**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 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 evapotranspiration 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 $(\max_{\text{conc}} - \min_{\text{conc}})/\max_{\text{conc}} \times 100 = \%$. 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.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Plant growth</th>
<th>Reduced plant growth</th>
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<th>Reduced plant growth</th>
<th>Plant growth</th>
<th>Reduced plant growth</th>
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<th>Reduced plant growth</th>
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<tbody>
<tr>
<td>Ca ppm</td>
<td>8,000 ppm</td>
<td></td>
<td>2,408 ppm</td>
<td></td>
<td>9 ppm</td>
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<td>12 ppm</td>
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<td>Mg ppm</td>
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<td>Cu ppm</td>
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<td>10 ppm</td>
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<td>Zn ppm</td>
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<td>As ppm</td>
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<td>0.65 ppb</td>
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</table>

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.

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References

K.A. Hulme & S.M. Hill. *Seasonal element variations of Eucalyptus camaldulensis biogeochemistry and implications for mineral exploration: an example from Teilta, Curnamona Province, western NSW.*


