Eucalyptus camaldulensis (river red gum) Biogeochemistry: An Innovative Tool for Mineral Exploration in the Curnamona Province and Adjacent Regions

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CHAPTER 3

DETAILED BIOGEOCHEMISTRY OF INDIVIDUAL TREES

3.1 TRACE ELEMENT BIOGEOCHEMICAL CYCLING IN THE BIOSPHERE

The biogeochemical cycle is defined as the pathway in which chemical elements move through both the biotic and abiotic compartments of the Earth. The chemical composition of plants is a function of several dynamic factors; such as external factors related to geology, landscape settings, soils and climate, to internal physiological factors of the plants themselves (Kovalevskii, 1979). The primary sources of trace elements for all life on land are predominately supplied from the soil (parent material from which they are derived) (Pendias & Pendias, 1984). The two primary inputs of trace elements in semi-arid & arid environments (biosphere) are via aerial and the terrestrial pathways, the later of which is the mostly considered in this study. The uptake of trace elements by plants is largely governed by the following:

- plant physiology (nutritional requirements and rooting depth);
- the interface between soil/soil solution and plant roots;
- translocation of trace elements to different organs; and,
- organ senescencing and the accumulation of litter (element recycling).

Plant physiology nutritional requirements and rooting depths

There is a myriad of information on the nutritional requirements of plants and in particular the ability of plants to accumulate both essential and non-essential trace elements such as; S, Fe, Mg, Mn, Cu, Zn, Mo, Ni, Co and Se (Kabata-Pendias & Pendias, 1991; Marschner, 1995; Campbell, 1996; Reuter & Robinson, 1997; and, Dunn, 2007) that are potentially indicavtive of buried mineralisation (see Table 1.1 and Table 1.2 this thesis).

A large proportion of trace element uptake is achieved via the plants root system from the surrounding soils. Studies have shown that Australian plants typically have varying rooting depths such as:

- very deep roots: *Triodia pungens* >30-50m (Reid *et al.*, 2008) and *E. camaldulensis* (Davis, 1953; Hulme and Hill, 2003);
- very widespread rooting systems: horizontal spread exceeds well beyond the bole and the aerial drip zone (Dexter, 1967); and,
- Rao's study in 2005 (cited in Field and Little 2008, p. 183) showed that shallow root mats and fungal mat associations have extensive root systems.

The morphology of the plant root system plays a crucial role in water and trace element uptake (Aspandiar *et al.*, 2006). The eucalypts are generally considered as a xeromorphic genus, which besides having efficient water use also tend to have lower than normal nutritional requirements, are able to extract nutrients from nutrient poor soils and they better utilise their nutrients (Beadle, 1968). In addition, the rooting structure and depth of the eucalypts is mostly descrided as dimorphic, including a set of lateral roots extending horizontally from the main crown and a main sinker or tap root, extending vertically into the substrate (Pate *et al.*, 1995). The main function of a dimorphic root system, in particular in arid and semi-arid environments, is the exploition of water from their immediate substrate to

ensure the plant's survival through the year (Pate *et a*l., 1999). Associated with this, water is the primary solute in which trace element transfer between the surrounding soils and root interface takes place.

Interface between soil/soil solution and plant roots

In order for plants to extract water from depth, a process termed hydraulic lift (or hydraulic redistribution) takes place. This includes the vertical movement of water from moist areas to dry areas, which takes place through the xylem and capillary rise. In addition, this process can carry trace metals (Aspandiar, *et al.*, 2006; Field & Little, 2008). The rhizosphere is a dynamic chemical environment where numerous biochemical reactions take place, and includes compounds such as ascorbic, aspartic, citric, fulvic, humic, hydroxybenzoic, malic, oxalic and tannic acids (Field & Little, 2008). There are multiple sources for these acids, however, this process is mostly possible due to the characteristics of the plant 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.

Translocation of trace elements to different organs

The translocation of both essential and non-essential elements is well documented, therefore only a brief overview is provided here. The uptake of elements takes place via the fine surface 'hairs' of the root. Transport is facilitated either through the cytoplasm of cells and from cell to cell through plasmodesmata, or throughout much of the plant through non-living spaces and within cell walls (Salisbury & Ross, 1992). The 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). The life and senescence of different plant organs, promotes different organic and inorganic substances to be accumulated as plant litter.

Organ senescencing and the accumulation of litter (element recycling)

Plant litter is composed of polysaccharides, polyphenols and terpenoids of varied abundance and composition (Gallo, *et al.*, 2009). The production of plant litter largely depends on the productivity of the plant, as well as rainfall, the length of the growing season and climate can contribute to the production of plant litter (Staaf, 1987 and Facelli, *et al.*, 1991). In particular, in arid and semi-arid environments there are shorter time lags between the growth of a plant organ and its deposition as plant litter, where in general leaf abscission takes place the moment leaves die (Noy-Meir, 1985). In addition, the production of plant litter in arid and semi arid environments is quite episodic due to drought and hot winds, which induces leaf mortality (West, 1979). The accumulation of plant litter can alter the physical and chemical properties of the immediate environment either directly and indirectly, as the decomposition of the plant litter may release both nutrient and phototoxic substances into the soil (Day, 1983). Additionally, the chemical composition of litter will vary with species, seasons and organs.

Long-lived organs usually have more lignin and secondary compounds, and the plant litter that is produced generally lasts longer (Feeny, 1970), as with the *E. camaldulensis* a fully expanded mature leaf is commonly between 1.5 - 2 years of age (Field, J. 2004, pers.comm., November), and decompose slowly due to poor litter quality and low nutrient concentrations (Adams and Attiwill, 1986). Maxium litterfall for many eucalypts takes place over summer or during dry periods (O'Connell and Grove, 1996). During the senescence of organs, compounds are either released in to the environment (substrate) by leaching or attaked by

decomposers. The chemical property of the leachates (toxicity, mineral content and solubility) will depend on the nature of the substance translocated and accumulated in the organ.

The accumulation of plant litter can alter the soil temperature by intercepting solar radiation and by insulating the soil from air temperature (McKinney, 1929). These changes in soil temperature may enhance the rate of decomposition mineral leaching and inturn nutrient availability (Knapp and Seastedt, 1986). As well plant litter can affect the exchange of water between the atmosphere and the soil, such that the plant litter can reduce evaporation, and increase infiltration (Larson and Whitman, 1942).

The accumulation of nutrients in the plant litter and their rate at which they are transferred to the soil can be grouped into three categories (O'Connell and Grove, 1996):

- potassium and sodium released rapidly mainly as a result of direct leaching by rainfall and throughfall;
- calcium and magnesium the loss of these elements is related to celluar decay of the litters components; and,
- nitrogen, phosphorous and sulphur takes place during the initial stages of litter accumulation.

The decomposition of plant litter (organic matter) contributes to the exchange capacity of cations and anions in the soil, and affects the retention, release and availability of nutrients to the plant.

In this semi-arid study area plant litter was generally sparse, largely due to its low preservation potential in the landscape, where litter is eroded by aeolian and due to the colonisation of river red gums in ephemeral stream channels, fluvial removal. It therefore is not included as a component of this study.

Plant Biogeochemical Cycling by Plants

There is a large amount of literature on the biogeochemical cycling of trace elements in terrestrial ecosystems (e.g. see review by Schlesinger, 1991). Most of these studies, however, are based in tropical and temperate ecosystems, particularly associated with forestry and agricultural systems (Jordan, 1983; Rai et al., 1986; Raich, 1998; Likens 19??), rather than arid and semi-arid settings. Net primary production in tropical to temperate systems is typically in the range of 5800 to 16,900 kg/ha/y, whereas in semi-arid and arid settings this is thought to be considerably lower and in the range of 1000-7000 kg/ha/y (Sala et al., 1988) and generally estimated to be more like 1500 kg/ha/y (Lieth, 1975). One of the main limitations in trying to constrain net primary production and associated biogeochemical cycling fluxes in arid and semi-arid settings is the assumption of steady-state ecosystems. This is certainly not the case in the semi-arid settings considered in this study, where there has been radical environmental and landscape change, within short time frames, in particular within the timeframe of pastoral settlement within the last 200 years (e.g. Fanning 1999). There are major and irregularly variable inputs and outputs from the 'open' landscape system, particularly by aeolian processes as well as poorly constrained colluvial sheetflooding and alluvial flooding events and large artesian groundwater systems, as well as 'catastrophic' herbivore grazing. Constraining all of these variables within the short-timeframe and constrained budget of this project is beyond the scope of this study. As a result this study is more focussed on empirical observations, associations and correlations, in particular between the E. Camaldulensis and the underlying geological substrate.

3.2 SIX INDIVIDUAL TREE STUDY SITES

The biogeochemical characteristics of *E. camaldulensis* organs (e.g. leaves, roots, twigs, fruit/buds and bark) and adjacent stream sediments are outlined from individual trees at 6 key orientation sites (Figure 3.1) across the region:

- Yunta Winnininnie Creek in the southern Olary Domain (potential Cu-Au mineralisation);
- Bindarrah Cutana Creek in the northern Olary Domain (potential Ag-Pb-Zn mineralisation);
- Flying Doctor Willawillyong Creek (adjacent to Ag-Pb-Zn mineralisation) in the Broken Hill Domain;
- Teilta Teilta Creek (Willyama Supergroup bedrock prospective for polymetallic mineralisation);
- Williams Peak Williams Creek (near Au and diamond mineralisation) in the Koonenberry Belt; and,
- Tibooburra Inlier Racecourse Creek (highly prospective for primary and secondary Au mineralisation).

For each of these trees this preliminary orientation study endeavoured to identify:

- the recommended biogeochemical sampling medium for mineral exploration;
- the recommended analytical suite suited for mineral exploration;
- the temporal influences on element uptake;
- the relationships between *E. camaldulensis* biogeochemistry and other landscapeenvironmental factors (e.g. regolith-architecture, existing regolith chemistry, existing hydrogeochemistry); and,
- the geochemical relationships with more traditional regolith sampling media, such as stream sediments.



Figure 3.1: A regional map of northwest New South Wales and central east South Australia, and the location of the six study sites (Yunta, Olary-Bindarrah, Broken Hill-Flying Doctor, Williams Creek, Teilta and Tibooburra.

3.3 ORGAN TISSUE BIOGEOCHEMISTRY

All plants require essential mineral elements for their survival (Table 3.1), such as, N, P, K, Ca, Mg, S, B, Cl, Fe, Mn, Zn, Cu, Mo and Ni. They are referred to as "macro"- and "micronutrients" (Salisbury & Ross, 1992). In addition to the essential elements are a suite of elements known as the beneficial elements, which promote plant growth, but are not necessary for completion of the plant's life cycle. They include Si, Na, Co and Se. Elements taken up by plants will be translocated to various plant organs (e.g. leaves, twigs, fruit, bark and roots) due to their different physiological roles in the plant (Brooks, 1972). This element distribution will induce a chemical heterogeneity within the plant that needs to be considered in the preliminary stages of a biogeochemical survey. Carlisle & Cleveland (1958) suggest that the elemental content of tree organs increases in the sequence: roots; bark; buds; twigs; and, leaves.

Table 3.1: The essential and beneficial elements and their concentration ranges required by plants for growth, survival and reproduction. Modified from (Kabata-Pendias & Pendias, 1991; Marschner, 1995; Campbell, 1996; Reuter and Robinson, 1997 and Dunn, 2007). *values reported for *E. camaldulensis*, # micronutrients not indicated as essential by Campbell 1996, + elements classified as beneficial but not essential Marschner 1997.

	Macro-nutrients typically > 1000 ppm in plant tissue									
Element	Available form	Typical concentration	Physiological role							
		ranges (ppm)								
Phosphorus (P)	$H_2PO_4^-$, HPO_4^{-2-}	*1800-2200	Nucleic acids, P-esters							
Potassium (K)	\mathbf{K}^+	*6000-8000	Major cytoplasmic cation, protein synthesis							
Nitrogen (N)	NH_4^+ , NO_3^-	*14000-21000	Protein, nucleic acids							
Sulfur (S)	SO_4^{2-}	*1100-1600	Cysteine, Methionine, redox reactions							
Calcium (Ca)	Ca^{2+}	*5000-10100	Cell walls and membranes stability							
Iron (Fe)	Fe, Fe ²⁺ & Fe ³⁺	*110-170	Redox reactions, cytochromes							
Magnesium (Mg)	Mg^{2+}	*1700-3700	Chlorophyll, protein and DNA							

	Micro-nutrients typically < 100 ppm in plant tissue.								
Element	Available form	Typical concentration	Physiological role						
		ranges (ppm)							
Manganese (Mn)	Mn^{2+}	*190-600	Respiration/photolysis enzyme cofactor						
Copper (Cu)	Cu^+ , Cu^{2+}	*3-5	Enzyme. plastocyanin, cytochrome oxidase						
Zinc (Zn)	Zn^{2+} , $Zn(OH)_2$	*13-41	Enzyme cofactors, chlorophyll synthesis						
Boron (B)	H_2BO^{3-}	*144-200	Pollen tube growth & orientation						
Molybdenum (Mo)	MoO_4^{+2}	<0.1-1.0	Nitrate reductase cofactor						
Nickel (Ni)	Ni ²⁺	0.1-6.5	Urease cofactor						
Chlorine (Cl)	Cl	*1700-4600	Oxygen evolving complex						

	Beneficial minerals typically < 50 ppm in plant tissue.								
Element	Available form	Typical concentration ranges in (ppm)	Physiological role						
Aluminium (Al)	N/A	*120-260	Controls colloidal cell properties						
Silicon (Si) # +	Si(OH) ₄	1000	Reduce transpiration and improve resistance to pathogens and phytoliths						
Sodium (Na) # +	Na^+	*2200-3600	C-4 generation of PEP step						
Cobalt (Co) # +	Co^{2+}	0.2	Enzyme cofactor, nitrogen fixation						
Selenium (Se)	N/A	N/A	Specific plants- avert phosphorus toxicity						

3.4 COMPARISON BETWEEN STREAM SEDIMENT CHEMISTRY AND TRACE ELEMENT BIOACCUMULATION (SOIL-PLANT TRANSFER) WITHIN EUCALYPTUS CAMALDULENSIS

Another variation to be considered for tree biogeochemical sampling is the difference in element concentrations within the selected media of leaves or twigs and their adjacent stream sediments. Stream sediment traditionally constitutes an important sampling medium in regional-scale reconnaissance geochemical surveys (Cohen, *et al.*, 1999), however the equivalent application of riparian vegetation is less well constrained. The ability of plants to absorb elements can vary, and different sediment size fractions may contribute differently to the element uptake. In order to determine the primary source for element uptake, the biological absorption coefficient (BAC) is estimated by: BAC = C_p/C_{ss} ; where C_p is the concentration of a selected element in the plant dry weight; and, C_{ss} is the concentration of the same element in the stream sediment (Kovalevsky, cited in Brooks, *et al.*, 1995). Results are plotted logarithmically as shown by (Kabata-Pendias & Pendias, 1984) the following modified parameters (Index of bioaccumulation) that define the degree of bioaccumulation:

- 0.0001 to 0.001 = very low;
- 0.001 to 0.01 = low;
- 0.01 to 0.1 = slight;
- 0.1 to 1 = medium; and,
- 1 to 10 = high.

3.5 TEMPORAL ELEMENTAL VARIABILITY WITHIN EUCALYPTUS CAMALDULENSIS

Fluctuations in element concentration over time in active plant tissue should be taken into account when sampling. The chemical content of plants in general should reflect, at least in part, the chemical composition of their surrounding substrate. However the strength of this relationship can be variable and will be influenced by different factors such as:

- bioavailability;
- ambient temperature; and,
- rainfall.

Temporal changes in element concentration are most important in photosynthetic tissue, such as leaves (Allen *et al.*, 1974). Several researchers have noted pronounced temporal variations in the element concentrations in plants elsewhere in the world. In general the highest trace element concentrations generally occur in spring (Dunn, 1983; Dunn; 1984, Stednick *et al.*, 1987), however, this research has previously been undertaken in cold to temperate climates rather than the semi-arid to arid setting of this study. Equivalent studies from semi-arid to arid terrains are more limited. To date, the general understanding is that in semi-arid and arid regions, such as inland 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:

- winter most species are dormant;
- spring reproduction has begun;
- summer summer rains give rise to peak reproduction activity; and,
- autumn peak biomass.

Initiation of flower bud production (spring) and an increase in bud, fruit and leaf production (summer), corresponds with increasing temperature, daylight lengths and available rainfall, which will enhance plant growth and many of the reproductive processes. Theoretically these factors will contribute to an increase in evapotranspiration rates, resulting in greater movement of elements through the xylem and then allocation to specific sites for their physiological role and the increase in cellular activity during the peak period of reproduction (Garland, 1981).

Abundant fruit, buds and leaf production in autumn and, minor fruit, bud and leaf production in winter, characterises these periods. These periods also coincide with reduced temperatures, reduced rainfall and shorter length of daylight, which will have an impact on plant growth and many of the reproductive processes.

In order to investigate the uptake and distribution of elements by the *E. camaldulensis*, an investigation into the seasonal variation in element composition of the *E. camaldulensis*

leaves was undertaken. Six orientation sites across the Curnamona Province and adjacent regions (Yunta, Bindarrah, Teilta, Tibooburra, Williams Creek and Flying Doctor) were studied (Hulme & Hill, 2003). Repeated sampling of *E. camaldulensis* leaves was conducted on a seasonal basis at these sites (autumn, winter, spring, and summer) for 2003 and 2004 (Hulme & Hill, 2004).

Through recognising the physiological role that the essential elements play in plant growth, there is also the potential to define periods corresponding to biogeochemical changes that are associated with either maximum or minimal growth development.

3.6 ELEMENTAL VARIABILITY

The importance of understanding the influence of climatic seasons on the essential element concentration in the *E. camaldulensis* is that it corresponds with periods of plant growth and development, conversely it also delineates periods of minimal changes, or stability, in elemental concentrations. 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 refers to the amount of fluctuation that an element may experience over a season. Examination of the elemental concentration of *E. camaldulensis* leaves enables the definition of the degree of variability as described by Markert & Weckert (1989). The degree of variability was estimated by: $\max_{(conc)} - \min_{(conc)} = X$; $X/\max_{(conc)}(x) 100 = \%$.

3.7 CELLULAR HEAVY METAL PARTITIONING

Metal ions taken up by the roots are then translocated to aerial organs via the transpiration stream (Briat & Lebrun, 1998). Once inside the plant cell, metals ions that have not been used for particular metabolic requirements need to be stored in isolated parts of the plant. The main strategies used for plants to tolerate toxic effects of excess metal ion accumulation include (Hanna & Grant, 1962; Memon *et al.*, 2001):

- binding of the metal ion to the negatively charged cell walls, which prevents entry into the cytoplasm;
- chelation including organic acids; and,
- compartmentation in vesicles (vacuoles), which prevents the metal ion interfering with metabolic functions.

To date no studies have been conducted on compartmentation of metal ions in *E. camaldulensis* leaves. In order to investigate the compartmentation of metal ions in *E. camaldulensis* leaves, samples were collected from three compass bearings around a *E. camaldulensis* tree near the Barrier Pinnacles mine. For the most part, the concentrations of metals in this tree are extremely high. Table 3.2 outlines concentration values recorded from this tree by XRF and ICP-MS analysis at Geoscience Australia (GA), Canberra.

Table 3.2: Outline the variations of metal concentrations within *E. camaldulensis* in leaves adjacent to the Pinnacles mine.

Organs	Pb (ppm)	As (ppm)	Cd (ppm)	Ag (ppm)	Zn (ppm)
Leaves N/E (hostrock)	412	4.50	2	BDL	283
Leaves S (contact)	433	5.42	2.2	BDL	317
Leaves S/W (ore zone)	460	5.03	2.9	0.6	396

3.8 YUNTA: WINNININNIE CREEK (SETTING)

Winnininnie Creek is about 10 km northeast of Yunta, in central eastern South Australia, approximately 337 km north of Adelaide. The *E. camaldulensis* tree sampled here is 200 m north of the Barrier Highway, on the Olary 1:250 000 topographic map (SI54-02), WGS84 reference 373462 mE; 6398388 mN.

The area experiences a semi-arid to arid climate, with an average annual rainfall of 236 mm, predominately falling in the summer. Temperatures range from an average summer maximum of 31.9° C to an average winter minimum of 3.5° C (Bureau of Meteorology, 2005a). The study site lies within the eastern pastoral province of South Australia, (Laut *et al.*, 1977).

The landscape immediately surrounding the *E. camaldulensis* consists of erosional rises with a low topographic relief of 0-9 m (Figure 3.2). To the north, the landscape has a higher topographic relief exceeding 300 m. The most elevated parts of this area are between 500 m and 700 m above sea level, within the Tatawuppa Hills in the west, Altandee Hills in the northeast, and Oulnina Hills in the southeast. Elevation generally decreases towards the low-lying alluvial plains in the south, which are approximately 260 m above sea level.



Figure 3.2: An image of the E. camaldulensis at Winnininnie Creek (Yunta), and the surrounding low-relief regolith dominated landscape.

Drainage across the study area occurs within ephemeral drainage depressions and outwash that ultimately flows towards alluvial overbank plains of the Murray Basin in the south.

The vegetation communities and dominant species are closely associated with the major landforms. The main vegetation community types in the area as described by Laut *et al.* (1977) are:

• open chenopod shrubland dominated by *Maireana sedifolia* and *Atriplex vesicaria* and tall shrubland subdominated by *Acacia – Eremophila – Dodonaea – Cassia*, and *Acacia aneura*. This shrubland typically colonises weathered bedrock on erosional rises and hills;

- open chenopod shrubland dominated by *Maireana sedifolia* and *Atriplex vesicaria* and low open woodland with minor *Casuarina cristata* and *Myoporum playtcarpum*. This community typically colonises colluvial and alluvial depositional plains; and,
- riparian woodlands dominated by *E. camaldulensis*, typically colonising low-lying landscape settings, such as major drainage channels and alluvial outwash plains.

3.8.1 Geology

Winnininnie Creek is on the Olary 1:250 000 geological mapsheet (SI 54-2) (Forbes, 1991). It is within the Adelaide Geosyncline, which includes a thick sequence of Neoproterozoic to Cambrian sedimentary rocks and volcanics, overlying Palaeoproterozoic to Mesoproterozoic basement (Preiss, 1983).

3.8.2 Mineralisation (Winnininnie)

Gold and base metal mineral exploration has been undertaken in the Adelaidean metasediments of the adjacent Nackara Arc, (McCallum, 1997). During the 1980s and mid-1990s Australian Anglo American, Mintech Resources PTY LTD and Equinox Resources NL held mineral exploration leases within the Winnininnie area, searching for stratabound Au, and structurally controlled base metal mineralisation in Adelaidean metasediments (McCallum, 1997). Table 3.3 shows that for the most part, previous exploration surveys returned disappointing or inconclusive results. The area is generally within an encouraging geological setting and some geophysical and drilling targets have been identified, but it has been difficult to thoroughly test these because of the extensive transported regolith.

Mineral Deposit	Company	Exploration Lease	Year	Method	Mineralisation Target	Results
Winnininnie Barite deposit	Australian Anglo American	EL 1302	1985	Stream Sediments and bedrock/rock chip sampling	Au mineralisation	No significant results returned
Teetulpa Goldfield	Mintech Resources PTY LTD	EL 1226	1996	Mapping, stream sampling, reprocessing aeromagnetics, ground magnetics and drilling	Stratiform & stratabound Au	Disappointing Au and basemetal values
Mannahill	Equinox Resources NL	El 1164	1995	Aeromagnetic and radiometric surveys, chip & soil sampling	Au and Zn-Pb-Ag mineralisation	Assay values for Zn, Au and Ag were low, with surficial deposits obscuring bedrock

Table 3.3: Summarises mineral exploration surveys undertaken across the Winnininnie area over the last 28 years, and outlines some known prospects from the area.

Known Prospects	Commodity	Province	Description
Old trick mine	Au, Bi and	Adelaide	E/W quartz gossan reef carries Au
	Pb	Geosyncline	
Ella Jones mine	Au	Adelaide	Gold from quartz vein, quartz and Fe gossan lodes
		Geosyncline	
Elsie May reef mine	Au, Ag, Bi	Adelaide	Quartz vein carries Au, and one small vein of galena
-	and Pb	Geosyncline	

3.9 WINNININIE CREEK EUCALYPTUS CAMALDULENSIS CHARACTERISTICS

The Winnininnie Creek *E. camaldulensis* is a gnarled tree with a girth of 5.20 m and a spreading open canopy that extends from ground level up to approximately 36 m. The bark is generally smooth, except near the base where it is rough with shedding patches. Twigs are red-brown, ranging between 2-5 mm in diameter. Buds are stalked and have a strongly beaked conical shape and are typically in clusters of 5-7. Leaves are alternating, pendulous and narrowly lanceolate approximately 12-15 cm long and 1- 1.5 cm wide, and pale green on both the adaxial and abaxial surface. The tree is part of a *E. camaldulensis* woodland corridor along the main drainage channel. Figure 3.3 illustrates the location of this *E. camaldulensis* and its position relative to adjacent *E. camaldulensis* trees (plan view), and a profile view of the channel, which is approximately 32.50 m wide and incised up to 1.55 m on the northeast and 1.60 m on the southwest bank.



Figure 3.3: A cartoon illustrating the location of the Winnininnie Creek (Yunta) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* (plan view) and a profile view of the channel.

The ephemeral channel hosting the *E. camaldulensis* has an approximate length of 38 km, flowing from north to south. The channel incises bedrock units, that elsewhere in the Olary region host Cu-Au, Ag, Bi and Pb mineralisation and the Winnininnie Dome barite deposit.

3.9.1 Organ Tissue Biogeochemistry Results

Sampling of leaves, twigs, buds and bark was undertaken during autumn 2003 at the Winnininnie Creek study site. Four samples per medium (leaves and twigs) and single composite samples of buds and bark were collected from the accessible N, NE, E and SW sectors around the *E. camaldulensis* canopy. Fifty-two elements were assayed by a combination of INAA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. In general, Sb, Ce, Cs, Cr, Eu, Ir, Lu, Mo, Rb, Se, Ag, Ta, Te, Th, W, U, Zr, Be, Bi, Cd, Ga, In, Nb, Pb, Ti and V were below analytical detection limits for all sampling media. The chemical compositions of twenty-two elements were detectable from the *E. camaldulensis* organ tissues sampled, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.4. All elements with > 25 % of their values below detection limits have been removed from the data set.

Table 3.4: Variations	s of metal concentrations wit	nin different oven dried tissue	s of an individual E. came	aldulensis, winnininnie Creek					
(Yunta). Initial value	represents the mean; values i	n brackets () are the range of v	alues; C= composite sampl	e and * signifies values below					
analytical detection limit. To calculate the means, below detection limit values were taken as half the lower analytical detection limit value.									
Values with a mean b	ut no range represent only one	sample in that data set. n= the	number of samples recovered	ed for each organ.					
Flomont (nnm)	$I_{0} = 0$	Twigs $(n-4)$	Bude (C)	Dork (n-1)					
Liement (ppm)		1 wigs (II-4)	Duus (C)	Dark(II-1)					
Na	1117 (910-1370)	562 (530-610)	1120	250					

Na	1117 (910-1370)	562 (530-610)	1120	250
Mg	2129 (1895-2237)	975 (565-1405)	421	1678
Al	53 (44-77)	45 (39-54)	35	*
Р	859 (781-951)	1769 (1123-2412)	1536	89
S	870 (788-1004)	363 (336-385)	886	152
K	8715 (7200-10300)	7745 (7320-8730)	13000	2850
Ca	11025 (9500-12700)	22675 (18700-24800)	8700	71000
Sc	0.02 (0.016-0.023)	0.016 (0.013-0.017)	0.009	*
Mn	56 (49-69)	74 (64-93)	41	17
Fe	50 (*-80)	37 (*-50)	*	*
Co	0.17 (*-0.24)	*	*	*
Ni	2.8 (2-4)	7.3 (3-13)	2	2
Cu	6.5 (6-7)	18.3 (13-21)	7	1
Zn	19.8 (16-27)	25.8 (22-31)	16	7
As	0.07 (*-0.084)	*	*	*
Br	8.2 (6.63-9.54)	2.7 (2.23-3.26)	8.5	2.5
Sr	50.2 (41.98-57.96)	122.8 (97.22-147.97)	49.27	427.09
Sn	0.16 (*-0.20)	0.23 (0.20-0.30)	*	*
Ba	28.3 (22.9-38.8)	24.4 (20.9-31)	27.1	38.3
La	0.054 (0.047-0.059)	0.039 (0.029-0.049)	0.019	0.015
Nd	0.03 (0.02-0.04)	0.033 (0.02-0.04)	0.02	*
Sm	0.019 (0.017-0.022)	0.020 (0.018-0.022)	0.021	*

Of the twenty-two detectable elements, Na, Mg, Al, Sc, Fe, Co, As and La had their greatest concentrations within the leaves. Concentrations of P, Mn, Ni, Cu, Zn, Sn, and Nd were highest within the twigs. Concentrations of S, K, Br and Sm were greatest in the buds. The elements, Ca, Sr and Ba were highest in the bark.

3.9.2 Comparison between element concentrations in *Eucalyptus camaldulensis* and

adjacent stream sediments

Fifty-three elements were assayed (Appendix C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Cd, In, Se, Te and Au were below analytical detection limit in one or more sectors for both size fractions. The chemical compositions of twenty-two elements were detectable for both *E. camaldulensis* leaves and twigs, while Co and As were only detectable within the leaves. For all media the elements Al, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm were detectable. Table 3.5 shows which sectors have the maximum and minimum trace element concentrations for *E. camaldulensis* leaves, twigs and adjacent stream sediments for the size fractions <75 μ m and 75-300 μ m.

Table 3.5: Shows which sector for E. camaldulensis leaves and twigs and adjacent stream sediments size fractions <75 µm and 75-	300 µm
have the maximum and minimum trace element concentrations. BDL = below detection limit.	

Element	Leaves	Leaves	Twigs	Twigs	Stream	Stream	Stream	Stream	
(DL)	Maximum	Minimum	Maximum	Minimum	sediments	sediments	sediments	sediments	
(ppm)	conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ	Maximum	Minimum	Maximum	Minimum	
					conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ	
	(ppm)	(ppm)	(ppm)						
				(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	
					<75 μm	<75 μm	75-300 μm	75-300 μm	
N. (100)	GWL (1050)			NF (720)	fraction	fraction	fraction	fraction	
Na (100)	SW (1370)	NE (910)	N (610)	NE (530)	NE (5300)	SW (4900)	E (4500)	NE (4050)	
Mg (20)	SW (2237)	NE (1895)	E (1405)	N (565)	SW (11600)	E (9450)	E (7400)	NE (6200)	
Al (20)	E (77)	SW (47)	E (54)	NE (39)	N (75800)	E (64200)	E (51600)	NE (44700)	
P (20)	SW (951)	NE (781)	N (2412)	SW (1123)	SW (500)	E (400)	NE & E (350)	SW (290)	
S (10)	E (1004)	N (788)	SW (385)	NE (336)	N, E & SW	NE (150)	E (150)	N, NE & SW	
					(200)			(100)	
K (1000)	SW (10300)	NE (7200)	N (8730)	NE (7180)	SW (22800)	E (17300)	E (13900)	NE (12300)	
Ca (5000)	NE (12700)	SW (9500)	SW (24800)	N (18700)	N (23700)	NE (18400)	SW (20200)	NE (14300)	
Sc (0.05)	E (0.023)	N (0.016)	NE (0.017)	N (0.013)	Not in assay	Not in assay	Not in assay	Not in assay	
					suite	suite	suite	suite	
Mn (1)	SW (69)	N (49)	SW (93)	N (64)	N & SW	NE & E	NE (900)	E & SW	
					(600)	(500)		(650)	
Fe (50)	E (80)	BDL	N & NW (50)	BDL	SW (45900)	E (36800)	NE (73700)	SW (32900)	
Co (0.24)	E (0.24)	BDL	BDL	BDL	SW (19)	E (16)	NE (47)	SW (18)	
Ni (1)	E (4)	NE & SW (2)	E (13)	N & SW (3)	N (33)	E (29)	NE (72)	SW (34)	
Cu (1)	E & SW (7)	N & NE (6)	N (21)	SW (13)	SW (45)	N & NE (37)	NE (40)	E (25)	
Zn (1)	E (27)	SW (16)	E (31)	N & SW (22)	NE (115)	E (80)	NE (94)	SW (68)	
As (0.05)	E (0.084)	BDL	BDL	BDL	N, E & SW	NE (9)	NE (46)	SW (15)	
					(10)				
Br (0.2)	SW (9.54)	NE (6.63)	E (3.26)	N (2.23)	Not in assay	Not in assay	Not in assay	Not in assay	
					suite	suite	suite	suite	
Sr (0.05)	N (57.96)	E (41.98)	SW (147.97)	NE (97.22)	N (130)	N & NE	E (88)	NE (72)	
						(120)			
Sn (0.1)	E & SW (0.20)	NE (BDL)	N (0.30)	NE, E & SW	N & SW (4)	E (3)	E (2.3)	NE (2.1)	
				(0.20)					
Ba (10)	NE (38.8)	SW (22.9)	SW (31)	E (20.9)	SW (430)	E (350)	NE (340)	SW (310)	
La (0.2)	E (0.059)	N (0.047)	NE (0.049)	N (0.029)	NE (52)	SW (40)	NE (46)	SW (29)	
Nd (0.01)	E (0.04)	SW (0.02)	E & SW (0.04)	N (0.02)	NE (43)	SW (34)	NE (41)	SW (26)	
Sm (0.01)	E (0.022)	NE (0.017)	NE (0.022)	SW (0.018)	NE (10)	SW (8)	NE (9)	SW (6)	

In general there does not appear to be a direct link between maximum/minimum vegetation element concentrations and maximum/minimum stream sediment element concentrations within the same sector. There may however be a connection between maximum concentrations in leaves and twigs in the E sector for Al, Nd, Ni and Zn. Of the twenty-two detectable elements, the E sector leaves, N, E and SW sector twigs; SW sector <75 μ m stream sediment; and, NE sector 75-300 μ m stream sediment had the most elements with the highest concentrations. With the NE sector leaves, N sector twigs; E sector <75 μ m; and, SW sector 75-300 μ m stream sediments with the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum concentrations: N (Sr), NE (Ba and Ca), E (Al, As, Co, Cu, Fe, La, Nd, Ni, S, Sc, Sm, Sn and Zn) and SW (Br, Cu, K, Mg, Mn, Na, P and Sn);
- leaves minimum concentrations: N (Cu, La, Mn and S), NE (Br, Cu, K, Mg, Na, Ni, P, Sc and Sn), E (Sm and Sr) and SW (Al, Ba, Ca, Nd, Ni and Zn);
- twigs maximum concentrations: N (Cu, Fe, K, Na, P and Sn), NE (Fe, La, Sc and Sm), E (Al, Br, Mg, Nd, Ni and Zn) and SW (Ba, Ca, Mn, Nd, S and Sr);
- twigs minimum concentrations: N (Br, Ca, La, Mg, Mn, Nd, Ni, Sc and Zn), NE (Al, K, Na, S, Sn and Sr), E (Ba and Sn) and SW (Cu, Ni, P, Sm, Sn and Zn);

- <75 μm fraction maximum concentrations: N (Al, As, Ca, Mn, Ni, S, Sn and Sr), NE (La, Na, Nd, Sm and Zn), E (As and Sr) and SW (As, Ba, Co, Cu, Fe, K, Mg, Mn, P, S and Sn);
- <75 μm fraction minimum concentrations: N (Cu and Sr), NE (As, Ca, Cu, Mn, S and Sr), E (Al, Ba, Co, Fe, K, Mg, Mn, Ni, Sn and Zn) and SW (La, Na, Nd and Sm);
- 75-300 µm fraction maximum concentrations: NE (As, Ba, Co, Cu, Fe, La, Mn, Nd, Ni, P, Sm and Zn), E (Al, K, Mg, Na, P, S, Sn and Sr) and SW (Ca); and,
- 75-300 μm fraction minimum concentrations: N (S), NE (Al, Ca, K, Mg, Na, S, Sn and Sr), E (Cu and Mn) and SW (As, Ba, Co, Fe, La, Mn, Nd, Ni, P, S, Sm and Zn).

For the rare earth elements, the maximum and minimum concentrations for both size fractions of the stream sediments and the maximum concentrations for the leaves are from the same sector, with maximum and minimum concentrations for several of the other elements for all media in more than one sector (Table 3.5). A number of the elements analysed for all media have elemental associations due to their similar chemical properties and occupy several sampling sectors, such as (Ba, Ca, Mg and Sr), (Fe, Co and Ni), (Ce, La, Sm and Nd), (Sc and La), and (K and Na).

3.9.3 Elemental Trends

Due to the small data set (n = 4), scatter diagrams (Figure 3.4) were constructed to determine whether or not any of the following detectable elements Al, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm within all media (leaves, twigs, 75 μ m and 300 μ m size fractions) revealed relationships approaching a linear trend. The results show that only a small group of elements have relationships possibly approaching linear trends. The following elements and their media: Na-leaves, Cu-twigs and Al-leaves within the <75 μ m size fraction and Ca-leaves and Cu-leaves within the 75-300 μ m size fraction revealed a trend approaching a negative relationship. In contrast, the S content in leaves and the 75-300 μ m size fraction of the stream sediments had a trend approaching a positive relationship. The overall negative trend possibly implies that as the elements become available within the pore/soil water the *E*. *camaldulensis* may be preferentially excluding them, or that other factors may be involved.



Figure 3.4: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and $75-300 \mu m$ at Winnininnie Creek (Yunta).

The stream sediment trace element concentrations revealed that the <75 μ m size fraction has higher concentrations of Al, K, Ca, Mg, Na, Ti, P, Ba, S, Sr, V, Rb, Ce, Cr, La, Nd, Y, Ga, Th, Pr, Nb, Sm, Cs, Gd, Dy, Sn, Tb, Er, U, Eu, W, Se, Ho. Tb, TI, Tm, Ag, Lu and In than the 75-300 μ m size fraction. The 75-300 μ m size fractions had higher concentrations of Fe, Mn, Zn, Cu, Ni, Co, Pb, As, Mo, Sb, Bi, Cd and Au (Figure 3.5).



Figure 3.5: Variations of metal concentrations within $<75 \ \mu m$ and $75-300 \ \mu m$ stream sediments size fractions surrounding the *E. camaldulensis*, Winnininnie Creek (Yunta). Straight line is 1:1. To calculate the means, below detection limit values were taken as half the detection limit value.



Figure 3.6: The elemental composition and index accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking $<75\mu$ m and $75-300\mu$ m stream sediments at Winnininnie Creek (Yunta). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The comparison of the elemental composition of the Winnininnie Creek *E. camaldulensis* leaves and twigs (Figure 3.6) shows that leaves have a higher concentration of K, Mg, Na, S, Al, Ba, Fe, and La, whereas twigs have greater concentrations of Ca, P, Mn, Sr, Zn, Cu, Ni, Nb, Nd and Sm. The elements Co and As are only detected within the leaves, which may reflect a preferential allocation of these elements within the *E. camaldulensis* organs.

In general there is a decrease in element concentration from elements classified as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.6) illustrates that for both size fractions (<75 μ m and 75-300 μ m), some elements are more bioavailable and readily taken up by *E. camaldulensis* than others. The following summarises the index of bioaccumulation from both size fractions (<75 μ m and 75-300 μ m) for leaves and twigs:

- <75 μm size fraction (twigs): S, P, Sr and Ca (high), K, Mg, Na, Zn, Cu, Mn and Ni (Medium), Ba (slight), and Nb, Sm, La and Al (low);
- <75 μm size fraction (leaves): S and P (high), K, Sr, Ca, Mg, Na, Zn and Cu (medium), Ba, Mn and Ni (slight), Nb, Sm, La and Al (low) and Nd, Co, As and Fe (very-low);
- 75-300 µm size fraction (twigs): S, P, Ca and Sr (high), K, Na, Zn, Cu, Mn and Ni (medium), Ba (slight), Nb and Sm (low) and Nd and Al (very-low), and,
- 75-300 µm size fraction (leaves): S and P (high), Ca, K, Sr, Na, Zn, Mg and Cu (medium), Mn, Ni and Ba (slight), Nb, Sm, La and Co (low) and As, Nd, Al and Fe (very-low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements. These results are consistent with similar relationship found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.10 WINNINNINIE CREEK TEMPORAL ELEMENT VARIATIONS WITHIN EUCALYPTUS CAMALDULENSIS

In general, Ba, Br, Ca, La, K, Sm, Na, Zn, Al, Cu, Mg, Mn, Nd, P, S and Sr are detectable in the leaves across all seasons for 2003 and 2004. Elements Fe, Sc and Ni recorded below analytical detection limit concentrations for either one or more seasons. All of the above elements, with the exception of Ba, Br, La, Sm, Na, Nd, Sc and Sr, are considered to be essential, although there have been some suggestions that Na (e.g. in C-4 generation of PEP step) could be "beneficial" to plants (Kabata-Pendias & Pendias, 1991; Marschner, 1986) likewise with Al, which can help control colloidal cell properties in plants (Dunn, 2007). Table 3.6 and Figure 3.7 - Figure 3.11 present the rainfall and the temporal fluctuations in element concentrations for *E. camaldulensis* leaves at Winnininnie Creek for all seasons for 2003 and 2004.

Table 3.6: Elemental composition of *E. camaldulensis* (leaves) sampled across all seasons for 2003 and 2004. High values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded for that year e.g. 2003 (Ba – 18 ppm; winter), while yellow represents the season in which the highest concentration was recorded for that year e.g. 2004 (Na – 1800 ppm; summer). BDL denotes (below detection limit).

Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
Ba ppm	28	18	27	34	33	30	50	47
Br ppm	8	9	9	10	10	9	10	11
Ca ppm	11025	9120	11100	13000	13000	13000	13000	16000
Fe ppm	50	BDL	BDL	73	78	72	BDL	110
La ppm	0.054	0.036	0.045	0.044	0.04	0.028	0.10	0.10
K ppm	8715	8770	8340	6430	9580	8080	6000	6000
Sm ppm	0.019	0.014	0.014	0.016	0.02	0.019	BDL	BDL
Sc ppm	0.020	0.013	0.013	0.020	0.023	0.021	BDL	BDL
Na ppm	1117	1130	1080	1330	1390	1460	1700	1800
Zn ppm	20	11	16	22	21	22	16	16
Al ppm	54	35	43	91	47	43	82	86
Cu ppm	7	5	6	10	5	4	6	6
Mg ppm	2129	2193	2351	2319	2295	2741	2311	2340
Mn ppm	56	74	78	97	82	104	124	131
Nd ppm	0.03	0.03	0.02	0.04	0.05	0.04	0.06	0.06
Ni ppm	3	2	1	5	2	1	BDL	2
P ppm	859	955	1139	936	691	617	694	714
S ppm	871	998	1122	982	781	942	1120	994
Sr ppm	50	66	57	62	67	77	79	81

The physical appearance of the *E. camaldulensis* sampled across 2003 and 2004, was:

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

The results outlined here show trends of groups of elements displaying similar behaviour.

Group A Elements (Periods of growth): more abundant during periods of growth. Spring and summer, are characterised by temperatures with an average maximum of 28.7°C and minimum of 12.2°C in 2003, and an average maximum of 28.4°C and minimum of 12.3°C in 2004. The average rainfall for these periods is 18.5 mm in 2003 and 13 mm in 2004. From September to February (spring and summer) 2003, Ba, Br, Ca, Fe, Sm, Sc, Na, Zn, Al, Cu, Mn, Nd, Ni and Sr, and for the same period in 2004 Br, Ca, Fe, Na, Al, Mg, Mn, Ni, P and Sr showed a gradual increase in concentration, recording their highest concentrations in the summer. In contrast, during the summer of 2003, La, K, Mg, P and S and for the same period in 2004 Ba and S had a decrease in concentrations.

Group B Elements (Periods of non-growth): reduced concentration levels during periods of non-growth. Autumn and winter are characterised by temperatures with an average maximum of 19.1°C and minimum of 5.3°C in 2003, and an average maximum of 19.9°C and minimum of 5.9°C in 2004. The average rainfall for these periods was 11.7 mm in 2003 and 8.6 mm in 2004. From March to August (autumn to winter) 2003 Ba, Ca, Fe, La, Sm, Sc, Zn, Al and Cu and for the same period in 2004 Ba, Br, Fe, La, Al, Cu, Nd and P showed a gradual decrease in abundance, and recorded their lowest concentrations in the winter.

During June 2003 and 2004 S, Mg, Mn and Na results showed a slight increase in concentrations two months after a period of significantly reduced rainfall in March. In contrast, Ni, La, Cu, Sc, Ba, Fe, Sm and Al all had a decrease in concentration for the same period.



Figure 3.7: Rainfall and the temporal fluctuations in Ba, Br, Ca and Fe for *E. camaldulensis* (leaves) at Winnininnie Creek (Yunta). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.8: Rainfall and the temporal fluctuations La, K, Sm and Sc for *E. camaldulensis* (leaves) at Winnininnie Creek (Yunta). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.9: Rainfall and the temporal fluctuations in Zn, Al, Cu and Mg for *E. camaldulensis* (leaves) at Winnininnie Creek (Yunta). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.10: Rainfall and the temporal fluctuations in Mn, Nd, Ni and P for *E. camaldulensis* (leaves) at Winnininnie Creek (Yunta). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.11: Rainfall and the temporal fluctuations in S and Sr for *E. camaldulensis* (leaves) at Winnininnie Creek (Yunta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)

3.10.1 Winnininnie Creek Eucalyptus camaldulensis Elemental Variability

The results in (Table 3.7) show the degree of element variability during periods of plant growth and reduced plant growth for the Winnininnie Creek *E. camaldulensis* during the 2003 and 2004 seasons.

defines the opt	imal sa	.mpliı	ng perio	od tha	t shou	ld be ı	utilised	for selec	ted ele	ments	s. BDL	denot	tes belc	w de	tection	limit.				
Parameters	N,	No se varia	asonal Ibility	l	v	Slight ariab	t seaso ility <:	nal 30%	L var	ow s iabili	easona ty ~ 3(d 0%	II sease	ntern onal y	nediat variat	te oility	H var	ligh s 'iabili	easona ty > 80	ıl D%
			•	<u>.</u>	•			00.4			•	<u>.</u>		~ >	0%				-	
Years	200)3	20	04	20	03	2	004	20	03	200	04	200)3	20	04	20	03	200)4
	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
Ba						*	*	*	*											
Br					*	*	*	*												
Ca			*		*	*		*												
Fe							*						*	*		*				
La				*		*			*		*									
Κ				*	*	*	*													
Sm					*	*	*	BDL												
Sc							*	BDL	*	*										
Na					*	*	*	*												
Zn				*		*	*		*											
Al							*	*	*					*						
Cu				*	*		*			*										
Mg					*	*	*	*												
Mn					*	*	*	*												
Nd	*			*			*							*						
Ni					*										*			*		*
P					*	*	*	*												
S					*	*	*	*												
Sr					*	*	*	*												

Table 3.7: Shows the degree of elemental variation for the *E. canaldulensis* studied at Winnininnie Creek (Yunta) between (2003 and 2004) periods of plant growth (G) shown by a green asterisk (*) and periods of reduced plant growth (RG) shown by a black asterisk (*), and defines the optimal sampling period that should be utilized for selected elements. BDL denotes below detection limit

The degree of variability across 2003 and 2004 is mostly slight (< 30%) for Ba, Br, Ca, K, Sm, Na, Zn, Cu, Mg, Mn, P, S and Sr; slight to low (< 30% - ~ 30%) for La and Sc; intermediate (~ 50%) for Fe; and, high (> 80%) for Ni. The slight to intermediate variations suggest that seasonal variations are less important for many of the elements, with the exception of Ni. This suggests that the most appropriate sampling period for typically expressing higher element contents is autumn.

3.11 BINDARRAH: CUTANA CREEK (SETTING)

Cutana Creek is approximately 35 km northeast of Olary, in central eastern South Australia, about 450 km north of Adelaide. The *E. camaldulensis*, sampled here is 300 m north of the Barrier Highway and on the Olary 1:250 000 topographic map (SI54-02), grid reference 468729 E; 6442323 N mN.

The area experiences a semi-arid to arid climate, with an average annual rainfall of 236 mm, mostly falling in the summer. Temperatures range from an average summer maximum of 31.9° C to an average winter minimum of 3.5° C (Bureau of Meteorology, 2005b). The study site lies within the eastern pastoral province of South Australia, which extends from the Lake Frome plain in the north to the Murray River in the south (Laut *et al.*, 1977).

The landscape immediately surrounding the sampled *E. camaldulensis* consists of alluvial and colluvial depositional plains with a low topographic relief of 0-9 m (Figure 3.12). The most elevated parts of the area are between 300 and 400 m above sea level within the MacDonald Hills in the west and the Nilpena Hills in the south. Elevation generally decreases towards the low-lying plains in the north-northwest, associated with the Lake Frome plain, which is approximately 12 m above sea level and part of a large internal drainage basin. The Lake Frome plain is an extensive dissected alluvial plain, partly overlain by sheetflow sand sheets and aeolian dunes. In the north-northeast are linear southwest-northeast trending dunes, with minor alluvial swamps, and lakes, associated with the Strzelecki Desert. The landscape of the immediate area mostly includes undulating rises in the west and south associated with the MacDonald Hills and Nilpena Hills, flanked by gently sloping erosional rises that extend into broad alluvial plains to the northwest and northeast.



Figure 3.12: An image of the E. camaldulensis at Cutana Creek (Bindarrah), and the surrounding low-lying regolith dominated landscape.

Drainage across the study area occurs within contemporary ephemeral drainage depressions and areas of outwash that ultimately flow towards alluvial overbank plains in the northnorthwest, and finally towards the Lake Frome plain. The vegetation communities and dominant species are closely associated with the major landform settings for this region. The main vegetation community types in the area as described by Laut *et al.* (1977) are:

- tall open shrubland dominated by *Acacia aneura A. brachystachya*. This community typically occurs on weathered bedrock on erosional rises and hills;
- open chenopod shrubland dominated by *Maireana sedifolia* and *Atriplex vesicaria* and tall shrubland sub-dominated by *Casuarina cristata*, *Acacia aneura A. brachystachya*. This community typically occurs on colluvial and alluvial depositional plains; and,
- riparian woodlands dominated by *E. camaldulensis* and open shrublands co-dominated by *Maireana sedifolia* and *Nitraria schoberi*.

3.11.1 Geology

Cutana Creek is within the Olary 1:250 000 geological map sheet (SI 54-2), which includes sections of the Willyama Inliers, Adelaide Geosyncline, and the northern margin of the Murray Basin and the southern margin of the Lake Eyre Basin (Forbes, 1991). The Willyama Supergroup in this area has been subdivided into two groups, the Curnamona Group and the Strathearn Group (Robertson, 2003). The study area is on the southwestern margin of the Kilabity Inlier, which is the largest of the Willyama Supergroup Inliers within the Olary Domain. The Willyama Supergroup inliers consist of Palaeoproterozoic-Mesoproterozoic metasediments and Mesoproterozoic granitoid/pegmatoid intrusives (Forbes, 1989; Robertson, 2003), which are extensively obscured by a Neoproterozoic to Recent sedimentary cover.

3.11.2 Mineralisation (Cutana)

The region proximal to Cutana Creek has hosted extensive periods of intermittent exploration. The largest operational mine in the region was at Radium Hill. The uranium-rich mineral, davidite was recognised and reported by the prospector, A.J. Smith, in 1906 (Sprigg, 1954). Extensive mining of the Radium Hill uranium deposit took place during 1944-1952, largely encouraged by its importance for military and industrial purposes (King & Campana, 1958). The following, Table 3.8, highlights that previous exploration surveys returned inconclusive results from the area surrounding this tree. The Cutana area however is within a generally prospective geological setting for mineral exploration. Some geophysical and drilling targets have been identified, but it has been difficult to fully test these because of the extensive transported regolith cover.

Table 3.8: Summarises the mineral exploration surveys undertaken across the Cutana region and the exploration methods that were employed (Lopes, 1970; Hatton, 2006).

Mineral Deposit	Company	Exploration	Year	Method	Mineralisation	Results
		Lease			Target	
Luxemburg	Austral	EL 1302	1969-1970	Induced	Cu-Au	No significant
Mine	Exploration Services Pty Ltd			polarization & magnetometer, Drilling	mineralisation	results returned
Wilkins Prospect	M.I.M Exploration Pty Ltd	EL 1976/2635	1995-2001	Mapping, sampling, reprocessing	Cu-Au mineralisation	Disappointing Au and basemetal values

Mineral Deposit	Company	Exploration Lease	Year	Method	Mineralisation Target	Results
				aeromagnetics, ground magnetics and drilling		
Cutana Copper Mine	M.I.M Exploration Pty Ltd	EL 1976/2635	1995-2001	Aeromagnetic and radiometric surveys, chip and soil sampling	Cu-Au mineralisation	Trace copper and gold
Green & Gold Mine	M.I.M Exploration Pty Ltd	EL 1976/2635	1995-2001	Aeromagnetic and radiometric surveys, chip and soil sampling	Cu-Au mineralisation	Shallow percussion drilling did not intersect sulphides

3.12 CUTANA CREEK EUCALYPTUS CAMALDULENSIS CHARACTERISTICS

The Cutana Creek *E. camaldulensis* is a gnarled tree with a girth of 7.70 m and a spreading open canopy that extends from ground level up to approximately 40 m. The bark is generally smooth, except near the base where it is rough with large shedding strips. Twigs are redbrown, ranging between 2-5 mm in diameter. Buds are stalked and have a strongly beaked conical shape and are mostly in clusters of 5-7. Leaves are alternating, pendulous and narrowly lanceolate approximately 11-15 cm long and 1.5-2 cm wide, pale green on both the adaxial and abaxial surface. The tree is one of many *E. camaldulensis* that from a woodland corridor along the main drainage channel. Figure 3.13 illustrates the location of the *E. camaldulensis* and its position (468729 mE; 6442323 mN) in relation to adjacent *E. camaldulensis* trees (plan view) and profile view of the channel. The channel is approximately 135.30 m wide and is incised up to 0.81 cm on the southeast and 0.30 cm on the northwest.



Figure 3.13: A cartoon illustrating the location of the Cutana Creek (Bindarrah) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* (plan view) and a profile view of the channel.

The ephemeral channel (Cutana Creek) hosting the *E. camaldulensis*, has an approximate length of 29 km, flowing southwest to northeast. The channel incises many different bedrock lithological units across the area, some of which host Cu-Au and Zn-Pb-Ag mineralisation.

3.12.1 Organ Tissue Biogeochemistry Results

Sampling of leaves, twigs, buds and bark was undertaken during autumn 2003 at the Bindarrah study site. Four samples per medium (leaves and twigs), and single composite samples of buds and bark were collected from the reachable N, NE, and E & SW sectors around the *E. camaldulensis* canopy. Fifty-two elements were assayed by a combination of INAA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. The elements Sb, Eu, Ir, Se, Ta, Te, Th, Zr, Be, Bi, Cd, Ga, In, Nb and Pb were below the lower analytical detection limits in all sampling media, while Cs, Cr, Au, Hf, Lu, Mo, Ag, Th, Yb, Ti and V were only detected in roots. The chemical compositions of thirty-two elements were detectable from the *E. camaldulensis* organ tissues, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.9. All elements with > 25 % of their values below analytical detection limits have been removed from the data set.

Table 3.9: Variations of metal concentrations within different oven dried tissues of an individual *E. canaldulensis*, Cutana Creek (Bindarrah). Initial value represents the mean; values in brackets () are the range of values; C= composite sample and * signifies values below detection limit. To calculate the 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

Element (ppm)	Leaves (n=4)	Twigs (n=4)	Buds (C)	Bark (n=1)	Roots (n=1)
Na	2005 (1880-2160)	668 (480-850)	3090	340	540
Mg	2200 (2121-2314)	1197 (1086-1386)	2339	1453	527
Al	102 (60-127)	53 (40-63)	61	30	292
Р	1149 (1095-1198)	1831 (1381-2192)	1949	411	153
S	1029 (901-1158)	398 (331-443)	1428	190	186
K	9705 (8830-10500)	4832 (4520-5200)	11800	2470	1640
Ca	8100 (7500-8300)	24850 (20000-28300)	11900	74500	11200
Sc	0.04 (0.024-0.052)	0.015 (0.008-0.019)	0.026	*	0.147
Ti	*	*	*	*	6
V	*	*	*	*	2
Cr	*	*	*	*	1.21
Mn	115 (62-199)	273 (83-562)	114	131	19
Fe	84 (*-170)	*	*	50	860
Co	*	*	0.63	*	1.21
Ni	3.50 (2-4)	2.6 (2-3)	3	3	2
Cu	8 (7-9)	10 (9-11)	13	2	3
Zn	28.2 (24-37)	32.2 (19-49)	39	15	7
As	0.05 (*-0.11)	0.03 (*-0.06)	*	*	0.054
Br	15.7 (12.10-21)	2.7 (1.97-3.69)	16	2.98	3.53
Sr	58.3 (54-62.45)	181 (169.58-196.49)	51.99	483.92	137.76
Mo	*	*	*	*	1.36
Ag	*	*	*	*	0.51
Sn	0.13 (0.1-0.2)	0.6 (0.20-0.70)	*	0.1	0.2
Cs	*	*	*	*	0.13
Ba	26 (21.5-41.7)	55.9 (40.1-73.1)	32.2	62.8	33.1
Lu	*	*	*	*	0.016
Hf	*	*	*	*	0.147
Au (ppb)	*	*	*	*	0.57
La	0.09 (0.05-0.11)	0.06 (0.04-0.082)	0.032	0.010	1.42
Ce	0.34 (*-0.56)	0.17 (*-0.27)	*	*	3.01
Nd	0.07 (0.04-0.09)	0.043 (0.02-0.05)	0.04	*	0.51
Sm	0.03 (0.024-0.036)	0.025 (0.02-0.03)	0.032	0.015	0.243

The Bindarrah *E. camaldulensis* showed elemental variability between the organs. Of the thirty-two elements assayed Al, Sc, Ti, V, Cr, Fe, Co, Mo, Ag, Cs, Lu, Hf, Au, La, Ce, Nd and Sm had the greatest concentration within the roots. Concentrations of P, Mn, Zn, Sn and Ba were highest within the twigs. Concentrations of Ni, As and Br were greatest in the leaves. Concentrations of Na, Mg, S, K and Cu were highest in the buds followed by Ca and Sr being more abundant in the bark.

3.12.2 Comparison Between Element Concentrations in Eucalyptus camaldulensis and

Adjacent Stream Sediment Chemistry

Fifty-three elements were assayed (Appendix. C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Cd, In, Sb, Te and Au were below analytical detection limit in one or more sectors for both size fractions. The chemical compositions of twenty elements were detectable for both *E. camaldulensis* leaves and twigs, while Fe was only detectable in the leaves and Rb was only detectable in the twigs. For all media, Al, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm were detectable. Table 3.10 shows which sectors for *E. camaldulensis* leaves, twigs and adjacent stream sediments size fractions.

Table 3.10: Shows which sector for *E. canaldulensis* leaves and twigs and adjacent stream sediments fractions $<75 \,\mu\text{m}$ and 75-300 μm have the maximum and minimum trace element concentrations DL = detection limit

Element (DL) (ppm)	Leaves Maximum conc ⁿ	Leaves Minimum conc ⁿ	Twigs Maximum conc ⁿ	Twigs Minimum conc ⁿ	Stream sediment Maximum	Stream sediment Minimum	Stream sediment Maximum	Stream sediment Minimum
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					<75 μm fraction	<75 μm fraction	75-300 μm fraction	75-300 μm fraction
Na (100)	NE (2160)	E (1880)	NE (850)	NE (480)	S (5150)	NE (3700)	NE & S (23100)	E (18600)
Mg (20)	E (2314)	NE (2121)	S (1386)	N (1086)	N (11400)	S (7650)	N (2400)	E(1900)
Al (20)	S (127)	N (60)	NE (63)	N (40)	N (86700)	S (62100)	NE (46700)	E (37100)
P (20)	E (1198)	S (1095)	NE (2192)	E (1381)	NE (600)	N (410)	E (400)	N, NE & S (320)
S (10)	E (1158)	N (901)	S (443)	N (331)	NE (300)	S (100)	NE (50)	BDL
K (1000)	E (105000)	N (8830)	N (5200)	E (4520)	NE (19600)	S (15500)	NE (8300)	E (6500)
Ca (5000)	N, NE & S (8300)	E (7500)	N (28300)	E (20000)	N (11000)	S (5450)	N & NE (4700)	E (3900)
Sc (0.05)	S (0.052)	N (0.024)	NE (0.019)	N (0.008)	Not in assay suite	Not in assay suite	Not in assay suite	Not in assay suite
Mn (1)	S (199)	N (62)	S (562)	N (83)	NE (550)	S (430)	E (850)	S (370)
Fe (50)	E(170)	BDL	BDL	BDL	E (53100)	S (44700)	E (136000)	NE (53500)
Ni (1)	N, E & S (4)	NE (2)	N, NE & S (3)	E(2)	NE (30)	S (22)	E(17)	NE & S (9)
Cu (1)	S (9)	NE (7)	N & S (11)	NE & E (9)	NE (45)	S (27)	S (18)	N & E (12)
Zn (1)	S (37)	N & NE (24)	S (49)	N (19)	NE (105)	N, E & S (100)	E (42)	NE (34)
As (0.05)	E (0.11)	N, NE & E (BDL)	S (0.059)	N, NE & S (BDL)	E (6)	S (5)	NE (1.5)	N & E (0.5)
Br (0.2)	S (41)	N (12)	NE (73)	N & E (40)	Not in assay suite	Not in assay suite	Not in assay suite	Not in assay suite
Rb (0.1)	BDL	BDL	S (2.36)	BDL	N (94)	S (72)	NE (31)	E(24)
Sr (0.05)	NE (62)	E (54)	S (196)	N (170)	N (145)	S (100)	NE (70)	E (54)
Sn (0.1)	NE (0.20)	N, E & S (0.10)	NE & S (0.70)	N (0.20)	E (3.8)	S (3.1)	E (4.8)	NE (3.3)
Ba (10)	S (42)	NE (19)	NE (73)	N & E (40)	N & NE (340)	S (310)	NE & S (22)	E(175)
La (0.01)	E & S (0.11)	N (0.053)	S (0.082)	N (0.037)	E (140)	N (54)	E (220)	NE (58)
Ce (0.20)	E (0.56)	BDL	E (0.27)	N & NE (BDL)	E (240)	N (100)	E (410)	NE(105)
Nd (0.01)	E & S (0.09)	N (0.04)	NE, E & S (0.05)	N (0.02)	E (110)	N (43)	E (185)	NE (46)
Sm (0.01)	E (0.036)	N (0.024)	S (0.030)	N (0.020)	E(20.5)	N (9)	E(35.5)	NE(10)

Overall there does not appear to be a direct link between maximum/minimum vegetation element concentration and maximum/minimum stream sediment element concentrations within the same sector. Of the four sectors sampled, however, there may be a connection between leaves, $<75 \mu m$ and $75-300 \mu m$ stream sediment size fractions in the E sector where there are maximum concentrations recorded for Ce, Fe, La, Nd and Sm and likewise for twigs maximum and $<75 \mu m$ size fraction minimum concentration in the S sector for As, Cu, Mg, Ni, Rb, S and Sr. Of the twenty-three elements analysed, the E sector leaves, S sector twigs;

NE sector $<75 \ \mu m$ size fraction; and, E sector 75-300 μm size fraction had the most elements with the highest concentration. With the N sector leaves, N sector twigs; S sector $<75 \ \mu m$ size fraction; and, E sector 75-300 μm size fraction having the most elements with the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum: N (Ca and Ni), NE (Ca, Na, Sn and Sr), E (As, Ce, Fe, K, La, Mg, Nd, P, S and Sm) and S (Al, Ba, Br, Ca, Cu, Mn, Ni, Sc and Zn);
- leaves minimum: N (Al, As, Br, K, La, Mn, Nd, S, Sc, Sm and Sn), NE (As, Ba, Ce, Cu, Mg, Ni and Zn), E (As, Ca, Na, Sn and Sr) and S (P and Sn);
- twigs maximum: N (Ca, Cu, K and Ni), NE (Al, Ba, Br, Na, Nd, Ni, P, Sc and Sn), E (Ce and Nd) and S (As, Cu, La, Mg, Mn, Nd, Ni, Rb, S, Sm, Sn, Sr and Zn);
- twigs minimum: N (Al, As, Ba, Br, Ce, La, Mg, Mn, Nd, Rb, Sm, Sn, Sr and Zn), NE (As, Ce, Cu, Na and Rb), E (Ba, Br, Ca, Cu, K, Ni and P) and S (As, S and Sc);
- <75 μm fraction maximum: N (Al, Ba, Ca, Mg, Nd, Rb and Sr), NE (Ba, Cu, K, Mn, Ni, P, S and Zn), E (As, Ce, Fe, La, Nd, Sm and Sn) and S (Na);
- <75 μm fraction minimum: N (Ce, La, Nd, P, Sm and Zn), NE (Na), E (Zn) and S (Al, As, Ba, Ca, Cu, Fe, K, Mg, Mn, Ni, Rb, S, Sn and Sr);
- 75-300 µm fraction maximum: N (Ca and Mg), NE (Al, As, Ba, Ca, K, Na, Rb, S and Sr), E (Ce, Fe, La, Mn, Nd, Ni, P, Sm, Sn and Zn) and S (Ba, Cu and Na); and,
- 75-300 µm fraction minimum: N (As, Cu and P), NE (Ce, Fe, La, Ni, Nd, P. Sm, Sn and Zn), E (As, Al, Ba, Ca, Cu, K, Mg, Na, Rb and Sr) and S (Mn, Ni and P).

The maximum and minimum concentrations for rare earth elements in both size fractions of the stream sediments and leaves are within the same sector; with several of the other elements having maximum and minimum concentrations in more than one sector for all media (Table 3.10). Some of the elements analysed for all media occupy similar sectors due to their similar chemical properties, such as, (Ba, Ca, Mg and Sr), (Ce, Nd and Sm), and (K, Na and Rb).

3.12.3 Elemental Trends

Due to the small data set (n = 4), scatter diagrams (Figure 3.14) were constructed to determine whether or not Al, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm within all media (leaves, twigs, <75 μ m and 75-300 μ m size fraction) revealed relationships approaching a linear trend. The results show that only a small group of elements revealed a trend possibly approaching a linear relationship. Elements and their media that revealed a trend approaching a negative relationship include, Nd-leaves, Cu-leaves, Mg-twigs, Ba-leaves and Sr-twigs with the <75 μ m size fraction, and Ni-twigs with the 75-300 μ m size fraction. In contrast, Sm-leaves for the <75 μ m and Ca-twigs for the 75-300 μ m size fraction produced a trend approaching a positive relationship. The overall negative trend possibly implies that as the elements become available within the pore/soil water the *E. camaldulensis* may be preffentially excluding them, or that other factors may be involved.



Figure 3.14: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and 75-300 μm at Cutana Creek (Bindarrah).

Stream sediment trace element concentrations show that the <75 μ m size fraction has higher concentrations of Al, K, Mg, Ca, P, Ba, S, Sr, Zn, Rb, Cu, Y, Ni, Pb, Co, Nb, Dy, As, Cs, Sn, Er, Yb, Eu, W, Ho, Mo, TI, Bi, Tm, Ag, Lu, Cd and In than the 75-300 μ m size fraction. The 75-300 μ m size fraction has higher concentrations of Fe, Ti, Na, Mn, Ce, V, La, Nd, Cr, Th, Ga, Pr, Sm, Gd, U, Tb, Se and Au (Figure 3.15).



Figure 3.15: Variations of metal concentrations within $<75 \ \mu m$ and 75-300 μm stream sediments size fractions surrounding the *E. camaldulensis*, Bindarrah (Cutana Creek). To calculate the means, below detection limit values were taken as half the detection limit value.


Figure 3.16: The elemental composition and index of accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking stream sediments at Bindarrah (Cutana Creek). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The comparison of the elemental composition of the Cutana Creek *E. camaldulensis* leaves and twigs (Figure 3.16) shows that leaves have higher concentrations of K, Mg, Na, S, Fe, Al, Ni, Ce, La, Nd and Sm than twigs, whereas twigs have higher concentrations of Ca, P, Mn, Sr, Zn, Ba, Cu and Sn. For the <75 μ m size fraction, Fe is only detected within the leaves, which may reflect a preferential allocation of this element within the *E. camaldulensis* organs.

In general there is a decrease in element concentration from elements classified as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.16) highlights that for both the (<75 μ m and 75-300 μ m) size fractions some elements are more bioavailable and readily taken up by the *E. camaldulensis* compared to others. The following summarises the index of bioaccumulation from both size fractions (<75 μ m and 75-300 μ m) for leaves and twigs:

- <75 μm size fraction (twigs): S, P, Ca and Sr (high), K, Na, Zn, Mn, Mg, Cu, Ni, Ba and Sn (medium), and Ce and Sm (low) and Al, La and Nd (very-low);
- <75 μm size fraction (leaves): P and P (high), Ca, K, Na, Sr, Zn, Mn, Mg,Cu and Ni (medium), Ba and Sn (slight), Ce, Fe, Sm and Al (low) and La and Nd (very-low);
- 75-300 µm size fraction (twigs): P, Ca and Sr (high), K, Mg, Zn, Cu, Ni, Mn, Ba and Sn (medium), Na (slight), Al, Ce and Sm (low) and La and Nd (very-low); and,
- 75-300 µm size fraction (leaves): P, Ca, K and Mg (high), Sr, Zn, Cu, Ni, Mn and Ba (medium), Na and Sn (slight), Al, Ce, Sm and Fe (low) and La and Nd (very-low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements. These results are consistent with similar relationships found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.13 CUTANA CREEK TEMPORAL ELEMENT VARIATIONS WITHIN EUCALYPTUS CAMALDULENSIS

In general, Ba, Br, Ca, K, Sm, Sc, Na, Zn, Ni, Al, Cu, Mg, Mn, P, S and Sr are detectable in leaves across all seasons for 2003 and 2004. Elements Fe, Sn and Nd recorded below analytical detections limit concentrations for either one or more seasons. All of these elements, with the exception of Ba, Br, Sm, Sc, Na and Sr, are considered to be essential for plants. Table 3.11 and Figure 3.17 - Figure 3.21 present the rainfall and temporal fluctuations in element concentrations for *E. camaldulensis* leaves at Cutana Creek for all seasons for 2003 and 2004.

Table 3.11: Elemental composition of *E. camaldulensis* (leaves) sampled at Cutana Creek (Bindarrah) across all seasons for 2003 and 2004. High values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded for that year e.g. 2003 (Ba – 25 ppm; spring), while yellow represents the season in which the highest concentration was recorded for that year e.g. 2004 (Ca 11000 ppm; summer). BDL denotes below detection limit.

Season sampled	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
Ba ppm	26	35	25	36	36	55	54	56
Br ppm	16	13	14	19	18	17	21	22
Ca ppm	8100	8440	10200	10700	10900	10400	10000	11000
Fe ppm	103	71	62	184	212	190	230	230
K ppm	9705	7130	6940	6200	6260	6620	6000	6000
Sm ppm	0.03	0.02	0.03	0.04	0.04	0.03	0.04	0.04
Sc ppm	0.04	0.04	0.05	0.06	0.07	0.06	0.07	0.07
Na ppm	2005	1880	1810	1710	1720	1460	1900	1800
Zn ppm	28	20	34	34	41	44	29	26
Al ppm	103	96	98	240	176	146	256	253
Cu ppm	8	8	9	10	7	8	9	10
Mg ppm	2200	2349	2459	2697	2688	3050	2502	2606
Mn ppm	116	127	157	180	158	220	209	143
Ni ppm	3	4	4	8	3	5	4	9
P ppm	1149	1351	1414	1323	1194	1412	1631	1496
S ppm	1029	1119	1058	1101	1092	1275	1420	1350
Sr ppm	58	69	75	82	84	80	85	95

The physical appearance of the *E. camaldulensis* sampled at Cutana Creek (Bindarrah) in 2003 and 2004 was noted as:

- 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.

Trends for groups of elements displaying similar behaviour are outlined here.

Group A Elements (Periods of growth): more abundant during periods of growth. Spring and summer are characterised by temperatures with an average maximum of 28.7°C and minimum of 12.2°C in 2003, and an average maximum of 28.4°C and minimum of 12.3°C in 2004. The average rainfall for these periods was 18.5 mm in 2003 and 13 mm in 2004. From September to February (spring and summer) 2003, Ba, Br Ca, Fe, Sm, Sc, Na, Al, Cu, Mg, Mn, Ni and Sr, and for the same period in 2004, Ba, Br, Ca, Cu, Ni and Sr showed a gradual increase in concentration, recording their highest concentrations in summer. For the same period, Zn (2003) and Fe, Sc, Sm (2004) remained unchanged. In contrast, during 2003 K, P and S, and for the same period in 2004 Zn, Al, P and S recorded a decrease in concentration for the summer period.

Group B Elements (Periods of non-growth): reduced concentration levels during periods of non-growth. Autumn and winter, are characterised by temperatures with an average maximum of 19.1°C and minimum of 5.3°C in 2003, and an average maximum of 19.9°C and minimum of 5.9°C in 2004. The average rainfall for these periods was 11.7 mm in 2003 and 8.6 mm in 2004. From March to August (autumn to winter) 2003, Br, Sm, Na, Zn and Al and for the same period in 2004, Br, Fe, Sm, Sc, Na and Al concentrations showed a gradual decrease, and recorded their lowest concentration in the winter. While for the same period Ca, Na, Cu,

Mg, Mn, Ni, P, S and Sr in 2003, and Cu, Ni, P, S and Sr in 2004 recorded their lowest concentration in the autumn.

During June 2003, Ba, Ca, Ni, Mg, Mn, P, S and Sr and for the same period in 2004, Ba, K, Ni, Zn, Cu, Mg, Mn, P and S recorded a slight increase in concentrations two months after a period (March) of significantly reduced rainfall. In contrast Br, Fe, Sm, Na and Al all had a decrease in concentration for the same periods.



Figure 3.17: Rainfall and the temporal fluctuations in Ba, Br, Ca and Fe for *E. camaldulensis* (leaves) at Cutana Creek (Bindarrah). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.18: Rainfall and the temporal fluctuations in K, Sm, Sc and Na for *E. camaldulensis* (leaves) at Cutana Creek (Bindarrah). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.19: Rainfall and the temporal fluctuations in Zn, cu, Al and Mg for *E. camaldulensis* (leaves) at Cutana Creek (Bindarrah). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.20: Rainfall and the temporal fluctuations in Mn, Nd, Ni and P for *E. camaldulensis* (leaves) at Cutana Creek (Bindarrah). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.21: Rainfall and the temporal fluctuations in S and Sr for *E. camaldulensis* (leaves) at Cutana Creek (Bindarrah). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).

3.13.1 Cutana Creek Elemental Variability

The results in Table 3.12 show the degree of element variability during periods of plant growth and reduced plant growth for the Cutana Creek (Bindarrah) *E. camaldulensis* during 2003 and 2004.

Table 3.12: Shows the degree of elemental variation for the E. camaldulensis studied at Cutana Creek (Bindarrah) between (2003 and 2004)
periods of plant growth (G) shown by the green asterisk (*) and periods of reduced plant growth (RG) shown by the black asterisk (*), and
defines the optimal sampling period that should be utilised for selected elements. BDL denotes below detection limit.

Parameters	ers No seasonal			Sli	ight sea	sonal		Lo	ow se	easona	ıl	In	term	nediat	e	Hi	High seasonal riability > 80% 2003 2004 3 G RG G		ıl	
	v	aria	bility		var	variability <30% va			vari	abili	ty ~ 30)%	seaso	nal v	ariab	ility	varia	abilit	y > 80)%
			-								~ 5	0%	-			-				
Years	200)3	200)4	20	03	200)4	200)3	200)4	200)3	200)4	200)3	200)4
	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
Ba					*		*	*		*										
Br					*	*	*	*												
Ca					*	*	*	*												
Ce				*	BDL	BDL	*													
Fe				*	*		*						*							
Κ		*			*		*	*												
Sm				*	*	*	*													
Sc				*	*	*	*													
Na					*	*	*	*												
Zn						*	*	*	*											
Al					*		*	*						*						
Cu		*	*					*					*							
Mg					*	*	*	*												
Mn				*	*	*	*													
Nd				*			*		*					*						
Ni		*			*		*	*												
Р					*	*	*	*												
S					*	*	*	*												
Sr					*	*	*	*												

The degree of variability across 2003 and 2004 for the Cutana Creek (Bindarrah) *E. camaldulensis* is mostly slight (< 30%) for Br, Ca, K, Sm, Na, Sc, Mg, Mn, Ni, P, S and Sr; slight to low (< 30% - ~ 50%) for Ba, Fe, Zn, Cu and Nd. The slight to intermediate variations suggest that seasonal variations are less important for all elements analysed.

3.14 FLYING DOCTOR: WILLAWILLYONG CREEK (SETTING)

Willawillyong Creek is approximately 8 km east of Broken Hill, in the central-eastern part of the Barrier Ranges, New South Wales. The *E. camaldulensis* sampled here is 200 m north of the Barrier Highway, on the Broken Hill 1:250 000 topographic map sheet (SH54-15), grid reference 550209 mE; 6468134 mN. The Flying Doctor Prospect is named due to its proximity to the former site of the Royal Flying Doctor Radio Control Centre (Tyne & Webster, 1988).

The area experiences a semi-arid climate, with an irregular annual rainfall of 221 mm, predominately falling in the summer. Temperatures range from an average summer maximum of 31.8° C to an average winter minimum of 4.5° C (Bureau of Meteorology, 2005c). The study site is centred on a tributary of Willawillyong Creek, which is part of the Stephens Creek catchment. The region surrounding the study site is classified as part of the Broken Hill Bioregion, which extends to the Bancannia Catchment in the north, Darling River Catchment in the east and the Lake Frome catchment in the west (Sahukar *et al.*, 2003).

The landscape immediately surrounding the *E. camaldulensis* has a low topographic relief of 0-9 m (Figure 3.22), grading up to higher topographic relief > 300 m. The highest parts in the area are between 300 m and 400 m (above sea level) with the Barrier Ranges in the north-northwest and Coonbaralba Range in the east. Elevation generally decreases towards the low-lying plains in the east and south associated with the Darling River drainage basin, which is approximately 60 m above sea level. The landscape of the area broadly consists of undulating rises in the north-northwest and east associated with the Barrier and Coonbaralba Ranges, flanked by gently sloping erosional rises, which eventually extend into broad alluvial plains and terminate into both perennial and non-perennial lakes (i.e. lakes Cawndilla, Menindee, Pamamaroo, Tandure, Nettlegoe and Tandou) to the southeast.



Figure 3.22: An image of the *E. camaldulensis* at Willawillyong Creek (Flying Doctor), and the surrounding low-lying regolith dominated landscape.

The vegetation communities and dominant species are closely associated with the major landform settings at this site. The main vegetation community types in the area as described by Copper (1975); Sahukar *et al.* (2003) and Hill *et al.* (2005) are:

- open shrubland dominated by minor *Acacia aneura* and *Acacia tetragonophylla*. This community typically colonises weathered bedrock on erosional rises and hills;
- open chenopod shrublands dominated by *Mairiana pyramidata* and *Atriplex vesicaria* and tall open shrubland subdominated by *Casuarina cristata*. This community typically colonises colluvial and alluvial depositional plains; and,
- riparian woodlands dominated by *E. camaldulensis* and open shrublands co-dominated by *Mairiana sedifolia* and grasses. This community typically colonises low-lying landscape settings, such as major drainage channels and alluvial outwash plains.

3.14.1 Geology

Willawillyong Creek is on the Mount Gipps 1:25 000 geological mapsheet (7234 111 S), which includes the Early to Middle Proterozoic Willyama Supergroup (Bradley, 1984). The study area lies to the southeast of the main Broken Hill ore body, and minerlisation extends along a linear zone, which extends for approximately 11 km northeast from the De Bavay Schist zone and lies close to the Globe Vauxhall Schist zone (Bradley, 1984; Burton, 1994). The major rock types include composite gneisses and migmatites, quartzo-feldspathic gneisses, amphibolite and mafic granulites and mafic and ultramafic intrusives (Bradley, 1984; Burton, 1994; Figure 3.23). The landscape is broadly characterised by north to south trending Palaeoproterozoic metasediments and meta-igneous rocks (Hill, 2005; Andrews, 1922). The dominant physiographic features of the study area are the exposed ridges, which form the eastern margin of the Barrier Ranges, with the adjacent erosional and alluvial plains forming the western margin of the Murray-Darling Basin, which gently slopes towards the Darling River system (Hill, 2005, Hill *et al.*, 2005).



Figure 3.23: An illustration of the bedrock geology and the stratiform and stratabound mineralisation (Pb, Zn, Ag and W) of the Flying Doctor Prospect after Willis *et al.* (1983) and Bradley (1980).

3.14.2 Mineralisation (Flying Doctor)

The Broken Hill-type deposits of the Northern Leases (Flying Doctor mineralisation) are along two main lines of lode: (i) the upper lode horizon; and, (ii) the main lode horizon. Both horizons are NE-trending linear zones within the undifferentiated Purnamoota Subgroup of the Willyama Supergroup (Burton, 1994). Proximal to the individual *E. camaldulensis* are the Barrier Main Lode and the Flying Doctor mineralisation, within the Upper Lode Horizon. This consists of blue quartz \pm gahnite \pm sulphide and minor garnet. The mineralisation is fine to coarse grained galena and sphalerite with minor chalcopyrite, pyrite and pyrrhotite, and occurs as disseminations, in massive forms as patches, irregular vein-like masses or reticular networks (Burton, 1994). The total recorded production from the Barrier Main Lode is estimated to be in the vicinity of 393.85 t resulting in 34 kg Ag and 57 t Pb (Burton, 1994). The Flying Doctor mineralisation 100 m below the surface with a strike length of 250 m (Burton, 1994). The deposit contains 300 000 t of mineralisation with average grades of 7% Pb, 60 g/t Ag, and 2.4% Zn (Department of Mineral Resources, 1981).

3.15 WILLAWILLYONG CREEK EUCALYPTUS CAMALDULENSIS CHARACTERISTICS

The Willawillyong Creek *E. camaldulensis* is a gnarled tree with a girth of 4.30 m and a spreading open canopy that extends from ground level up to approximately 74 m. The bark is generally smooth, except near the base where it is rough with large shedding strips. Twigs are brown, ranging between 2-5 mm in diameter. Buds are stalked and have a beaked conical shape and are typically in clusters of 5-6. Leaves are alternating, pendulous and narrowly lanceolate approximately 7.5-11 cm long, 1- 1.5 cm wide, pale green on the adaxial and abaxial surface. The tree is approximately 70 m from the main drainage channel, surrounded by *Atriplex vesicaria* (bladder saltbush) and *Atriplex nummularia* (old man saltbush). Figure 3.24 illustrates the location of the *E. camaldulensis* and its position in relation to a neighbouring *E. camaldulensis* tree (plan view) and a profile view of the channel, which is approximately 4 m wide and is incised up to 1 m on the southeast and 1 m on the northwest.



Figure 3.24: A cartoon illustrating the location of the Willawillyong Creek (Flying Doctor) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* s (plan view) and a profile view of the channel.

The alluvial depositional plain (Apd), hosting the *E. camaldulensis* is characterised by redbrown quartzose silts and sands with fine quartz and lithic fragments (Hill, *et al.*, 2005). This ephemeral channel has an approximate length of 5 km, terminating in the Stephens Creek Reservoir. The alluvial depositional plain and adjacent channel incises different lithological units that host Broken Hill-type mineralisation (Pb-Ag-Zn). In close proximity (i.e. within 2 km) to the *E. camaldulensis* there are twenty-four recorded mineral occurrences. Table 3.13 outlines some of the known deposits proximal to the *E. camaldulensis*.

detect mineralisation.			
Mineral Deposit	Mineralisation Target	Lithology	Pathfinder elements
Consolidated Broken Hill	Pb-Zn-Ag mineralisation	Broken Hill Group	Hg, As and Zn
Round Hill	Pb-Zn-Ag mineralisation	Broken Hill Group	Hg, As and Zn
Barrier Main Lode	Pb-Ag-Zn mineralisation	Retrograde schist/Purnamoota Group	Hg, As and Zn
New Silver Peak	Pb-Ag-Zn mineralisation	Sundown Group	Hg, As and Zn
Old Silver Peak	Pb-Ag-Zn mineralisation	Retrograde schist/Purnamoota Group	Hg, As and Zn

Table 3.13: Outlines the known mineralisation in the Flying Doctor (Northern Leases) area, and examples of pathfinder elements used to detect mineralisation.

3.15.1 Organ Tissue Biogeochemistry Results

Samples of leaves, twigs, buds, fruit and bark were taken during autumn 2003 from the Willawillyong Creek study site. Five samples per medium (leaves and twigs), and single composite samples of buds, fruit and bark were collected from the reachable N, NE, E, S and NW sectors around the *E. camaldulensis* canopy. Fifty-two elements were assayed by combined INNA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. In general, Sb, Cs, Cr, Co, Eu, Au, Hf, Lu, Mo, Rb, Se, Ag, Ta, Te, Th, W, U, Yb, Zr, Be, Bi, Ga In, Nb, Pb, Ti and V were below analytical detection limits for all sampling media. The concentrations of twenty-four elements were detectable from the *E. camaldulensis* organ tissues, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.14. All elements with > 25 % of their values below detection limits have been removed from the data set.

Table 3.14: Variations of metal concentrations within different oven dried tissues of an individual *E. camaldulensis*, at Willawillyong Creek (Flying Doctor). Initial value represents the mean; values in brackets () are the range of values; C = composite sample and * signifies values below detection limit. To calculate the 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.

Element (ppm)	Leaves (n=5)	Twigs (n=5)	Buds (C)	Fruit (n=1)	Bark (n=1)
Na	1082 (970-1330)	650 (240-1160)	880	2060	190
Mg	1590 (1387-1788)	388 (226-603)	1794	1246	944
Al	77 (65-89)	57 (33-112)	51	75	*
Р	1103 (1031-1200)	782 (701-914)	1690	1147	86
S	815 (730-908)	284 (266-317)	928	592	120
Κ	11140 (10300-12500)	4166 (3000-5320)	13400	14200	980
Ca	7940 (6300-10600)	12220 (7500-16800)	10000	10900	71600
Sc	0.028 (0.023-0.033)	0.018 (0.011-0.026)	0.007	0.035	*
Mn	44 (29-78)	22 (16-33)	48	42	44
Fe	67 (*-80)	*	*	*	*
Co	0.27 (*-0.39)	*	*	*	*
Ni	1.8 (1-2)	1.5 (*-2)	2	2	2
Cu	7.6 (6-9)	8.2 (6-11)	10	6	2
Zn	28 (23-37)	29.2 (15-44)	27	22	22
As	0.07 (*-0.081)	*	*	*	*
Br	12.14 (10.20-17.50)	2.6 (1.63-3.68)	10.40	14.40	10.40
Sr	44.23 (36.73-52.87)	76.3 (49.96-110.96)	67.93	64.35	567.40
Cd	0.24 (0.20-0.30)	0.38 (0.30-0.50)	0.4	0.2	0.2
Sn	0.12 (0.1-0.2)	0.32 (0.20-0.50)	0.1	0.2	0.1
Ba	7.5 (*-17.4)	*	*	*	15.4
La	0.067 (0.046-0.081)	0.06 (0.028-0.092)	*	0.050	*
Ce	0.27 (*-0.44)	0.21 (*-0.38)	*	0.52	*
Nd	0.046 (0.03-0.06)	0.03 (0.01-0.05)	0.03	0.05	*

Element (ppm)	Leaves (n=5)	Twigs (n=5)	Buds (C)	Fruit (n=1)	Bark (n=1)
Sm	0.023 (0.019-0.025)	0.020 (0.014-0.023)	0.017	0.025	*

The Willawillyong Creek *E. camaldulensis* showed elemental variability between the organs. Of the twenty-four elements measured, Al, Fe, Co, As and La had the greatest concentration within the leaves. Concentrations of Zn and Sn were most abundant within the twigs. Concentrations of Mg, P, S, Mn, Ni, Cu and Cd were highest in the buds. Concentrations of Na, K, Ni, Br, Sc, Ce, Nd and Sm were highest in the fruit. The elements Ba, Ni, Sr and Ba were more abundant in the bark.

3.15.2 Comparison Between Element Concentrations in Eucalyptus camaldulensis and

Adjacent Stream Sediment Chemistry

Fifty-three elements were assayed (Appendix. C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Se and Te were below analytical detection limit in one or more sectors for both size fractions. The chemical composition of twenty elements were detectable in both leaves and twigs, with the abundance of Fe, As and Ba only detected within the *E. camaldulensis* leaves. For all media, Al, Ca, Cd, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm were detectable. Table 3.15, shows which sector for *E. camaldulensis* leaves, twigs and adjacent stream sediment <75 μ m and 75-300 μ m size fractions have the maximum and minimum trace element concentrations.

Element (DL) (ppm)	Leaves Maximum conc ⁿ	Leaves Minimum conc ⁿ	Twigs Maximum conc ⁿ	Twigs Minimum conc ⁿ	Stream sediments Maximum conc ⁿ	Stream sediments Minimum conc ⁿ	Stream sediments Maximum conc ⁿ	Stream sediments Minimum conc ⁿ
	(ppm)	(ppm)	(ppm)	(ppm)	(nnm)	(nnm)		
					(ppm)	(ppm)		75-300 um
					<75 μm fraction	<75 μm fraction	75-300 μm fraction	fraction
Na (100)	E (1330)	NW (970)	N (1160)	NE (240)	N (4650)	E (3100)	N (6800)	E (2450)
Mg (20)	NE (1788)	N (1387)	N (603)	NE (226)	E (9250)	N (6550)	E (8800)	N (5650)
Al (20)	N (89)	S (65)	N (112)	E (33)	S (82200)	N (65200)	NW (66500)	N (53900)
P (20)	N (1200)	NE (1031)	E (914)	NW (701)	N & E (700)	NW (470)	E (800)	NW (480)
S (10)	E (908)	S (730)	E (317)	NE (266)	E (800)	NW (350)	E (950)	NW (300)
K (1000)	NE (12500)	NW (10300)	E (5320)	N (3000)	NW (20000)	N (16400)	NW (19200)	N (15500)
Ca (5000)	S (10600)	NE (6300)	E (16800)	NE (7500)	E (20400)	NW (8300)	E (16200)	NE (8750)
Sc (0.005)	NW (0.033)	E & S (0.023)	S (0.026)	NE (0.011)	Not in assay suite	Not in assay suite	Not in assay suite	Not in assay suite
Mn (1)	S (78)	NE & E (29)	S (33)	E & S (16)	N (3550)	E (1650)	NW (3650)	E (1450)
Fe (50)	NW (80)	E, S & NW (BDL)	S & NW (50)	N, NE & E (BDL)	NE (44300)	N (37100)	S (40400)	N (34100)
Ni (1)	N, NE, E & S (2)	NW (1)	NE (2)	N, E & NW (BDL)	NE (29)	N (21)	S (27)	N (17)
Cu (1)	NW (9)	E (6)	N (11)	E (6)	NE (68)	N (48)	E (62)	N (35)
Zn (1)	S (37)	NE (23)	N (44)	NE (15)	NW (3250)	N & E (2150)	NW (2950)	N (1500)
As (0.05)	E, S & NW (0.08)	N & NE (BDL)	BDL (all sectors)	BDL (all sectors)	NE (18)	E (12.5)	NW (16)	NE (6)
Br (0.2)	E (17.50)	NW (10.20)	N (3.68)	NE (1.63)	Not in assay suite	Not in assay suite	Not in assay suite	Not in assay

Table 3.15: Shows which sector for *E. camaldulensis* leaves and twigs and adjacent stream sediments size fractions $<75 \ \mu m$ and 75-300 μm have the maximum and minimum trace element concentrations at Willawillyong Creek (Flying Doctor). DL = detection limit.

Element (DL) (ppm)	Leaves Maximum conc ⁿ	Leaves Minimum conc ⁿ	Twigs Maximum conc ⁿ	Twigs Minimum conc ⁿ	Stream sediments Maximum conc ⁿ	Stream sediments Minimum conc ⁿ	Stream sediments Maximum conc ⁿ	Stream sediments Minimum conc ⁿ
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)		
					<75 μm fraction	<75 μm fraction	75-300 μm fraction	75-300 μm fraction
								suite
Sr (0.05)	N (52.87)	NE (36.73)	N (110.96)	NE (49.96)	E (185)	N (105)	E (145)	N & NE (96)
Cd (0.1)	S & NW (0.3)	N, NE & E (0.2)	N & NW (0.5)	NE (0.2)	NW (12)	N (7)	S & NW (12)	N (6)
Sn (0.1)	NE (0.20)	N, E, S & NW (0.10)	S (0.50)	NE & E (0.20)	NW (3.8)	N (2.7)	S & NW (3)	N (2)
Ba (10)	E (17.40)	N, NE, S & NW (BDL)	BDL (all sectors)	BDL (all sectors)	NW (370)	E (310)	NW (350)	E (280)
La (0.01)	N (0.081)	S (0.046)	S (0.092)	NE (0.028)	N (86)	E (36)	N (49)	E (28)
Ce (0.20)	E (0.44)	N & S (BDL)	N (0.38)	NE, S & NW (BDL)	N (150)	E (66 pm)	N (88)	E (52)
Nd (0.01)	E (0.06)	S (0.03)	N (0.05)	NE (0.01)	N (66)	E (29)	N (39)	E (24)
Sm (0.01)	NW (0.025)	S (0.024)	S (0.023)	NE (0.020)	N (13)	E (6)	N (8)	E (5)

In general there does not appear to be a link between maximum/minimum vegetation element concentration and maximum/minimum stream sediment element concentrations within the same sector. There may, however, be a connection between twigs and the <75 μ m and 75-300 μ m size fractions maximum concentrations in the N sector for Ce, Na and Nd. Of the twenty-three elements measured, the E sector leaves, N sector twigs; N sector <75 μ m size fraction; and, NW sector 75-300 μ m size fraction had the most elements with the highest concentration. The S sector leaves, NE sector twigs; N sector <75 μ m size fraction; and, N sector 300 μ m size fraction have the most elements with the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum: N (Al, La, Ni, P and Sr), NE (K, Mg, Ni and Sn), E (As, Ba, Br, Ce, Na, Nd, Ni, and S), S (As, Cd, Ca, Mn, Ni and Zn) and NW (As, Cd, Cu, Fe, Sc and Sm);
- leaves minimum: N (As, Ba, Cd, Ce, Mg and Sn), NE (As, Ba, Ca, Cd, Mn, P, Sr and Zn), E (Cd, Cu, Fe, Mn, Sc and Sn), S (Al, Ba, Ce, Fe, La, Nd, S, Sc, Sm and Sn) and NW (Ba, Br, Fe, K, Na, Ni and Sn);
- twigs maximum: N (Al, Br, Cd, Ce, Cu, Mg, Na, Nd, Sr and Zn), NE (Ni), E (Ca, K, P and S), S (Fe, La, Mn, Sc, Sm and Sn) and NW (Cd and Fe);
- twigs minimum: N (K, Fe and Ni), NE (Br, Ca, Cd, Fe, La, Mg, Na, Nd, S, Sc, Sm, Sr and Zn), E (Al, Cu, Fe, Mn, Ni, and Sn), S (Mn) and NW (Ni and P);
- <75 μm fraction maximum: N (Ce, La, Mn, Na, Nd, P and Sm), NE (As, Cu, Fe and Ni), E (Ca, Mg, P, S and Sr), S (Al) and NW (Ba, Cd, K, Sn and Zn);
- <75 μm fraction minimum: N (Al, Cd, Cu, Fe, K, Mg, Ni, Sn and Sr), E (As, Ba, Ce, La, Mn, Na, Nd and Sm) and NW (Ca, P and S);
- 75-300 μm fraction maximum: N (Ce, La, Na, Nd and Sm), E (Ca, Cu, Mg, P, S and Sr), S (Cd, Fe, Ni and Sn) and NW (Al, As, Ba, Cd, K, Mn, Sn and Zn); and,
- 75-300 μm fraction minimum: N (Al, Cd, Cu, Fe, K, Mg, Ni, Sn, Sr and Zn), NE (As, Ca and Sr) and E (Ba, Ce, La, Mn, Na, Nd and Sm).

The maximum and minimum values for rare earth elements in both size fractions of stream sediments are within the same sectors (Table 3.15). Some of the elements analysed within all media have similar distribution patterns between sectors due to their similar chemical

properties, such as: (Ba, Ca, Mg and Sr), (Ce, Nd and Sm), (La and Sc), (Fe and Ni), (Cd and Zn), and (K, Na and Rb).

3.15.3 Elemental Trends

Due to the small data set (n =5) scatter diagrams (Figure 3.25) are constructed to determine whether or not Al, Ca, Cd, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm within all media (leaves, twigs, <75 μ m and 75-300 μ m size fractions) conform to a linear relationship. The results show that only two of elements possibly approach a linear relationship. Copper within twigs and the 75-300 μ m stream sediment size fraction revealed a trend approaching a negative relationship. In contrast, P in twigs for the 75-300 μ m stream sediment size fraction broadly approximates a positive relationship. The overall negative trend possibly implies that as the elements become available within the pore/soil water the *E. camaldulensis* maybe preferentially excluding them, or that other factors may be involved. Further data is needed to provide more reliable patterns.



Figure 3.25: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and 75-300 μm at Willawillyong Creek (Flying Doctor).

In the stream sediments the <75 μ m size fraction has higher concentrations of Al, Fe, Km Ca, Mg, Ti, Zn, Pb, P, S, Sr, Ce, V, Rb, Cu, La, Nd, Cr, Ni, Y, Ga, Th, As, Co, Pr, Sb, Sm, Gd, Dy, Cs, Sn, W, U, Yb, Er, Eu, Ho, Tb, Bi, Tm and Lu than the 75-300 μ m size fraction. The 75-300 μ m size fraction had higher concentrations of Na, Mn, Cd, Ag, Mo, Se and Au, whilst Nb, TI and In had equivalent concentrations for both size fractions (Figure 3.26).



300 μm log Concⁿ (ppm) Figure 3.26: Variations of metal concentrations within <75 μm and 75-300 μm stream sediments size fractions surrounding the *E. camaldulensis*, Willawillyong Creek (Flying Doctor). To calculate the means, below detection limit values were taken as half the detection limit value.



Figure 3.27: The elemental composition and index accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking stream sediments at Willawillyong Creek (Flying Doctor). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The comparison of the composition of the Willawillyong Creek *E. camaldulensis* leaves and twigs (Figure 3.27) reveals higher concentrations of K, Mg, P, Na, S, Al, Fe, Mn, Ba, Ni, Ce,

Co, As, La, Nd and Sm in leaves compared to the twigs, whereas the twigs have greater concentrations of Ca, S, Sr, Zn, Cu, Ce, Cd, Sn and La. The elements Ba, Co and As are only detectable within the leaves, which may reflect a preferential allocation of these elements within the *E. camaldulensis* organs, although once again a greater data set would be useful to test this relationship further.

In general there is a decrease in element concentration from elements classified as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.27) illustrates that for both the <75 μ m and 75-300 μ m stream sediment size fractions some elements appear to be more bioavailable and readily taken up by *E. camaldulensis* than others. The following summarises the index of bioaccumulation from both size fractions (<75 μ m and 75-300 μ m) compared with leaves and twigs:

- <75 μm size fraction (twigs): P, S and Ca (high), K, Sr, Na, Cu and Sn (medium), Mg, Ni, Cd and Zn (slight), Mg, Zn, Ba, Ni and Cd (medium), Fe, Mn, Ce, As and Sm (slight), Mn, Ce, Sm, Fe and La (low) and Nd and Al (very-low);
- <75 μm size fraction (leaves): P and S (high), Ca, K, Sr, Na, Mg and Cu (medium), Ni, Ba, Sn, Cd, Co, Mn and Zn (slight) and As, Ce, Sm, Fe, La, Nd and Al (low);
- 75-300 µm size fraction (twigs): P, S and Ca (high), K, Sr, Na, Cu and Sn (medium), Mg, Ni, Cd and Zn (slight), Mn, Ce, Sm, La and Fe (low) and Nd and Al (very-low); and,
- 75-300 µm size fraction (leaves): P and S (high), Ca, K, Sr, Na, Mg and Cu (medium), Ni, Ba, Sn, Cd, Co, Mn and Zn (slight) and As, Ce, Sm, La, Fe, Nd and Al (low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements. These results are consistent with similar relationship found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.16 WILLAWILLYONG CREEK TEMPORAL ELEMENT VARIATIONS WITHIN EUCALYPTUS CAMALDULENSIS

In general, Br, Ca, La, K, Sm, Na, Zn, Ni, Al, Cu, Mg, Mn, Nd, P, S and Sr are detectable in the leaves across all seasons for 2003 and 2004. Elements As, Fe, Sc, Sn and Cd, recorded below analytical detection limit concentrations for either one or more seasons. All of these elements, with the exception of Br, La, Sm, Na, Nd, Sr, As, Sc, Sn and Cd, are considered to be essential for plant function. Table 3.16 and Figure 3.28 – Figure 3.33 presents the rainfall and temporal fluctuation in element concentrations for *E. camaldulensis* leaves at Willawillyong Creek for all seasons for 2003 and 2004.

Table 3.16: Elemental composition of *E. camaldulensis* (leaves) sampled across all seasons for 2003 and 2004. High values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded e.g. 2003 (Br - 10 ppm; spring), while yellow represents the season in which the highest concentration was recorded e.g. 2004 (Ca - 9000 ppm; summer). Orange denotes no seasonal elemental change. BDL denotes below detection limit.

Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
As (ppm)	0.05	BDL	0.07	0.07	BDL	BDL	0.08	BDL
Br (ppm)	11	11	10	12	15	11	12	12
Ca (ppm)	7940	9560	10400	13100	7960	8190	6000	9000
Fe (ppm)	50	BDL	55	107	71	68	BDL	110
La (ppm)	0.07	0.05	0.07	0.09	0.038	0.044	0.010	0.010
K (ppm)	11140	8420	6860	5730	9620	7780	5000	5000
Sm (ppm)	0.023	0.021	0.021	0.019	0.014	0.013	0.010	0.010
Sc (ppm)	0.028	0.018	0.024	0.032	0.016	0.016	BDL	BDL
Na (ppm)	1082	1410	1760	1540	1250	1420	2100	2100
Zn (ppm)	28	26	33	42	42	35	25	34
Al (ppm)	77	37	73	145	69	53	92	108
Cu (ppm)	8	10	11	9	9	8	10	11
Cd (ppm)	0.24	0.30	0.20	0.30	BDL	0.3	0.3	0.4
Mg (ppm)	1590	1750	1811	1816	2277	1719	1612	1731
Mn (ppm)	45	65	69	102	74	71	82	104
Nd (ppm)	0.046	0.040	0.040	0.070	0.16	0.04	0.05	0.07
Ni (ppm)	1	3	2	6	2	2	2	2
P (ppm)	1103	1244	1304	1379	1298	1164	953	985
S (ppm)	815	1106	1247	974	1087	973	1115	1194
Sn (ppm)	0.12	0.10	BDL	0.20	0.30	0.30	0.05	0.05
Sr (ppm)	44	59	58	75	58	48	45	56

The physical appearance of the E. camaldulensis sampled across 2003 and 2004, was:

- 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.

The results outlined here show trends of groups of elements displaying similar behaviour.

Group A Elements (Periods of growth): more abundant during periods of growth. Spring and summer are characterised by temperatures with an average maximum of 29.8°C and minimum of 15.7°C in 2003, and an average maximum of 28.7°C and minimum of 15.2°C in 2004. The average rainfall for these periods was 16.9 mm in 2003 and 18.43 mm in 2004. From September to February (spring and summer) 2003, Br, Ca, Fe, La, Sc, Zn, Al, Cd, Mg, Mn, Nd, Ni, P, Sn and Sr, and for the same period in 2004, Ca, Fe, Na, Al, Cu, Cd, Mn and S showed a gradual increase in concentration, recording their highest concentrations in summer. While for the same period element As in 2003 and Br, K, Sm, Sc, Na, Ni and Sn in 2004 remained unchanged. In contrast, during 2003 K, Sm, Na, Cu and S, and for the same period in 2004 As concentration showed a decrease in the summer.

Group B Elements (Periods of non-growth): reduced concentration levels during periods of non-growth. Autumn and winter, are characterised by temperatures with an average maximum of 20.1°C and minimum of 9.6°C in 2003, and an average maximum of 21°C and minimum of 9.8°C in 2004. The average rainfall for these periods was 20.97 mm in 2003 and 12.13 mm in 2004. From March to August (autumn to winter) 2003, As, Fe, La, Sc, Zn, Al and Nd and for the same period in 2004, Br, Al, Cu, Mn, Nd, S and Sn concentrations showed a gradual decrease, and recorded their lowest concentration in winter.

The rainfall pattern across 2003 appears to be quite consistent, while the rainfall pattern across 2004 was more erratic. There is also a significant reduction in rainfall (28.4 mm) during the transition from periods of growth (spring-summer) in 2003, to periods of nongrowth (autumn-winter) in 2004 (Bureau of Meteorology, 2005c). Results show that concentrations between March-June (Autumn-Winter) 2003 and March-June (Autumn-Winter) 2004 are comparable, even though there is a reduction of 7 mm in available rainfall. This suggests that the rainfall that fell during September-December 2003 provided a soil/pore water nutrient-rich source during periods of reduced rainfall in March-June 2004. However concentrations for As, Ca, Fe, La, K, Sm, Sc, Zn, Al, Mg, Nd, Ni, P, Sn and Sr are reduced during September-December 2004 (Spring-Summer) compared to September-December (Spring-Summer) 2003. It is possible that the reduced elemental concentrations reflect the chemical composition of the surrounding groundwater which is either deficient in these elements or that they are not in a readily available form. Elements Br, Na, Cu, Cd and S are higher in concentration during September-December 2004 (Spring-Summer) compared to September-December (Spring-Summer) 2003, suggesting that leaves that are senescing, retranslocate the more mobile elements or the extensive root system is penetrating further into the underlying substrate and sourcing the groundwaters that host these elements in an available form (e.g. in solution).



Figure 3.28: Rainfall and the temporal fluctuations in As, Br, Ca and Fe for *E. camaldulensis* (leaves).) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year)



Figure 3.29: Rainfall and the temporal fluctuations in La, K, Sm and Sc for *E. canaldulensis* (leaves) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year)



Figure 3.30: Rainfall and the temporal fluctuations in Na, Zn, Al and Cu for *E. camaldulensis* (leaves) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.31: Rainfall and the temporal fluctuations in Cd, Mg, Mn and Nd for *E. camaldulensis* (leaves) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.32: Rainfall and the temporal fluctuations in Ni, P, S and Sn for *E. camaldulensis* (leaves) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.33: Rainfall and the temporal fluctuations in Sr for *E. camaldulensis* (leaves) at Willawillyong Creek (Flying Doctor). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year)

3.16.1 Flying Doctor (Willawillyong Creek) Elemental Variability

The results shown in Table 3.17 show the degree of element variability during periods of plant growth and reduced plant growth for the Willawillyong Creek (Flying Doctor) *E. camaldulensis* during the 2003 and 2004 seasons.

Parameters	rs No seasonal variability		ability	Sli	ght s	eason	al	Lo	ow se	easona	l	In	tern	nediat	e	Hi	gh se	easona	al	
					vari	abili	ty <30)%	vari	abili	ty ~ 30)%	seaso	nal y	ariab	ility	varia	abili	ty > 80	0%
									~ 50%											
Years	2003 2004		04	200	2003 2004		200)3	200)4	2003 200		200)4	2003		2004			
	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
As		*	BDL										*			*				
Br				*	*	*	*													
Ca					*	*	*					*								
Fe							*						*	*		*			*	
La				BDL	*	*	*													
Κ				*	*	*	*													
Sm				BDL	*	*	*													
Sc			*	BDL		*			*											
Na				*	*	*	*													
Zn					*	*	*	*												
Al							*	*					*	*						
Cu					*	*	*	*												
Cd					*			*		*									*	
Mg					*	*	*	*												
Mn							*	*	*	*										
Nd					*			*		*					*					
Ni			*	*					*					*						
Р					*	*	*	*												
S					*	*	*	*												
Sn			*	BDL	*									*						
Sr					*	*	*	*												

Table 3.17: Shows the degree of elemental variation for the *E. camaldulensis* studied at Willawillyong Creek (Flying Doctor) between (2003 and 2004) periods of plant growth (G) shown by a green asterisk (*) and periods of reduced plant growth (RG) shown by a black asterisk (*) and defines the optimal sampling period that should be utilised for selected elements.

The degree of concentration variability across 2003 and 2004 for the *E. camaldulensis* is mostly slight (< 30%) for Br, La, K, Sm, Na, Zn, Cu, Mg, P, S and Sr; slight – low (< 30% - ~ 30%) for Ca, Sc and Mn; intermediate (~ 50%) for As; intermediate – high (~ 50% - > 80%) for Fe; and, variable for Al, Cd, Nd, Ni and Sn with concentration variability lying within more than one parameter. The slight to intermediate variations suggest that for many of the elements, seasonal variations are of low importance, with the exception of Fe. This suggests that the most appropriate sampling period is not distinctivelt discrimitated, except perhaps a slight preference towards summer.

3.17 WILLIAMS PEAK: WILLIAMS CREEK (SETTING)

Williams Creek is approximately 44 km west of White Cliffs, in central-northwest New South Wales, and approximately 300 km northeast of Broken Hill. The *E. camaldulensis* tree sampled is 250 m south of Henry Roberts Rd on the White Cliffs 1:250 000 topographic mapsheet (SH54-12) and Kayrunnera 1:100 000 geological mapsheet (7436), grid reference 660106 mE; 6593320 mN.

The area experiences a hot, semi-arid climate, with an average annual rainfall of 246 mm, falling mostly in the summer. Temperatures range from an average summer maximum of 33.9°C to an average winter minimum of 5.8°C (Bureau of Meteorology, 2005d). The sample site lies on the northeast margin of the Coturaundee Range, which is part of the Mulga Lands Bioregion, which extends north and east across inland northern New South Wales and into Queensland (Sahukar *et al.*, 2003).

The landscape immediately surrounding the *E. camaldulensis* includes erosional rises with a low topographic relief of 0-9 m (Figure 3.34). The highest parts in the region are associated with the Coturaundee Range to the southwest with an elevation of 423 m above sea level and Koonenberry Mountain in the northeast with an elevation up to 407 m above sea level. Elevation generally decreases towards the low-lying plains in the north and northwest, associated with the Bulloo River Overflow and the Bancannia Basin, where both are approximately between 80-90 m above sea level.



Figure 3.34: An image of the *E. camaldulensis* at Williams Creek (Williams Peak), and the surrounding low-lying regolith dominated landscape.

The landscape of the region broadly consists of northwest to southeast trending erosional mountains associated with the Coturaundee Range and Koonenberry Mountain, flanked by gently sloping colluvial sheetflow erosional rises and plains. To the north, creeks such as Williams Creek, Turkey Creek, Box Creek, Kayrunnera Creek and Yanda Watercourse, unite to form the channel of Yancannia Creek, which eventually drains northeast and flows into the non-perennial lakes Ulenia and Yantara, which are on the southern margin of the Bulloo River Overflow Catchment. Aeolian sediments are widespread, and are a major component of the surficial regolith material.

The contemporary ephemeral drainage across the study area occurs within sandy, braided alluvial channels, with all of their headwaters within the Coturaundee Range.

The vegetation communities and dominant species are closely associated with the major landform settings for this region. The main vegetation community types in the area as described by Hill (2005), Sahuka *et al.* (2003) and Mills (2002) are:

- open woodlands dominated by *Acacia aneura*, mostly in areas with exposed bedrock or subcrop on erosional rises and hills;
- open chenopod shrublands dominated by *Maireana pyramidata* and *Atriplex vesicaria* with *Casuarina pauper* and *Acacia cambagei*. This community typically colonises alluvial and colluvial depositional plains; and,
- riparian woodlands dominated by *E. camaldulensis* and open shrublands co-dominated by *Maireana pyramidata* and grasses. This community typically colonises the low-lying landscape settings, such as major drainage channels and alluvial outwash plains.

3.17.1 Geology

Williams Creek is on the Kayrunnera 1:100 000 geological mapsheet (7436) (Mills & Hicks, 2001), which includes the eastern margin of the Koonenberry fold and thrust belt. The general geology consists of Palaeozoic rocks, with Cretaceous sediments associated with the Eromanga Basin onlapping the Palaeozoic rocks in the east and north (Mills, 2002). The landscape is characterised by a northwesterly trending range of Devonian quartzites and quartz sandstones (Coturaundee Range). Immediately flanking the range are sediments mostly from the Jurassic-Cretaceous (Eromanga Basin), and are onlapped by an assortment of alluvial and colluvial sediments derived from the Coturaundee Range, and reworked and deposited throughout the Cainozoic to the present day.

3.17.2 Mineralisation

After the initial Au-rush to the Albert Goldfield (Tibooburra, Mt Browne, New Bendigo and the Warratta inliers), smaller parties of prospectors began to explore further into the Koonenberry region. This led to the discovery of a number of local finds such as at Williams Peak. Mineral exploration proximal to Williams Creek since early 1880 revealed Au at Peak Tank (Williams Peak Goldfield), and silver and copper at Wertago (Nuntherungie Silverfield and Wertago Copperfield) (Mills, 2002). Mineralisation across the region is generally confined to either reefs (Au and/or Cu bearing), vein systems or possible stratiform 'lode' (Cu, Zn, Pb/Ag, or Au-bearing) and placer/alluvial Au deposits (Fleming, 1995).

Williams Peak Goldfield (formerly known as Peak Tank Goldfield, Candy Peak and Kandie Peak; Steel, 1881; Rodgerson, 1890; Rodgerson, 1891 and Mills, 2002) is approximately 2 km northeast of the sample tree. Williams Peak is described by Pitman, (1894, p. 112) as "an isolated conical hill of Upper Silurian slate, unconformably capped by Upper Cretaceous quartz and ironstone conglomerate. The tenant of the Peak Government Tank (Peter Riley) has obtained a reasonable amount of alluvial gold, by following the ironstone conglomerate, and working the gullies with which it intersects such as Williams Creek". Recent mapping by Mills (2002) reports that Pitman's findings were correct and the Au is contained in the Mesozoic basal quartz pebble conglomerate, and that Williams Peak Goldfield possibly has a

significant association with a number of small granitic intrusions and a major fault (Xmas Tank Fault) within the Teltawongee Beds. Mining included driving 20-30 m adits and shallow shafts into the side of the hill and following Au placer deposits at the unconformity between the basal quartz conglomerate and metasediment basement. The grade and production is unknown but is suggested to be low, as primary reefs were explored without success. Table 3.18 summarises mineral exploration surveys that have been conducted in the area, and the exploration methods employed (Barnes, 1974; Lewis, 1976; Wood, 1988 and Fleming, 1995).

Mineral Deposit	Company	Exploration Lease	Year	Method	Mineralisation Target	Results
Nuntherungie	Esso Exploration & Production Australia Inc.	EL 824	1975-1977	Airborne EM survey, rock chip sampling and drilling	Pb/Ag mineralisation	Average grades 55oz/t Ag, 26% Pb
Big Wertago Mine	Lone Star Exploration NL	EL 437	1971-1972	Mapping, sampling, and diamond drilling	Cu/Pb mineralisation	5000 tones Cu produced
Nil Desperandum	M.IM exploration Pty Ltd	EL 1976/2635	1995-2001	Aeromagnetic and radiometric surveys, chip and soil sampling	Cu and Au mineralisation	Ore proven to 32 m depth. Production 1890's 183 oz/t Ag and 1 oz/t Au
Kayrunnera Diatreme	CRA Exploration	EL 2649 Brunker and 2650 Silverfield	1986	Aeromagnetic surveys, ground magnetics, and soil sampling	Kimberlitic pipes Diamonds	No diamond or microdiamonds were recovered

Table 3.18: Shows that for the most part, previous exploration in the Williams Creek (Williams Peak) area for polymetallic minerals such as Cu, Au, Pb and Ag has been quite successful; however the ore grades are generally low and the deposit size small to medium.

3.18 WILLIAMS CREEK EUCALYPTUS CAMALDULENSIS CHARACTERISTICS

The Williams Creek *E. camaldulensis* is a gnarled tree with a girth of 1.94 m and a spreading open canopy that extends from ground level up to approximately 35 m. The bark is smooth, except near the base where it is rough with large shedding strips. Twigs are brown, ranging between 2-5 mm in diameter. Buds are stalked and have a beaked conical shape and are typically in clusters of 5-6. Leaves are alternating, pendulous, narrowly lanceolate approximately 11-13 cm long and 1- 1.5 cm wide, pale green on both the adaxial and abaxial surface. The sampled *E. camaldulensis* is one part of a *E. camaldulensis* riparian woodland along the main drainage channel. Figure 3.35 illustrates the location of the *E. camaldulensis* and its position in relation to adjacent *E. camaldulensis* trees (plan view) and a profile view of the channel, which is approximately 42.70 m wide and is incised up to 5.90 m on the west and 0.30 – 0.50 m on the east.



Figure 3.35: A cartoon illustrating the location of the Williams Creek (Williams Peak) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* s (plan view) and a profile view of the channel.

The ephemeral channel (Williams Creek) hosting the *E. camaldulensis* has an approximate length of 25 km, flowing southwest to northeast. The channel incises many different bedrock lithological units across the area, some hosting known Cu, Au, Pb and Ag mineralisation.

3.18.1 Organ Tissue Biogeochemistry Results

Samples of leaves, twigs, fruit, buds and bark were taken during autumn 2003 at the Williams Creek study site. Eight samples per medium (leaves and twigs), and single samples of composite buds, fruit and bark were collected from the reachable N, NE, E, SE, S, SW, W and NW sectors around the *E. camaldulensis* canopy. Fifty-two elements were assayed by combined INAA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. The elements Sb, Cs, Eu, Hf, Ir, Lu, Mo, Rb, Se, Ag, Ta, Te, Th, W, U, Zr, Be, Bi, Cd, Ga, In, Nb, Pb, Ti and V were below analytical detection limits in all sampling media, while Co was only detected in leaves. The concentrations of twenty-five elements were detectable from the *E. camaldulensis* organs, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.19. All elements with > 25 % of their values below detection limits have been removed from the data set.

Table 3.19: Variations of metal concentrations within different oven dried tissues of an individual *E. camaldulensis*, at Williams Creek (Williams Peak). Initial value represents the mean; values in brackets () are the range of values; C = composite sample and * signifies values below detection limit. To calculate the means, below detection limit values were taken as half the detection limit value. Values with a mean but no range reperied paragraphic action and the data set no the number of samples reconversed for each organ.

Element (ppm)	Leaves (n=8)	Twigs (n=8)	Fruit (8)	Buds (C)	Bark (n=1)
Na	43 (20-80)	171 (90-350)	200	40	200
Mg	2128 (1793-2523)	2269 (1440-3485)	1991	1939	1338
Al	161 (103-216)	101 (76-164)	145	65	10
Р	1278 (1192-1394)	864 (481-1703)	1554	1804	217
S	1065 (998-1179)	437 (400-488)	647	190	186
Κ	9567 (9060-11900)	4178 (2420-7890)	9170	11600	2350
Ca	9837(8600-11500)	25250 (17100-35100)	12300	7300	69100
Sc	0.07 (0.047-0.088)	0.03 (0.024-0.037)	0.037	0.017	*
Cr	0.41 (*- 0.71)	*	0.51	0.30	*
Mn	111 (75-150)	130 (87-174)	102	84	280
Fe	198 (140-240)	84 (50-110)	110	70	25
Co	0.27 (0.21-0.33)	*	0.51	0.3	*
Ni	1.44 (*-2)	2.5 (*-8)	2	2	*
Cu	7.9 (7-9)	19 (15-22)	7	10	2

Element (ppm) Leaves (n=8)		Twigs (n=8)	Fruit (8)	Buds (C)	Bark (n=1)
Zn	18 (16-22)	21 (17-26)	15	22	11
As	0.08 (*-0.14)	0.03 (*-0.068)	*	*	*
Br	10.3 (8.30-11.50)	3.4 (2.54-4.23)	8.92	7.70	1.73
Sr	55.09 (50.25-60.21)	172 (124.12-233.34)	83.46	42.86	368.87
Sn	0.23 (*-0.5)	0.29 (0.20-0.50)	0.20	0.20	0.20
Ba	42.1 (29.8-51.7)	59.4 (38.2-83.1)	46.6	36.9	59.5
Au ppb	0.17 (*-0.32)	0.64 (*-1.31)	*	*	1.15
La	0.18 (0.13-0.23)	0.11 (0.09-0.12)	0.103	0.043	0.011
Ce	0.57 (0.44-0.73)	0.31 (*-0.46)	0.51	0.22	*
Nd	0.14 (0.1-0.2)	0.095 (0.07-0.11)	0.13	0.04	*
Sm	0.04 (0.033-0.048)	0.029 (0.025-0.032)	0.027	0.015	0.011

Of the twenty-five elements assayed, Na, Mg, Ni, Cu, Zn, Sn, Ba and Au were of highest concentrations within the twigs. Elements Al, S, K, Sc, Cr, Fe, As, Br, La, Ce, Nd and Sm were most abundant in the leaves. The concentration of P was highest in the buds followed by Ca, Sr and Mn being more abundant in the bark.

3.18.2 Comparison Between Element Concentrations in Eucalyptus camaldulensis and

Adjacent Stream Sediment Chemistry

Fifty-three elements were assayed (Appendix. C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Cd, In, Sb, Se and Te were below detection limit in one or more sectors for both stream sediment size fractions. The chemical compositions of twenty-five elements were detectable in both leaves and twigs, while Co was only detectable in the leaves. For all media, Al, As, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm were detectable. Table 3.20 shows which sector for *E. camaldulensis* leaves, twigs and adjacent stream sediment <75 μ m and 75-300 μ m size fractions have the maximum and minimum trace element concentrations.

Element	Leaves	Leaves	Twigs	Twigs	Stream	Stream	Stream	Stream
(DL) (ppm)	conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ	Maximum	Minimum	Maximum	Minimum
(ppin)	conc	conc	cone	conc	conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ
	(ppm)	(ppm)	(ppm)	(ppm)				
					(ppm) <75 μm	(ppm) <75 μm	(ppm) 75-300 µm	(ppm) 75-300 µm
					fraction	fraction	fraction	fraction
Na (100)	SW (80)	W (20)	SW (350)	W (90)	E (3550)	N (3200)	NW (1900)	N (1200)
Mg (20)	E (2523)	W (1793)	S (3485)	W (1440)	SW (3850)	NE (2450)	NW (2300)	N (1450)
Al (20)	E (216)	NW (103)	W (164)	NW (69)	SW (52100)	NE (35700)	NW (29700)	N (19300)
P (20)	SE (1394)	NW (1192)	NW (1703)	S (481)	W (230)	NE (140)	NW (175)	N (100)
S (10)	N (1179)	E (998)	NW (488)	SW (400)	SW (250)	NE (100)	S & SW (200)	N, NE, E, SE,
								W & NW
								(150)
K (1000)	SW (11900)	E (1150)	NW (78900)	S (2420)	SW (12400)	NE (9600)	NW (8950)	N (6250)
Ca (5000)	N (11500)	S (9000)	S (35100)	NE (17100)	SW (4500)	NE (2550)	SW (2450)	N (1150)
Sc (0.05)	E (0.088)	N (0.037)	N (0.047)	SE (0.024)	Not in assay	Not in assay	Not in assay	Not in assay
					suite	suite	suite	suite
Cr (0.30)	NW (0.71)	N, SW & W	W (0.43)	E, S & SW	N, S & W (37)	NW (28)	W (22)	N (14)
		(BDL)		(BDL)				
Mn (1)	N (150)	S (75)	SE (174)	W (87)	N (330)	NW (240)	NW (190)	N, NE & SE
								(140)
Fe (50)	E (240)	W (140)	N (110)	SW (50)	W (25900)	NE (19900)	NW (17300)	N (13200)
Co (0.20)	NE (0.33)	W (0.21)	BDL (all	BDL (all	SW & W (8.5)	NE (5.5)	NW (5.5)	NE (3.8)
			sectors)	sectors)				
Ni (1)	N, E, SW &	SE (BDL)	S (8)	SE (BDL)	SW (18)	NE (10)	E, SW & NW	SE (9)
	NW (2)						(11)	
Cu (1)	NE & SE (9)	E, S & W (7)	NE (22)	N & E (15)	NW (30)	SE (19)	NW (22)	N (14)

Table 3.20: Shows which sector for *E. canaldulensis* leaves and twigs and adjacent stream sediments size fractions <75 µm and 75-300 µm have the maximum and minimum trace element concentrations at Williams Creek (Williams Peak).

Element (DL)	Leaves Maximum	Leaves Minimum	Twigs Maximum	Twigs Minimum	Stream sediments	Stream sediments	Stream sediments	Stream sediments
(ppm)	conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ	Maximum	Minimum	Maximum	Minimum
					conc ⁿ	conc ⁿ	conc ⁿ	conc ⁿ
	(ppm)	(ppm)	(ppm)	(ppm)				
					(ppm)	(ppm)	(ppm)	(ppm)
					<75 μm	<75 μm	75-300 μm	75-300 μm
					fraction	fraction	fraction	fraction
Zn (1)	SE (22)	E, S & W (16)	S & NW (26)	W (17)	W (60)	NE (42)	S & NW (28)	NE & SE (21)
As (0.05)	S (0.142)	N & NW	E (0.068)	NE, SE, S,	SW (4)	W (1)	NW (3.5)	NE & W (2)
		(BDL)		SW, W & NW				
				(BDL)				
Br (0.2)	N & SW	W (8.30)	S (4.23)	W (2.54)	Not in assay	Not in assay	Not in assay	Not in assay
	(11.50)				suite	suite	suite	suite
Sr (0.05)	NE (60.21)	NW (50.25)	S (233.34)	NE (124.12)	SW (94)	E (70)	NW (52)	N & NE (40.5)
Sn (0.1)	N (0.50)	SW & W	NE & SW	N, E, S, SW,	SW & W (2.3)	SE (2)	NW (1.4)	NE (0.9)
		(BDL)	(0.50)	W & NW				
				(BDL)				
Ba (10)	N (51.70)	S (29.80)	S (83.10)	W (38.20)	S (370)	NE & SE (300)	SW (290)	NE (250)
Au (0.30	N (0.32 ppb)	NE, E, SE, S,	NW (1.31 ppb)	NE (0.41 ppb)	N (8 ppb)	NW (BDL)	W (4 ppb)	E & NW (1
ppb)		SW, W & NW						ppb)
		(BDL)						
La (0.01)	E (0.23)	N (0.12)	N (0.12)	SE (0.09)	W (60)	NW (37.5)	NW (23)	N (18.5)
Ce (0.20)	E (0.73)	N (0.44)	NW (0.46)	S (BDL)	W (105)	NW (62)	SW (42.5)	E (31.5)
Nd (0.01)	E (0.20)	NW (0.10)	N, NE, E & SE	NW (0.07)	N & W (45.5)	NW (28.5)	NW (18.5)	N (14)
			(0.11)					
Sm (0.01)	SE & S (0.044)	N (0.033)	NW (0.032)	SE (0.025)	N & W (9)	NW (5.5)	NW (3.8)	N (2.8)

There does not appear to be a link between maximum/minimum vegetation element concentration and maximum/minimum stream sediment element concentrations for each of the sectors. There may be a relationship between leaves and twigs minimum concentration in the W sector for Br, Mg, Na, Sn and Zn. Of the twenty-five elements detected, the N & E sector leaves, S & NW sector twigs, SW & W sector <75 μ m size fraction and NW sector 75-300 μ m size fraction have the most elements with the highest concentration. The W sector leaves, W sector twigs, NE sector <75 μ m size fraction and N sector 75-300 μ m size fraction have the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum: N (Au, Ba, Br, Ca, Mn, Ni, S and Sn), NE (Co, Cu and Sr), E (Al, Ce, Fe, La, Mg, Nd, Ni and Sc), SE (Cu, P, Sm and Zn), S (As and Sm), SW (Br, K, Na, and Ni) and NW (Cr and Ni);
- leaves minimum: N (As, Au, Ce, Cr, La, Sc and Sm), NE (Au), E (Au, Cu, K, S and Zn), SE (Au and Ni), S (Au, Ba, Ca, Cu, Mn and Zn), SW (Au, Cr and Sn), W (Au, Br, Co, Cu, Fe, Mg, Na, Sn and Zn) and NW (Al, As, Au, Nd, P and Sr);
- twigs maximum: N (Fe, La, Nd and Sc), NE (Cu, Nd and Sn), E (As, Nd), SE (Mn and Nd), S (Ca, Ba, Br, Mg, Ni, Sr and Zn), SW (Na and Sm), W (Al and Cr) and NW (Au, Ce, K, P, S, Sm and Zn);
- twigs minimum: N (Cu and Sn), NE (As, Au, Ca and Sr), E (Cr, Cu and Sn), SE (As, La, Ni, Sc and Sm), S (As, Ce, Cr, K, P and Sn), SW (As, Cr, Fe, S and Sn), W (As, Ba, Br, Mg, Mn, Na, Sn and Zn) and NW (Al, As, Nd and Sn);
- <75 μm fraction maximum: N (Au, Cr, Mn, Nd and Sm), E (Na), S (Ba and Cr), SW (Al, As, Ca, Co, K, Mg, Ni, S, Sn and Sr), W (Ce, Co, Cr, Fe, La, Nd, P, Sm, Sn and Zn) and NW (Cu);
- <75 μm fraction minimum: N (Na), NE (Al, Ba, Ca, Co, Fe, K, Mg, Ni, P, S and Zn), E (Sr), SE (Ba, Cu and Sn), W (As) and NW (Au, Ce, Cr, La, Mn, Nd and Sm);
- 75-300 µm fraction maximum: E (Ni), S (S and Zn), SW (Ba, Ca, Ce, Ni and S), W (As and Cr) and NW (Al, As, Co, Cu, Fe, K, La, Mg, Mn, Na, Nd, Ni, P, Sm, Sn, Sr and Zn); and,

75-300 μm fraction minimum: N (Al, Ba, Ca, Cr, Cu, Fe, K, La, Mg, Mn, Na, Nd, P, S, Sm and Sr), NE (As, Co, Mn, S, Sr and Zn), E (Au, Ce and S), SE (Mn, Ni, S and Zn), W (As and S) and NW (Au and S).

The maximum and minimum rare earth element contents in the stream sediments for both size fractions are within the same sectors, and several of the other elements for all media have maximum and minimum concentrations in more than one sector (Table 3.20). Some of the elements assayed for all media sampled are similarly distributed between sectors due to their similar chemical properties, such as: (Au and Cu), (Ba, Ca, Mg and Sr), (Ce, Nd and Sm), (La and Sc), (Co, Ni and Fe), and (K, Na and Rb).

3.18.3 Elemental Trends

Due to the small data set (n = 8), scatter diagrams (Figure 3.36) were constructed to determine whether or not the relationships between Al, As, Ca, Cu, K, Mn, Nb, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm within different media (leaves, twigs, $<75 \ \mu m$ and 75-300 μm size fractions) conforms to a linear relationship. The results show that only a small group of elements produced a trend possibly approaching a linear relationship. The results for Sn in twigs and the $<75 \ \mu m$ stream sediment size fraction, and Fe in twigs, and Nd in twigs and the 75-300 μm size fraction revealed a trend approaching a negative relationship. In contrast, Na in leaves and the $<75 \ \mu m$ size fraction produce a trend approaching a positive relationship. The overall negative trend possibly implies that as the elements become available within the pore/soil water the *E. camaldulensis* may preferentially exclude them, or that other factors are involved.



Figure 3.36: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and 75-300 μm at Williams Creek (Williams Peak).
Stream sediment trace element concentrations revealed that the $<75 \mu m$ size fraction had higher concentrations compared to the 75-300 μm size fraction for Al, Fe, K, Ti, Na, Ca, Mg, Ba, Mn, P, S, Ce, Sr, V, Rb, Zn, La, Nd, Cr, Cu, Y, Th, Ni, Pb, Ga, Nb, Pr, Sm, Co, Gd, Dy, As, U, Yb, Cs, Sn, Er, Eu, W, Ho, Ag, Tm, Mo, Lu, TI, Bi and Au (Figure 3.37).



Figure 3.37: Variations of metal concentrations within $<75 \ \mu m$ and $75-300 \ \mu m$ stream sediments size fractions surrounding the *E. canaldulensis*, Williams Creek (Williams Peak). To calculate the means, below detection limit values were taken as half the detection limit value.



Figure 3.38: The element composition and index accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking stream sediments at Williams Creek (Williams Peak). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The compositions of the Williams Creek *E. camaldulensis* leaves and twigs (Figure 3.38) shows that leaves have a higher concentration of K. P, S, Fe, Al. Cr, Sn, Co, La, Nd, As and

Sm compared to the twigs, which have higher concentrations of Ca, Mg, Mn, Sr, Na, Ba, Zn, Cu, Ni, Sn and Au. Only the leaves had detectable Co, possibly reflecting a preferential allocation of this element within the *E. camaldulensis* leaves.

In general, there is a decrease in element concentration from elements classified as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.38) illustrates that for both the <75 μ m and 75-300 μ m size fractions some elements are more bioavailable and readily taken up by the *E. camaldulensis* than others. The following summarises the index of bioaccumulation from both size fractions (75 μ m and 300 μ m) for leaves and twigs:

- <75 μm size fraction (twigs): P, S, Ca and Sr (high), K, Mg, Mn, Zn, Cu, Sn, Ba, Ni and Au (medium), As, Cr and Na (slight) and Fe, Sm, La, Nd and Al (low);
- <75 μm size fraction (leaves): P, S and Ca (high), K, Sr, Mg, Mn, Zn, Cu, Sn, Ba and Ni (medium), Au, Co, As, Cr and Na (slight) and Fe, Sm, La, Nd and Al (low);
- 75-300 µm size fraction (twigs): Ca (very-high), P, S, Sr, Mg and Cu (high), K, Zn, Mn, Sn, Ba, Ni, Au and Na (medium) and Cr and As (slight) and Fe, Sm, La, Nd and Al (low); and,
- 75-300 μm size fraction (leaves): P, S, Ca, K, Sr and Mg (high), Zn, Mn, Cu, Sn, Ba, Ni and Au (medium), Co, Cr, As, Na, Fe and Sm (slight) and La, Nd and Al (low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements, these results are consistent with similar relationships found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.19 WILLIAMS CREEK TEMPORAL ELEMENT VARIATIONS WITHIN A *EUCALYPTUS CAMALDULENSIS*

In general, Ba, Br, Ca, Ce, Fe, La, K, Sm, Sc, Zn, Al, Cu, Mg, Mn, Nd, P, S and Sr are detectable in the leaves across all seasons for 2003 and 2004. Elements As, Cr, Au, Na and Ni recorded below analytical detection limit concentrations for either one or more seasons. All of these elements, with the exception of Br, Ba, Na, Ce, La, Sm, Sc, As, Nd, Au, Cr and Sr, are considered to be essential. Table 3.21 and Figure 3.39 - Figure 3.44 presents the rainfall and temporal fluctuations in element concentrations for *E. camaldulensis* (leaves) at Williams Creek for all seasons for 2003 and 2004.

Table 3.21: Elemental composition of *E. camaldulensis* (leaves) sampled at Williams Creek (Williams Peak) across all seasons for 2003 and 2004. High values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded e.g. 2003 (Ba – 42 ppm; autumn), while yellow represents the season in which the highest concentration was recorded e.g. 2004 (Ca – 19000 ppm; summer) BDL denotes below detection limit.

ppin, summer) DDL	denotes below det	cetion mint.						
Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
As ppm	0.07	BDL	BDL	0.10	BDL	BDL	BDL	0.11
Ba ppm	42	47	59	74	64	81	97	100
Br ppm	10	8	6	9	12	9	7	8
Ca ppm	9838	14500	17500	15700	15300	15500	17000	19000
Ce ppm	0.57	0.25	0.25	0.54	0.25	0.25	0.50	0.50
Cr ppm	0.41	BDL	BDL	0.63	0.87	BDL	BDL	BDL
Au ppb	0.32	0.93	BDL	BDL	BDL	BDL	BDL	BDL
Fe ppm	199	96	111	173	208	187	210	220
La ppm	0.18	0.11	0.13	0.19	0.21	0.19	0.20	0.30
K ppm	9568	8120	7150	7890	9860	6800	5000	5000
Sm ppm	0.04	0.03	0.03	0.04	0.05	0.04	0.04	0.04

Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
Sc ppm	0.07	0.03	0.04	0.06	0.08	0.06	0.07	0.08
Na ppm	44	33	43	43	41	59	BDL	50
Zn ppm	18	13	18	18	32	24	19	23
Al ppm	161	59	86	246	246	138	159	218
Cu ppm	7	7	7	8	6	5	5	7
Mg ppm	2128	2186	2474	2276	2451	2934	2570	2774
Mn ppm	111	145	166	117	105	147	191	209
Nd ppm	0.14	0.08	0.08	0.20	0.21	0.16	0.17	0.17
Ni ppm	1	2	1	7	2	BDL	2	BDL
P ppm	1279	1150	1523	1265	1056	1082	1319	1739
S ppm	1065	1036	1130	840	950	957	1080	1190
Sr ppm	55	86	89	77	80	93	116	125

The physical appearance of the *E. camaldulensis* sampled at Williams Creek across 2003 and 2004, was:

- 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.

Group A Element (Periods of growth): more abundant during periods of growth. Spring and summer, are characterised by temperatures with an average maximum of 32.6°C and minimum of 17.7°C in 2003, and an average maximum of 31.9°C and minimum of 17.7°C in 2004. The average rainfall for these periods was 19 mm in 2003 and 10 mm in 2004. From September to February (spring and summer) 2003, As, Ba, Cr, La, Sm, Al, Cu, Mg, Mn, Nd and Ni, and for the same period in 2004, As, Ba, Ca, Fe, La, Sc, Cu, Mn, P, S and Sr showed a gradual increase in concentration, recording their highest concentrations in summer. While in 2003 Au and Zn and in 2004 Ce, Cr, Au, K, Sm and Nd remained unchanged. In contrast, during the summer of 2003 Ca, Na, Mg, Mn, P, S and Sr recorded a decrease in concentration.

Group B Elements (Periods of non-growth): reduced concentration levels during periods of non-growth. Autumn and winter, are characterised by temperatures with an average maximum of 22.65°C and minimum of 9.8°C in 2003, and an average maximum of 23.2°C and minimum of 9.8°C in 2004. The average rainfall for these periods was 26.5 mm in 2003 and 15.2 mm in 2004. From March to August (autumn to winter) 2003, Ce, Fe, La, Sm, Sc, Na, Zn, Al, Cu, Nd and P and for the same period in 2004, Fe, La, Sm, Sc, Al, Cu and Nd concentration showed a gradual decrease, and recorded their lowest concentration in the winter. While elements Ba, Ca, Mg, Mn and Sr in 2003, and elements Ba, Ca, Ce, Mg, Mn, P, S and Sr in 2004 recorded their lowest concentration in the autumn.

There is little difference in the minimum and maximum temperatures between 2003 and 2004. The rainfall pattern for 2003 is quite consistent, compared to the rainfall for 2004, which is more erratic. The general trend across 2003 is that As, Ba, Ca, Cr, La, Sm, Zn, Al, Cu, Mg, Mn, Nd, Ni, P and Sr and for the same period in 2004 As, Br, Ca, Ce, Fe, La, Sc, Cu, Mn, P, S and Sr have higher concentrations during periods of growth (spring/summer). During periods of non-growth (autumn/winter) all of the above elements in 2003 and in 2004 have reduced concentrations. However Br, Ce, Au, Fe, K, Sc and Na in 2003, and Br, Cr, K, Sm, Na, Zn, Al, Mg, Nd and Ni 2004 do not follow this general trend. The overall rainfall difference between 2003 and 2004 is 10.62 mm (Bureau of Meteorology, 2005d). The results show that

elements As, Ba, Ca, Ce, Fe, La, Sm, Sc, Zn, Al, Mg, Mn, Nd, P, S and Sr in 2004 have a higher concentrations compared to 2003. This possibly suggests that the consistent rainfall, which fell at this site during 2003, continued to provide a soil/pore water nutrient-rich source that was available throughout 2004.



Figure 3.39: Rainfall and the temporal fluctuations in As, Ba, Br and Ca for *E. camaldulensis* (leaves) at Williams Creek (Williams Peak). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.40: Rainfall and the temporal fluctuations in Ce, Cr, Au and Fe for *E. camaldulensis* (leaves) at Williams Creek (Williams Peak). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).





Figure 3.42: Rainfall and the temporal fluctuations in Na, Zn, Al and Cu for *E. camaldulensis* (leaves) at Williams Creek (Williams Peak). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.43: Rainfall and the temporal fluctuations in Mg, Mn, Nd and Ni for *E. camaldulensis* (leaves) at Williams Creek (Williams Peak). - ---- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.44: Rainfall and the temporal fluctuations in P, S and Sr for *E. camaldulensis* (leaves) at Williams Creek (Williams Peak). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year).

3.19.1 Williams Creek Elemental Variability

The results shown in Table 3.22 show the degree of element variability during periods of either enhanced plant growth or reduced plant growth for the Williams Creek (Williams Peak) *E. camaldulensis* during the 2003 and 2004 seasons.

Table 3.22: Shows the degree of elemental variation for the *E. camaldulensis* studied at Williams Creek (Williams Peak) between (2003 and 2004) periods of plant growth (G) shown by a green asterisk (*) and periods of reduced plant growth (RG) shown by a black asterisk (*) and defines the optimal sampling period that should be utilised for selected elements. BDL = below detection limit.

Parameters	Nos	seasona	ıl varia	bility	Sli; vari	ght s abili	eason ty <30	al 0%	Lo varia	ow se abili	easona ty ~ 30	al 0%	In	tern seas	nediat onal	e	Hi varia	gh se abilit	easona ty > 80	al 0%
Voors	21	003	20	04	200	03	200	04	200	13	200	14	varia 200	aDIII 13	<u>1y ~ 5</u> 201	070 M	200	13	200	14
1 cars	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
As			BDL			Ŭ		Ŭ		Ŭ		Ŭ	*	*		*		Ŭ		<u> </u>
Ba					*	*	*	*												
Br					*		*	*		*										
Ca						*	*	*	*											
Ce			*	*									*	*						
Cr				BDL									*	*					*	
Au		BDL	BDL	BDL													*			
Fe							*	*		*			*							
La						*	*		*			*								
K				*	*	*					*									
Sm				*		*	*		*											
Sc							*	*		*			*							
Na					*	*	*													*
Zn		*			*		*	*												
Al								*					*	*	*					
Cu					*	*	*	*												
Mg					*	*	*	*												
Mn					*	*	*	*												
Nd				*			*						*	*						
Ni					*										*	*		*		
Р					*	*	*	*												
S					*	*	*	*												
Sr						*	*	*	*											

The degree of concentration variability across 2003 and 2004 for the *E. camaldulensis* is mostly slight (< 30%) for Ba, K, Sm, Na, Zn, Cu, Mg, Mn, P and S; slight – low (< 30% - ~ 30%) for Br, Ca, La, Sc and Sr; intermediate (~ 50%) for As; intermediate – high (~ 50% - > 80%) for Ni and variable for Fe, Al and Nd with concentration variabilities lying within more than one parameter. The slight to intermediate variation suggests that seasonal variations are less important for many of the elements, with the exception of Ni, which suggests that the most appropriate sampling period for expressing higher content is summer.

3.20 TEILTA: TEILTA CREEK (SETTING)

Teilta Creek is approximately 150 km north-northwest of Broken Hill. The *E. camaldulensis* tree sampled here is approximately 47 km west of the Silver City Highway, on the Cobham Lake 1:250 00 topographic mapsheet (SH54-11), and the Teilta 1:100 000 mapsheet (Hill, 2005) (Figure 3.47). Grid reference 524669 mE; 6578007 mN.

The area experiences a semi-arid climate, with warm to very hot summers and cool winters, and an unpredictable and generally low annual rainfall predominately in the summer. The closest meteorological station to the site is at Fowlers Gap AWS (Automatic Weather Station). The annual rainfall for the area is 272.4 mm with temperatures ranging from an average summer maximum of 31.3°C to an average winter minimum 12.3°C (Croft, D. 2007, pers.comm.). The region surrounding the study site is classified as the Simpson-Strzelecki Dunefield Bioregion (Sahukar, *et al.*, 2003).

The landscape immediately surrounding the *E. camaldulensis* includes erosional rises with low topographic relief of 0-9 m (Figure 3.45). The highest parts in the area are between 100 m and 200 m (above sea level) with Mount Westwood and neighbouring peaks, and a north-south trending ridge of rises and low hill associated with the northern margin of the Woowoolahrah Range, south of Joulnie Homestead (Kenny, 1934; Hill, 2004). Elevation generally decreases westwards towards the low-lying northeast trending longitudinal dunes associated with the Strzelecki Desert, which is approximately 68 m above sea level and eastward towards the western slope of Mount Westwood, which is characterised by alluvial and sheetwash sediment plains mantled by gibber plains (Hill, 2005).



Figure 3.45: An image of the E. camaldulensis at Teilta Creek (Teilta), and the surrounding low-lying regolith dominated landscape.

Drainage across the study area occurs within ephemeral drainage depressions, flowing from east to west, extending west from Mount Westwood and the Woowoolahrah Range, ultimately terminating in alluvial swamps and lacustrine depressions within the Strzelecki Desert (Hill, 2005) and finally towards the Lake Frome plains.

The vegetation communities and dominant species in the region are very closely associated with the major landform settings. The general characteristics in the area as described by Hill (2005) are:

- open chenopod shrubland dominated by saltbush (*Atriplex spp.*) and bluebush (*Maireana spp.*), with some areas of open woodland with mulga (*Acacia aneura*), belah (*Casuarina pauper*) and rosewood (*Alectryon oleofolius*). This community typically colonises weathered bedrock rises and hills;
- open chenopod shrubland dominated by saltbush (*Atriplex spp.*) and bluebush (*Maireana spp.*) with communities of mitchell grass (*Astrebla pectinata*). This community generally colonises regions of colluvial and alluvial outwash plains;
- open woodlands dominated by white cypress pine (*Callitris columellaris*) and belah (*Casuarina pauper*), with minor mulga (*Acacia aneura*). This community typically colonises aeolian dunefields, and hopbush (*Dodonaea* spp.) colonises aeolian sandplains; and,
- riparian woodlands dominated by *E. camaldulensis* colonise major drainage channels in the south, while major drainage channels in the north are colonised by coolibah (*Eucalyptus microtheca*) and beefwood (*Grevillea striata*), with smaller tributaries colonised by prickly wattle (*Acacia victoriae*).

3.20.1 Geology

Teilta Creek is within the Cobham Lake 1:250 000 geological mapsheet (SH 54-11) (Brunker & O'Connell., 1967). Prior to mid-1990 little was known about the underlying bedrock geology, as the area has minimal bedrock exposure (Hill, 2005), with an estimated transported regolith thickness >300 m (Cameron, 1993a). Mineral exploration drilling and geophysics conducted during the mid-1960s to the late 1980s and early 1990s by companies such as Kennecott Exploration, CRAE and BHP minerals within the Teilta region, have interpreted the underlying bedrock to include the Palaeo-Proterozoic Willyama Supergroup composed predominately of metasediments and metavolcanics that are unconformably overlain by Neoproterozoic Adelaidean metasediments and metavolcanics (Cameron, 1993a & b; de Caritat & Kirste, 2004; Hill, 2005; Ruperto, 2004). To the east, Neoproterozoic Adelaidean metasediments form the northwest margin of the Barrier Ranges, and previously undescribed exposures proximal to Teilta and Joulnie homesteads (Hill, 2005), while to the west the area is within the southeastern margins of the Mesozoic Eromanga Basin (Krieg & Rogers, 1995). Although extensive towards the northwest, their surface expression is poor due to northeast trending longitudinal linear aeolian dunes and or shallow gibber surface lags associated with surficial sheetwash sediments (Hill, 2005), and sediments associated with the Cainozoic Lake Eyre Basin (Alley, 1998).

3.20.2 Mineralisation

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. They were searching for base metal (Cu-Au and Zn-Pb-Ag) mineralisation within covered Palaeo-proterozoic Willyama Supergroup and Neo-proterozoic Adelaidean metasediments (Cameron, 1993a & b). Table 3.23 summarises mineral exploration surveys

undertaken across the Teilta region over the last 28 years and the exploration methods that were employed.

Table 3.23: An overview of selected exploration surveys undertaken across Teilta. 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.

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

3.21 TEILTA CREEK EUCALYPTUS CAMALDULENSIS CHARACTERISTICS

The Teilta Creek *E. camaldulensis* is a gnarled tree with a girth of 5.97 m and a spreading open canopy that extends from the ground level up to approximately 38 m. The bark is smooth, except near the base where it is rough with large shedding strips. Twigs are brown, ranging between 2-5 mm in diameter. Buds are stalked and have a beaked conical shape and are typically in clusters of 5-6. Leaves are alternating, pendulous, narrowly lanceolate approximately 11-15 cm long and 1- 2 cm wide, pale green on both the adaxial and abaxial surface. The tree is part of a *E. camaldulensis* woodland corridor along the main drainage channel. Figure 3.46 illustrates the location of the *E. camaldulensis* and its position in relation to adjacent *E. camaldulensis* trees (plan view) and a profile view of the channel, which is approximately 24.7 m wide and is incised up to 0.87 m on the southwest and 0.9 m on the northeast.



Figure 3.46: A cartoon illustrating the location of the Teilta Creek (Teilta) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* (plan view) and a profile view of the channel.

The ephemeral channel (Teilta Creek) hosting the *E. camaldulensis* has an approximate length of 20 km, flowing southwest to northeast. The channel incises many different bedrock

lithological units across the area, in which some host minor Cu-Au and Ag-Pb-Zn mineralisation. To date there are no known mineral deposits proximal to the Teilta Creek *E. camaldulensis*.

3.21.1 Organ Tissue Biogeochemistry Results

Sampling of leaves, twigs, buds, root and bark was undertaken at the Teilta Creek study site. Five samples of leaves and twigs, and single composite samples of buds, root and bark were collected from the reachable N, E, SW, W and NW sectors around the *E. camaldulensis* canopy. Fifty-two elements were assayed by combined INAA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. The elements Sb, Cs, Co, Eu, Hf, Ir, Lu, Mo, Se, Ag, Ta, Te, Th, W, U, Yb, Zr, Be, Bi, Cd, Ga, In, Pb, Ti and V were below analytical detection limits in all sampling media. The element Cr was only detectable in leaves and root samples. The chemical compositions of twenty-seven elements were detectable from the *E. camaldulensis* organ tissues, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.24. All elements with > 25 % of their values below detection limits have been removed from the data set.

Table 3.24: Variations of metal concentrations within different oven dried tissues of an individual *E. camaldulensis*, at Teilta Creek (Teilta). Initial value represents the mean; values in brackets () are the range of values; C= composite sample and * signifies values below detection limit. To calculate the 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.

Element (ppm)	Leaves (n=5)	Twigs (n=5)	Buds (C)	Roots (n=1)	Bark (n=1)
Na	436 (210-730)	644 (300-890)	580	900	280
Mg	2408(2178-2790)	1226 (723-1610)	2464	1086	1272
Al	177(140-223)	100 (89-121)	64	1447	33
Р	1213(1007-1778)	1909 (1239-3487)	2072	338	177
S	871(736-1087)	413 (369-532)	989	846	157
Κ	9154(7760-11500)	7404 (5750-11200)	12300	1750	1580
Ca	8000(7100-9400)	21120 (16400-27100)	9200	12300	68000
Sc	0.061 (0.047-0.068)	0.03 (0.026-0.037)	0.018	0.0653	0.005
Cr	0.41 (*- 0.65)	*	*	7.48	*
Mn	43 (36-52)	25 (18-39)	40	125	8
Fe	188 (150-230)	77 (*-110)	50	2610	25
Co	0.27 (*-0.36)	*	0.25	1.50	*
Ni	3 (1-8)	3.7 (*-12)	3	3	2
Cu	9 (8-11)	12 (10-14)	11	6	2
Zn	19.4 (17-20)	19 (17-23)	22	9	5
As	0.092 (0.059-0.16)	0.037 (*-0.061)	0.050	0.434	*
Br	14.12 (10.30-16.70)	3.33 (2.79-3.99)	11	5.06	2.51
Rb	3.61 (2.67-4.85)	2.61(*-5.74)	7.16	6.02	*
Sr	54.04 (49.95-64.96)	169 (148.11-187.66)	59.51	88.16	430.37
Nb	0.13 (0.09-0.18)	0.062 (0.05-0.08)	0.03	3.13	0.02
Sn	0.16 (0.1-0.2)	0.16 (0.10-0.20)	0.30	1.3	0.30
Ba	13.58 (*-23.80)	27.86 (20.1-32.1)	27.6	83.4	33.1
Au ppb	0.25(*-0.65)	0.62 (0.38-1.03)	*	*	0.39
La	0.142 (0.11-0.17)	0.07 (0.065-0.084)	0.050	3.220	0.015
Ce	0.324 (0.10-0.49)	0.26 (*-0.47)	0.25	6.68	*
Nd	0.13 (0.09-0.18)	0.062 (0.05-0.08)	0.03	3.13	0.02
Sm	0.034 (0.028-0.040)	0.023 (0.020-0.028)	0.022	0.570	0.012

The Teilta Creek *E. camaldulensis* showed elemental variability between the organs. Of the twenty-seven elements assayed, Na, Al, Cr, Mn, Fe, Co, As, Nb, Sn, Ba, La, Ce, Nd and Sm were of highest concentrations within the root sample. The concentrations of P, Ni, Cu, Zn and Au were greatest in the twigs. The concentrations of Mg, S, Sc and Br were highest in the

leaves. The concentration of K and Rb were greatest in the buds, followed by Ca, and Sr being more abundant in the bark.

3.21.2 Comparison Between Element Concentrations in Eucalyptus camaldulensis and

Adjacent Stream Sediment Chemistry

Fifty-three elements were assayed (Appendix. C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Cd, In, Sb, Se and Te were below analytical detection limit in one or more sectors for both size fractions. The chemical composition of twenty-seven elements were detectable in both *E. camaldulensis* leaves and twigs, while the chemical composition of Cr and Co were only detectable within the *E. camaldulensis* leaves. For all media, Al, As, Au, Ca, Cu, K, Mn, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm were detectable. Table 3.25, shows which sector for *E. camaldulensis* leaves, twigs and adjacent stream sediments size fractions <75 μ m and 75-300 μ m have the maximum and minimum trace element concentrations.

Table 3.25: Shows which sector for *E. camaldulensis* leaves and twigs and adjacent stream sediments size fractions $<75 \mu m$ and 75-300 μm have the maximum and minimum trace element concentrations at Teilta Creek (Teilta).

Element (DL)	Leaves Maximum	Leaves Minimum	Twigs Maximum conc ⁿ	Twigs Minimum	Stream sediments	Stream sediments	Stream sediments	Stream sediments
(ppm)	conc"	conc"	(ppm)	conc"	Maximum conc ⁿ	Minimum conc ⁿ	Maximum conc ⁿ	Minimum conc ⁿ
	(ppm)	(ppm)		(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
					<75 µm fraction	<75 μm fraction	75-300 μm fraction	75-300 μm fraction
Na (100)	W (730)	NW (210)	W (890)	NW (300)	SW (4800)	N & W (4550)	W (2500)	N (2050)
Mg (20)	W (2790)	NW (2178)	W (1610)	NW (723)	N (4650)	W (3850)	E (1850)	N (1550)
A1 (20)	NW (223)	N & SW (140)	NW (121)	W (89)	E (38400)	W (34300)	W (16100)	SW (14000)
P (20)	NW (1778)	N (1007)	NW (3487)	N (1239)	E (300)	NW (240)	E (145)	N, SW & NW (120)
S (10)	NW (1087)	SW (736)	NW (532)	W (358)	E (200)	N, SW & W (100)	E, W & NW (100)	N (BDL)
K (1000)	NW (11500)	W (7760)	NW (11200)	W (6110)	E (11100)	W (10200)	E & W (5500)	NW (4950)
Ca (5000)	E (9400)	SW (7100)	E (27100)	NW (16400)	E (6800)	W (4900)	E (1900)	N (1300)
Sc (0.05)	W & NW (0.068)	N (0.047)	E (0.037)	W (0.026)	Not in assay suite	Not in assay suite	Not in assay suite	Not in assay suite
Cr (0.30)	N (0.71)	E & W (BDL)	BDL (all sectors)	BDL (all sectors)	E (38)	NW (32)	NW (11)	SW (9)
Mn (1)	E (52)	E (34)	SW (39)	E (18)	E (490)	NW (430)	NW (160)	SW (125)
Fe (50)	NW (230)	N (150)	N & E (110)	W (BDL)	E (30200)	NW (26700)	NW (15900)	SW (12400)
Co (0.20)	NW (0.36)	N (BDL)	BDL (all sectors)	BDL (all sectors)	E (9)	N & NW (8)	E & W (4)	SW (3.2)
Ni (1)	NW (8)	N (1)	SW (12)	N (BDL)	E (13)	SW (9)	E (10)	SW & W (8)
Cu (1)	NW (11)	N & SW (8)	NW (14)	SW (10)	E (27)	SW (21)	E (20)	SW (7)
Zn (1)	NW (22)	W (17)	NW (23)	N & W (17)	W (78)	NW (62)	E (38)	SW (22)
As (0.05)	W (0.159)	SW (0.059)	E (0.061)	N, SW & NW (BDL)	N & W (5.5)	SW & NW (4.5)	N (4)	SW (2.5)
Br (0.2)	W (16.70)	N (10.30)	W (3.99)	NW (2.79)	Not in	Not in	Not in	Not in
					assay suite	assay suite	assay suite	assay suite
Rb (0.1)	NW (4.85)	W (2.67)	NW (5.74)	SW & W (BDL)	E (48.5)	W (44)	N, E, W & NW (0.2)	SW (0.1
Sr (0.05)	E (64.96)	SW (41.51)	W (187.66)	N (148.11)	E (82)	W (72)	E & W (28)	SW (22.5)
Nb (0.05)	E (0.18)	NW (BDL)	N (0.25)	NW (0.07)	E &W (16)	N,SW & NW (14)	BDL (all sectors)	BDL (all sectors)
Sn (0.1)	E, W & NW (0.20)	N & SW (0.10)	E, SW & W (0.20)	N & NW (0.10)	W (2.3)	NW (1.8)	W (0.8)	N, SW & NW (0.5)
Ba (10)	E (23.80)	NW (11.40)	E (32.10)	W (20.10)	E (320)	N & NW (300)	N & E (195)	SW (180)
Au (0.30 ppb)	N (0.65 ppb)	E, SW, W NW (BDL)	E (1.03 ppb)	N (0.38 ppb)	SW (3 ppb)	N, E W & NW (2 ppb)	N & E (5 ppb)	SW, W & NW (1 ppb)
La (0.01)	W (0.167)	N (0.114)	E (0.084)	W (0.065)	E (125)	SW (88)	E (16.5)	N (13.5)
Ce (0.20)	W (0.49)	E (BDL)	W (0.47)	N & W (BDL)	E (210)	SW (150)	E (29)	N (21)
Nd (0.01)	W (0.18)	SW (0.090)	NW (0.080)	N & E (0.05)	E (92)	SW & NW (68)	E (14)	N (11.5)
Sm (0.01)	W (0.040)	N (0.028)	NW (0.028)	N (0.020)	E (18)	N & SW (13)	E & NW (2.9)	N (2.3)

In general, there does not appear to be a link between maximum/minimum vegetation element concentration and maximum/minimum stream sediment element concentrations within the same sectors. There is however a possible relationship within the NW sector for leaves and the <75 μ m size fraction maximum concentration for Co, Fe, P, Sn and Zn, and leaves and the twigs maximum concentration for Al, Cu, K, Rb, S and Zn.

Of the twenty-seven elements analysed, the NW sector leaves, NW sector twigs; NW sector <75 μ m size fraction; and, E sector 75-300 μ m size fraction had the most elements with the highest concentration. With the N sector leaves, N & W sector twigs; E sector <75 μ m size fraction; and, SW sector 75-300 μ m size fraction having the most elements with the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum: N (Au and Cr), E (Ba, Ca, Mn, Nb, Sn and Sr), W (As, Br, Ce, La, Mg, Na, Nd, Sc, Sm and Sn) and NW (Al, Co, Cu, Fe, K, Ni, Rb, S, Sc, Sn and Zn);
- leaves minimum: N (Al, Br, Co, Cu, Fe, La, Ni, P, Sc, Sm and Sn), E (Au, Ce, Cr and Mn), SW (Al, As, Au, Ca, Nd, S, Sn and Sr), W (Au, Cr, K, Rb and Zn) and NW (Au, Ba, Na, Nb and Mg);
- twigs maximum: N (Fe and Nb), E (As, Au, Ba, Ca, Fe, La, Sc and Sn), SW (Mn, Ni and Sn), W (Be, Ce, Mg, Na, Sn and Sr) and NW (Al, Cu, K, Nd, P, Rb, S, Sm and Zn);
- twigs minimum: N (As, Au, Ce, Ni, Nd, P, Sm, Sn, Sr and Zn), E (Mn and Nd), SW (As, Cu and Rb), W (Al, Ba, Ce, Fe, K, La, Rb, S, Sc and Zn) and NW (As, Ca, Br, Mg, Nb and Sn);
- <75 μm fraction maximum: N (As and Mg), E (Al, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Mn, Ni, Nb, Nd, P, Rb, S, Sm and Sr), SW (Au and Na) and W (As, Nb, Sn and Zn);
- <75 μm fraction minimum: N (Au, Ba, Co, Na, Nb, S and Sm), E (Au), SW (As, Ce, Cu, La, Nb, Nd, Ni, S and Sm), W (Al, Au, Ca, K, Mg, Na, Rb, S and Sr) and NW (As, Au, Ba, Co, Cr, Fe, Mn, Nb, Nd, P, Sn and Zn);
- 75-300 µm fraction maximum: N (As, Au, Ba and Rb), E (Au, Ba, Ca, Ce, Co, Cu, K, La, Mg, Nd, Ni, P, Rb, S, Sm, Sr and Zn), W (Al, Co, K, Na, Rb, S, Sm, Sn and Sr) and NW (Cr, Fe, Mn, Rb and S); and,
- 75-300 µm fraction minimum: N (Ca, Ce, La, Mg, Na, Nd, P, S, Sm and Sn), SW (Al, As, Au, Ba, Co, Cr, Cu, Fe, Mn, Ni, P, Rb, Sn, Sr and Zn), W (Au and Ni) and NW (Au, K, P and Sn).

The maximum and minimum values for rare earth elements in the stream sediments for both size fractions are within the same sector, and maximum and minimum concentrations for several of the other elements for all media are in more than one sector (Table 3.25). Some of the elements assayed for all media sampled have similar characteristics in similar sectors due to their similar chemical properties, such as: (Au and Cu), (Ba, Ca, Mg and Sr), (Ce, Nd and Sm), (La and Sc), (Co, Ni and Fe), and (K, Na and Rb).

3.21.3 Elemental Trends

Due to the small data set (n = 5), scatter diagrams (Figure 3.47) were constructed to determine whether or not associations between Al, As, Au, Ca, Cu, K, Mn, P, S La, Nd, Ba, Mg, Na, Ni, Zn, Sr and Sm within all media (leaves, twigs, $<75 \mu m$ and $75-300 \mu m$ size fractions) approach linear relationships. The results show that a small group of elements revealed a

trend possibly approaching a linear relationship. Barium in leaves and the <75 μ m stream sediment size fraction, and Sr in leaves, and Ca in leaves and the 75-300 μ m size fraction have broad trends approaching positive relationships. The overall positive trend possibly implies that as the element concentration within the pore/soil water increases the *E. camaldulensis* is not excluding them, or that other factors may be involved. Further data would be needed to better refine this.



Figure 3.47: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and 75-300 μm at Teilta Creek (Teilta).

Stream sediment trace element concentrations revealed that the <75 μ m size fraction has higher concentrations of Al, Fe, K, Ti, Ca, Na, Mg, Mn, Ba, P, Ce, S, La, Sr, Nd, Zn, V, Rb, Th, Cr, Y, Cu, Pr, Nb, Sm, Ni, Ga, Co, Gd, Dy, As, U, Yb, Er, Sn, Cs, Eu, W, Ho, Tb, Ag, Tm, Mo, Lu, Bi and TI than the 75-300 μ m size fraction. The 75-300 μ m size fraction had higher concentrations of Pb and Au than the 75 μ m (Figure 3.48).



Figure 3.48: Variations of metal concentrations within $<75 \ \mu m$ and $75-300 \ \mu m$ stream sediments size fractions surrounding the *E. camaldulensis*, Teilta Creek (Teilta). To calculate the means, below detection limit values were taken as half the detection limit value.



Figure 3.49: The elemental composition and index accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking stream sediments at Teilta Creek (Teilta). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The elemental composition of the Teilta Creek *E. camaldulensis* leaves and twigs (Figure 3.49) shows that leaves have higher concentrations of K, Mg, S, Fe, Al, Mn, Zn, Cr, Co, La,

Nd, As and Sm, compared to the twigs, whereas the twigs have greater concentrations of Ca, P, Na, Sr, Ba, Cu, Ni, Sn, Nd and Au. The elements Co and Cr are only detected within the leaves, which may reflect a preferential allocation of these elements between the *E. camaldulensis* organs.

In general, there is a decrease in element concentration from elements classified as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.49) illustrates that for both the <75 μ m and 75-300 μ m stream sediment size fractions some elements are more bioavailable and more readily taken up by the *E. camaldulensis* than others. The following summarises the index of bioaccumulation from both size fractions (<75 μ m and 75-300 μ m) for leaves and twigs:

- <75 μm size fraction (twigs): S, P, Ca and Sr (high), K, Mg, Cu, Au, Zn, Ni and Na (medium), Mn, Sn, Ba, As and Nb (slight), Fe, Al and Sm (low), Nd and La (very-low);
- <75 μm size fraction (leaves): S, P and Ca (high), K, Sr, Mg, Cu, Au, Zn and Ni (medium), Na, Mn, Sn, Ba, Co, As and Cr (slight) and Nb, Fe, Al, Sm, Nd and La (low);
- 75-300 µm size fraction (twigs): P and Ca (very-high), S, Sr and K (high), Mg, Zn, Cu, Ni, Mn, Sn, Au, Nd and Ba (medium), As (slight) and Fe, Sm, Al, Nd and La (low); and,
- 75-300 µm size fraction (leaves): S (very-high), P, Ca, Sr, K and Mg (high), Zn, Cu, Ni, Mn, Sn, Au and Na (medium), Co, Ba, Cr, As, Fe, Sm, Al and Nd (slight) and La (low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements, these results are consistent with similar relationship found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.22 TEILTA CREEK TEMPORAL ELEMENTAL VARIABILITY WITHIN EUCALYPTUS CAMALDULENSIS

In general, As, Ba, Br, Ca, Fe, La, K, Rb, Sm, Na, Al, Cu, Mg, Mn, Nd, Ni, P, S Sr and Zn are detectable in leaves across all seasons for 2003 and 2004. In contrast, Ce, Cs, Cr, Au, Sc, Nb and Sn are below analytical detections limit concentrations for either one or more seasons. All of these elements, with the exception of As, Ba, Br, Ce, Cs, Cr, Au, La, Rb, Sm, Sc, Na, Nb, Nd and Sn, are considered to be essential. Table 3.26 and Figure 3.50 – Figure 3.56 presents the rainfall and temporal fluctuations in element concentrations for *E. camaldulensis* (leaves) at Teilta Creek for all seasons for 2003 and 2004.

Table 3.26: Elemental composition of *E. camaldulensis* (leaves) sampled at Teilta Creek (Teilta) across all seasons for 2003 and 2004. High values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded e.g. 2003 (Na ppm; autumn), while yellow represents the season in which the highest concentration was recorded e.g. (K - 9520 ppm; autumn). BDL denotes below detection limit.

Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer
As ppm	0.092	0.166	0.120	0.105	0.070	0.082	0.1	0.150
Ba ppm	13.58	17.90	22.90	24.40	29.00	35.20	51.00	45.00
Br ppm	14.12	13.1	12.3	16.5	17.5	13.8	17	17
Ca ppm	8000	14500	16700	14900	15000	13500	17000	16000
Ce ppm	0.324	BDL	BDL	BDL	BDL	BDL	0.200	0.300
Cr ppm	0.408	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Au ppb	0.3	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Fe ppm	188	119	95	158	124	112	150	160
La ppm	0.142	0.093	0.128	0.119	0.104	0.06	0.1	0.1
K ppm	9154	7910	6430	8290	9520	6630	6000	6000
Rb ppm	3.6	2.2	1	3.5	3.2	2.8	2	3
Sm ppm	0.034	0.026	0.031	0.027	0.027	0.020	0.030	0.030
Sc ppm	0.061	0.036	0.049	0.050	0.039	0.031	BDL	BDL
Na ppm	436	758	1190	1110	874	626	1200	1300
Zn ppm	19	16	21	23	25	23	18	25
Al ppm	177	44	101	189	138	87	108	146
Cu ppm	9	10	12	12	9	10	13	21
Mg ppm	2408	2810	3148	2985	3203	3073	3091	3512
Mn ppm	43	55	71	68	68	75	109	110
Nb ppm	0.097	0.06	0.06	BDL	BDL	0.1	0.07	BDL
Nd ppm	0.130	0.05	0.08	0.1	0.1	0.06	0.09	0.08
Ni ppm	3	2	3	5	2	1	1	2
P ppm	1213	964	994	1049	1011	915	1080	1315
S ppm	872	916	948	930	1005	1041	1138	1377
Sn ppm	0.16	0.1	0.1	0.2	0.2	0.2	BDL	BDL
Sr ppm	54	94	95	89	88	85	119	107

The physical appearance of the *E. camaldulensis* sampled at Williams Creek across 2003 and 2004, was:

- 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.

Group A Elements (Periods of growth): more abundant during periods of growth. Spring and summer, are characterised by temperatures with an average maximum of 29.8°C and minimum of 15.7°C in 2003, and an average maximum of 28.7°C and minimum of 15.2°C in 2004. The average rainfall for these periods was 15 mm in 2003 and 11.6 mm in 2004. From September to February (spring and summer) 2003, Ba, Br, Al, Ni, Sn and Zn and for the same period in 2004, As, Ce, Fe, Na, Al, Cu, Mg, Mn, Ni, P S and Zn showed a gradual increase in concentration, recording their highest concentrations in summer. Throughout the same period Cu in 2003 and Br, La, K and Sm in 2004 remained unchanged, with Ce, Cr and Au in 2003 and Cr, Au, Sc and Sn in 2004, recorded a below analytical detection limit values. Elements Ca, Na, Cu, Mg, Mn, S and Sr in 2003, and Ba, Ca and Sr in 2004 recorded their highest concentration in the spring. In contrast, during 2003 As, Ca, La, Sm, Na, Mg, Mn, S and Sr and for the same period in 2004 Ba, Ca, Nd and Sr recorded a decrease in concentration for summer. **Group B Elements (Periods of non-growth):** reduced concentration levels during periods of non-growth. Autumn and winter are characterised by temperatures with an average maximum of 20.1°C and minimum of 9.6°C in 2003, and an average maximum of 21°C and minimum of 9.8°C in 2004. The average rainfall for these periods was 20.43 mm in 2003 and 13.8 mm in 2004. From March to August (autumn to winter) 2003, La, Sm, Sc, Al, Nd, Ni, P, Sn and Zn and for the same period in 2004, Fe, La, Sm, Na, Al, Mg, Nd, Ni, P and Sr showed a gradual decrease in concentration, recording their lowest concentration in the winter. Elements Ce, Cr and Au in 2003 and Cr, Au, Sc, and Sn in 2004, recorded below analytical detection limit values. With the following As, Ba, Na, Cu, Mg, Mn, S and Sr in 2003, and Cu, Mn and S in 2004 recorded their lowest detectable concentration in autumn.

The rainfall pattern for 2003 and for 2004 appears to be quite consistent. However through out 2003 three months (January, March and September), and through out 2004 five months (January, March, April, September and December) recorded no rainfall. These periods of no rainfall resulted in a difference of (8.95 mm) in average annual rainfall between 2003 and 2004. The results show that during 2004, Ba, Br, Ca, Rb, Na, Zn, Cu, Mg, Mn, P, S and Sr recorded a higher concentration compared to 2003. In contrast, As, Au, Fe, La, K, Sm, Sc, Al, Nd and Ni recorded a decrease in concentration compared to 2003.



Figure 3.50: Rainfall and the temporal fluctuations in As, Ba, Br and Ca for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.51: Rainfall and the temporal fluctuations in Ce, Cr, Au and Fe for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.52: Rainfall and the temporal fluctuations in K, La, Rb and Sm for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.53: Rainfall and the temporal fluctuations in Na, Sc, Al and Cu for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year).



Figure 3.54: Rainfall and the temporal fluctuations in Mg, Zn, Mn and Nb for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.55: Rainfall and the temporal fluctuations in Nd, P, Ni and S for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year).



Figure 3.56: Rainfall and the temporal fluctuations in Sr for *E. camaldulensis* (leaves) at Teilta Creek (Teilta). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year).

3.22.1 Teilta Creek Elemental Variability

The results shown in Table 3.27 show the degree of element variability during periods of plant growth and reduced plant growth for the Teilta Creek *E. camaldulensis* during 2003 and 2004.

Parameters	No s	easonal	l varia	ability	Sli; vari	ght s abili	eason ty <30	al)%	Lo varia	ow se abili	easona ty ~ 30	d 0%	In seaso	tern nal v ~ 5	nediat variab 0%	e ility	Hi vari:	gh se abilit	easona ty > 80	al 0%
Years	20)03	20)04	200)3	200	04	200)3	200)4	200)3	200)4	200)3	200)4
	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
As						*	*					*	*							
Ba					*	*	*	*												
Br				*	*	*	*													
Ca						*	*	*					*							
Au		BDL	*	BDL									*							
Fe							*	*	*	*										
La				BDL		*			*						*					
Κ				*	*	*			*											
Rb							*		*			*		*						
Sm				*	*	*	*													
Sc				BDL		*	*						*							
Na						*	*	*					*							
Zn					*	*	*	*												
Al								*			*		*	*						
Cu		*			*		*					*								
Mg					*	*	*	*												
Mn					*	*	*	*												
Nd						*		*					*		*					
Ni									*	*					*	*				
Р					*	*	*	*												
S					*	*	*	*												
Sr						*	*	*					*							

Table 3.27: Shows the degree of elemental variation for the *E. camaldulensis* studied at Teilta Creek (Teilta) between (2003 and 2004) periods of plant growth (G) shown by a green asterisk (*) and periods of reduced plant growth (RG) shown by a black asterisk (*) and defines the optimal sampling period that should be utilised for selected elements. BDL = below detection limit.

The degree of concentration variability across 2003 and 2004 for the *E. camaldulensis* is mostly slight (< 30%) for Ba, Br, Ca, Sm, Na, Zn, Mg, Mn, P, S and Sr; slight – low (< 30% - \sim 30%) for Fe and K; low – intermediate (~ 30 - \sim 50%) for Ni; and variable for As, Au, La, Rb, Sc, Al, Cu and Nd with concentration variability lying within more than one parameter. The slight to intermediate variations for all elements assayed suggest that at Teilta Creek temporal variations are unlikely to have a significant impact on choosing suitable sampling periods.

3.23 TIBOOBURRA: RACECOURSE CREEK

Tibooburra is in the far northwest of New South Wales, and is within one of several bedrock inliers in the Tibooburra-Milparinka region. The regional Tibooburra Inlier consists of granite, bounded by folded metasediments. The inlier is unconformably overlain by Late Jurassic to Cretaceous sediments and Cainozoic sediments, such as the Tertiary Eyre Formation (Thalhammer *et al.*, 1998), which have been worked for Au since 1881 (Kenny, 1934). For more detailed geological setting and mineralisation prospectivity information see chapter 4.

3.23.1 Racecourse Creek Eucalyptus camaldulensis characteristics

The Racecourse Creek *E. camaldulensis* is a gnarled tree with a girth of 5 m and a spreading open canopy that extends from ground level up to approximately 36 m. The bark is smooth, except near the base where it is quite rough with large shedding strips. Twigs are brown, ranging between 2-5 mm in diameter. Buds are stalked and have a beaked conical shape and are typically in clusters of 5-6. Leaves are alternating, pendulous and broad, approximately 8 - 10 cm long and 2 - 3 cm wide, pale green on both the adaxial and abaxial surface. The tree is part of a *E. camaldulensis* riparian woodland within the main drainage channel. Figure 3.57 illustrates the location of the *E. camaldulensis* and its position (598496 E; 6741356 N) in relation to adjacent *E. camaldulensis* trees (plan view) and a profile view of the channel, which is approximately 43.60 m wide and incised up to 0.80 m on the west and 0.30 m on the east.



Figure 3.57: A cartoon illustrating the location of the Racecourse Creek (Tibooburra) *E. camaldulensis* and its position in relation to neighbouring *E. camaldulensis* (plan view) and a profile view of the channel.

The ephemeral channel (Racecourse Creek), which hosts the *E. camaldulensis*, has an approximate length of 5.13 km, flowing from north to south. The channel incises many different bedrock lithological units across the area. There are no known mineral deposits proximal to the Racecourse Creek *E. camaldulensis*.

3.23.2 Organ Tissue Biogeochemistry Results

Sampling of leaves, twigs, fruit and bark was undertaken at the Racecourse Creek study site. Five samples of leaves and twigs, and single composite samples of fruit, were collected from the reachable N, NE, E, SE and S sectors around the *E. camaldulensis* canopy. Bark samples were collected from the N, SE and W sectors. Fifty-two elements were assayed by combined INAA, ICP-MS and ICP-OES. Results from the organ tissue biogeochemistry survey are detailed in Appendix B. The elements Sb, Cs, Cr, Eu, Hf, Ir, Lu, Mo, Rb, Se, Ag, Ta, Te, Th, W, U, Yb, Zr, Be, Bi, Cd, Ga, In, Pb, Ti and V were below analytical detection limits in all sampling media, while Co was detected in leaves, and Nb in the twigs, fruit and bark. The concentrations of twenty-eight elements were detectable within one or more of the *E. camaldulensis* organ tissues, and showed some degree of chemical heterogeneity. The range of chemical heterogeneity for the different media is shown in Table 3.28. All elements with > 25 % of their values below analytical detection limits have been removed from the data set.

Table 3.28: Variations of metal concentrations within different oven dried tissues of an individual *E. camaldulensis*, at Racecourse Creek (Tibooburra). Initial value represents the mean; values in brackets () are the range of values; C= composite sample and * signifies values below detection limit. To calculate the 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

Element (ppm)	Leaves (n=5)	Twigs (n=5)	Fruit (C)	Bark (n=3)
Na	28 (20-60)	38 (30-50)	60	517 (300-820)
Mg	2931(2387-3604)	1313 (890-1596)	1509	1183 (939-1487)
Al	72 (65-83)	62 (50-83)	74	30 (24-41)
Р	1689 (1509-2008)	1292 (1015-1607)	1403	269 (202-403)
S	1681 (1543-1880)	436 (415-454)	825	262 (234-312)
Κ	11202 (9460-14200)	4192 (3880-4480)	12000	2897 (1750-5040)
Ca	9300 (8000-13100)	15740 (11900-19900)	9000	50267 (47700-54900)
Ti	3.20 (*-6)	*	*	*
Sc	0.022 (0.019-0.024)	0.012 (0.009-0.015)	0.019	*
Cr	0.19 (*- 0.37)	0.24 (*- 0.58)	*	*
Mn	150 (111-240)	75 (57-100)	94	54 (37-81)
Fe	106 (90-120)	21.5 (*-50)	80	*
Со	0.31 (0.27-0.34)	*	*	0.14 (*-0.21)
Ni	3 (2-5)	1.7 (*-3)	*	2.8 (*-6)
Cu	7 (6-8)	5.2 (4-8)	4	2
Zn	29 (24-32)	15 (11-19)	15	12 (10-17)
As	0.14 (*-0.235)	0.039 (*-0.062)	0.056	*
Br	15.22 (13.10-17)	1.97 (1.77-2.27)	13	6.38 (5.83-7.27)
Rb	1.53 (*-3.67)	*	2.14	1.4 (*-2.24)
Sr	59.94 (46.38-86.57)	148.34 (127.83-170.02)	69.57	368.87 (356.50-377.26)
Nb	*	0.059 (*-0.08)	0.07	0.107 (0.10-0.11)
Sn	0.22 (0.10-0.40)	0.26 (0.20-0.40)	0.10	0.30 (0.20-0.40)
Ba	21.50 (12.30-32.60)	21.08 (14.40-30.20)	19.30	28.83 (27.50-29.70)
Au ppb	0.40(*-0.68)	1.40 (*-6.41)	*	*
La	0.054 (0.043-0.070)	0.049 (0.036-0.080)	0.037	0.0.008 (*-0.013)
Ce	0.164 (*-0.49)	0.22 (*-0.38)	*	*
Nd	0.062 (0.04-0.14)	0.040 (0.02-0.06)	0.04	0.013 (0.01-0.03)
Sm	0.020 (0.017-0.022)	0.017 (0.013-0.023)	0.015	0.008 (*-0.010)

The Racecourse Creek *E. camaldulensis* showed elemental variability between the organs. Of the twenty-eight elements assayed Mg, P, S, K, Ti, Sc, Mn, Fe, Co, Zn, As, Br, Rb, Ba, La, Ce and Nd were most abundant within the leaves. Elements Cr, Au and Sm were at greatest levels in the twigs. Elements Na, Ca, Ni, Sr and Nb were more abundant in the bark, and Al and Cu have equivalent concentration in both leaves and twigs, and Sn was most abundant in leaves, twigs and bark.

3.23.3 Comparison Between Element Concentrations in Eucalyptus camaldulensis and

Adjacent Stream Sediment Chemistry

Fifty-three elements were assayed (Appendix. C) by ICP-MS (3M) & (3R) and AA 10 for the detection of Au in the stream sediments. In general, Cd, In, Sb, Se, Te and Au were below analytical detection limit in one or more sectors for both stream sediment size fractions. The chemical composition of twenty-eight elements were detectable in both *E. camaldulensis* leaves and twigs, while Co was only detected within the *E. camaldulensis* leaves. For all media, Al, Ba, Ca, Cu, K, Mn, P, S, Mg, Na, Ni, Zn, Sr and Sn were detectable. Table 3.29 shows which sectors for *E. camaldulensis* leaves, twigs, bark and adjacent stream sediment size fractions <75 μ m and 75-300 μ m have the maximum and minimum trace element concentrations.

Table 3.29: Shows which sector for *E. camaldulensis* leaves and twigs and adjacent stream sediments size fractions <75 µm and 75-300 µm have the maximum and minimum trace element concentrations at Racecourse Creek (Tibooburra).

Element	Leaves	Leaves	Twigs	Twigs	Bark	Bark	Stream	Stream	Stream	Stream
(DL)	Maximum	Minimum	Maximum	Minimum	Maximum	Minimum	sediments	sediments	sediments	sediments
(nnm)	Conc ⁿ	Conc ⁿ	Conc ⁿ	Conc ⁿ	Conc ⁿ	Conc ⁿ	Maximum	Minimum	Maximum	Minimum
(Ppm)	(nnm)	(nnm)	(nnm)	(nnm)	(nnm)	cone	Conc ⁿ	Conc ⁿ	Conc ⁿ	Conc ⁿ
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)		(ppm)	(ppm)	(ppm)	(ppm)
							(ppm)	(ppm)	(ppm)	(ppm)
							75 um	75 um	300 um	300 um
							fraction	fraction	fraction	fraction
Na (10)	N (60)	NF F SF &	NF (50)	F & SE (30	W (820)	SE (300)	F & SF	NF (4700)	N (11300)	S (10000)
144 (10)	11 (00)	S (20)	THE (50)	$D \approx DE(50)$	(020)	SE (500)	(5450)	IL (4700)	(11500)	5 (10000)
$M_{\alpha}(20)$	SE (2604)	S (20)	N (1506)	PIII) SE (800)	N (1497)	W(020)	(3430)	NE (4250)	S (1100)	NE (2250)
Mg(20)	SE (3004)	NE(2307)	IN(1390)	SE (890)	N(1407)	W (939)	N(7430)	NE (4550)	S (4400)	NE(3330)
AI (20)	SE (83)	5 (05)	E (83)	N (50)	N (41)	SE & W (24)	IN (04000)	NE (43000)	5 (48400)	E (43300)
P (20)	S (2008)	NE (1509)	N (1607)	SE (1015)	N (403)	SE & W	NE (650)	N & S	S (340)	N (290)
						(202)		(550)		
S (10)	N (1880)	SE (1543)	E (454)	SE (415)	N (312)	W (234)	N, NE &	E & S	E, SE, & S	N & NE
. ,	× /	· · · ·	. ,	, ,	``´´	, , ,	SE (200)	(150)	(100)	(50)
K (1000)	S (14200)	N (9460)	NE (4480)	SE (3880)	N (5040)	W (1750)	SE (14600)	NE	SE (18600)	E (16600)
(,				(/				(10600)	(,	(,
Ca	SE (13100)	N & S	N (19900)	SE (11900)	SE (54900)	W (47700)	N (8700)	E (8150)	N (10400)	E (9450)
(5000)	52 (10100)	(8000)		52 (11) 00)	52 (0 1900)		1 (0,00)	2 (0100)		2 (> .20)
$S_{\rm C}(0.05)$	E (0.024)	S(0.019)	NE (0.015)	E (0.009)	BDL (all	BDL	Not in	Not in	Not in	Not in
	2 (0:02 !)	5 (0101))	(01010)	2 (0.00))	sectors)	(all sectors)	assay suite	assay suite	assay suite	assay suite
Cr(0.30)	E (0 37)	N NE SE &	N (0.58)	NE E SE &	BDL (all	BDL (all	N(43)	S (33)	E(17)	N(15 pm)
CI (0.50)	E (0.57)	S (BDI)	11 (0.50)	S(BDI)	sectors)	sectors)	1((13)	5 (55)	L (17)	it (is pill)
Mn (1)	SF (240)	E (111)	N (100)	S (BBE) SE (57)	N (81)	W (37)	N & SF	\$ (330)	N F SF &	NF (300)
WIII (1)	SL (240)		14 (100)	SL (37)	(01)	•• (37)	(410)	5 (550)	S (310)	ILL (300)
Fe (50)	E (120)	N (90)	N & F (50)	NF SF & S	BDL (all	BDL (all	N (31300)	NF	F & S	SE (21000)
10(30)	L (120)	11(()0)	IT & E (50)	(BDL)	sectors)	sectors)	11 (51500)	(23100)	(21800)	SE (21000)
$C_{0}(0.20)$	SE (0.34)	S (0.27)	BDL (all	BDL (all	BDL (all	BDL (all	N(10.5)	(23100)	(21000)	N NE & SE
CO (0.20)	SE (0.54)	3 (0.27)	Soctors)	BDL (all	Sectors)	BDL (all	N (10.5)	$\mathbf{NE}(T)$	$L \alpha S(I)$	(6.5)
NG (1)	N (5)	NEEP.C	$\mathbf{S}(2)$	SECIOIS)	N(6)	W (PDI)	N & CE	S (11)	E(10)	N NE SE
INI (I)	IN (3)	(2)	3(3)	SE (BDE)	IN (0)	W (BDL)	(17)	5(11)	L (10)	$k \in (0)$
$C_{\rm PL}(1)$	c (2)	(2) NE & E (6)	N & S (7)	NE E & CE	NSERW	NCERW	(17) N (25)	NE(16)	N (10)	E(10)
Cu (1)	5 (6)	$\mathbf{NE} \propto \mathbf{E}(0)$	$n \alpha S(1)$	(4)	(2)	(2)	IN (23)	NE (10)	IN (19)	E (10)
$7_{22}(1)$	SE (22)	N (24)	N 8 6 (10)	(4) SE (11)	(2) N (17)	(2) CE & W	E (70)	NIE 9 C	C (44)	$\mathbf{N} \in \mathbf{E}(2\mathbf{C})$
Zn (1)	SE (32)	IN (24)	N & S (19)	SE (11)	N (17)	$SE \propto W$	E(70)	$NE \propto S$	5 (44)	$N \propto E(30)$
A (0.05)					DDL (11	(10)	NT (5)	(30)	0 (2 5)	
As (0.05)	NE(0.235)	SE (BDL)	NE(0.062)	N, SE & S	BDL (all	BDL (all	IN (5)	5 (2.5)	S (3.5)	(2,5)
		NE (12.10)		(BDL)	sectors)	sectors)	NT . 1	NT . *	NT . *	(2.5)
Br (0.2)	N (17)	NE (13.10)	NE (2.27)	SE (1.77)	N (7.27)	W (5.83)	Not in	Not in	Not in	Not in
a (0.05)		G (16 00)				an (an (no)	assay suite	assay suite	assay suite	assay suite
Sr (0.05)	SE (86.57)	S (46.38)	E (170.02)	SE (127.83)	W (377.26)	SE (356.50)	N & SE	NE & S	N (210)	S (185)
							(140)	(120)		
Nb (0.05)	BDL (all	BDL (all	N (0.08)	NE (BDL)	N & W	SE (0.10)	N, E & SE	NE & S	N, NE, E,	N, NE, E,
	sectors)	sectors)			(0.11)		(16)	(14)	SE & S (10)	SE & S (10)
Sn (0.1)	NE (0.40)	E & S (0.10)	E (0.40)	N, NE & SE	SE (0.40)	N (0.20)	N & SE	NE (2.7)	N (2.6)	NE (1.9)
				(0.20)			(3.3)			
Ba (10)	SE (23.60)	S (12.30)	N (30.20)	SE (14.40)	W (29.70)	N (27.50)	N & SE	NE (310)	NE & SE	N & E (380)
							(370)		(420)	
Au (0.30	E (0.68 ppb)	N & SE	N (6.41 ppb)	NE, E, SE &	BDL (all	BDL (all	NE (14	SE & S (1	E (3 ppb)	N, NE, SE

Element (DL)	Leaves Maximum	Leaves Minimum	Twigs Maximum	Twigs Minimum	Bark Maximum	Bark Minimum	Stream sediments	Stream sediments	Stream sediments	Stream sediments
(ppm)	Conc ⁿ (ppm)	Conc ⁿ	Maximum Conc ⁿ (ppm) 75 μm	Minimum Conc ⁿ (ppm) 75 μm	Maximum Conc ⁿ (ppm)	Minimum Conc ⁿ (ppm)				
							fraction	fraction	fraction	fraction
ppb)		(BDL)		S (BDL)	sectors)	sectors)	ppb)	ppb)		& S (BDL)
La (0.01)	SE (0.070)	S (0.070)	N (0.080)	SE (0.036)	BDL (all	BDL (all	SE (50)	S (43.5)	N & E	NE & S
					sectors)	sectors)			(24.5)	(23)
Ce (0.20)	N (0.27)	NE, E & SE	N (0.38)	SE & S	BDL (all	BDL (all	SE (90)	S (72)	NE (45.5)	S (39.5)
NJ (0.01)	NE (0.14)		NEE		DDL (-11	DDL (-11	NIE (20)	NI (25)	E (10)	NE(165)
Na (0.01)	NE(0.14)	$E, SE \ll S$	$N \propto E$	S (0.02)	BDL (all	BDL (all	NE (38)	IN (35)	E (19)	NE(10.5)
		(0.04)	(0.060)		sectors)	sectors)				
Sm	E & SE	N (0.017)	N (0.023)	SE (0.013)	BDL (all	BDL (all	NE (8.5)	S (7)	E (4.5)	SE (3.4)
(0.01)	(0.022)				sectors)	sectors)				

In general, there does not appear to be a close association between maximum/minimum vegetation element concentration and maximum/minimum stream sediment element concentrations within the same sectors. Although the maximum for leaves and the minimum for twigs for the SE sector may show a relationship for elements Ba, Ca, La, Mg, Mn, Sm, Sr and Zn and similarly with twigs and the <75 μ m stream sediment size fraction maximum concentrations for Ba, Ca, Cr, Cu, Fe, Mg, Mn and Nb. Of the twenty-six elements assayed, the SE sector leaves, N sector twigs, N sector bark, N sector <75 μ m size fraction and E & S sector leaves, SE sector twigs, W sectors bark, S sector <75 μ m size fraction and N sector 75-300 μ m size fraction have the most elements with the lowest concentrations. The following summarises the maximum and minimum element concentrations for all media and their distribution:

- leaves maximum: N (Br, Ce, Na, Ni and S), NE (As, Nd and Sn), E (Au, Cr, Fe, Sc and Sm), SE (Al, Ba, Ca, Co, La, Mg, Mn, Sm, Sr and Zn) and S (Cu, K and P);
- leaves minimum: N (Au, Ca, Cr, Fe, K, Sm and Zn), NE (Br, Ce, Cu, Mg, Na, Ni and P), E (Ce, Cu, Mn, Na, Nd, Ni and Sn), SE (As, Au, Ce, Cr, Na, Nd and S) and S (Al, Ba, Ca, Co, Cr, La, Na, Nd, Ni, Sc, Sn and Sr);
- twigs maximum: N (Au, Ba, Ca, Ce, Cr, Cu, Fe, La, Mg, Mn, Nb, Nd, P, Sm and Zn), NE (As, Br, K, Na and Sc), E (Al, Fe, Nd, Sn and Sr) and S (Cu, Ni, S and Zn);
- twigs minimum: N (Al, As and Sn), NE (Au, Cr, Cu, Fe, Nb and Sn), E (Au, Cr, Cu, Na and Sc), SE (As, Au, Ba, Br, Ca, Ce, Cr, Cu, Fe, K, La, Mg, Mn, Na, Ni, P, S, Sm, Sn, Sr and Zn) and S (As, Au, Ce, Cr, Fe and Nd);
- bark maximum: N (Al. Br, Cu, K, Mg, Mn, Nb, Ni, P, S and Zn), SE (Ca, Cu and Sn) and W (Ba, Cu, Na, Nb and Sr);
- bark minimum: N (Ba, Cu and Sn), SE (Al, Cu, Nb, P, Sr and Zn) and W (Al, Br, Ca, Cu, K, Mn, Ni, P, S and Zn);
- <75 μm fraction maximum: N (Al, As, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Nb, Ni, S, Sn and Sr), NE (Au, Nd, P, S and Sr), NE (Au, Nd, P, S and Sm), E (Na, Nb and Zn) and SE (Ba, Ce, K, La, Mn, Na, Nb, Ni, S, Sn and Sr);
- <75 μm fraction minimum: N (Nd and P), NE (Al, Ba, Co, Cu, Fe, K, Mg, Na, Nb, Sn, Sr and Zn), E (Ca and S), SE (Au) and S (As, Au, Ce, Cr, La, Mn, Nb, Ni, P, S, Sm, Sr and Zn);
- 75-300 μm fraction maximum: N (Ca, Cu, La, Mn, Na, Nb and Sr), NE (Ba, Ce, and Nb), E (Au, Co, Cr, Fe, La, Mn, Nb, Nd, Ni, S and Sm), SE (Ba, K, Mn, Nb and S) and S (Al, As, Co, Fe, Mg, Mn, Nb, P, S, Sn and Zn); and,
75-300 μm fraction maximum: N (Au, Ba, Co, Cr, La, Mb, Nd, Ni, P, S and Zn), NE (As, Au, Co, Mg, Mn, Nb, Ni, S and Sn), E (Al, As, Ba, Ca, Cu, K, Nb and Zn), SE (As, Au, Co, Fe, Nb, Ni and Sm) and S (Au, Ce, La, Nb, Ni and Sr).

The maximum and minimum concentrations for several of the elements for all media are in more than one sector (Table 3.29). Some of the elements assayed for all media occur within similar sectors due to their similar chemical properties, such as: (Au and Cu), (Ba, Ca, Mg and Sr), (Ce, Nd and Sm), (La and Sc), (Co, Ni and Fe), and (K, Na and Rb).

3.23.4 Elemental Trends

Due to the small data set (n = 5) scatter diagrams (Figure 3.58) were constructed to determine whether or not relationships between Al, Ba, Ca, Cu, K, Mn, P, S, Mg, Na, Ni, Zn, Sr and Sn within all media (leaves, twigs, <75 μ m and 75-300 μ m size fractions) approach linear relationships. The results show that only a small group of elements provide a trend possibly approaching a linear relationship. Sodium in twigs and K in twigs and the <75 μ m size fraction, and As in leaves within the 75-300 μ m stream sediment size fraction revealed a trend approaching a negative relationship. In contrast, Cu in twigs and the <75 μ m stream sediment size fraction have an association approaching a positive relationship. The overall negative trend possibly implies that as the elements become available within the pore/soil water the *E*. *camaldulensis* may be preferentially excluded, or that other factors may be involved.



Figure 3.58: Scatter plots illustrating trends that best approach a linear relationship between leaves, twigs, $<75 \mu m$ and 75-300 μm at Racecourse Creek (Tibooburra).

The stream sediment trace element results show that the <75 μ m size fraction has higher concentrations of Al, Fe, Mg, Ti, P, Mn, S, Ce, V, Zn, La, Cr, Nd, Y, Th, Cu, Nb, Ga, Ni, Pr, Co, Sm, Gd, Dy, U, As, Cs, Sn, Yb, Er, W, Eu, Ho, Tb, Ag, Tm, Mo, Lu, TI, Bi and Au compared to the 75-300 μ m size fraction. The 75-300 μ m size fraction has higher concentrations of K, Ca, Na, Ba, Sr, Rb and Pb (Figure 3.59).



Figure 3.59: Variations of metal concentrations within $<75 \ \mu m$ and $75-300 \ \mu m$ stream sediments size fractions surrounding the *E. camaldulensis*, Racecourse Creek (Tibooburra). To calculate the means, below detection limit values were taken as half the detection limit value.



Figure 3.60 The elemental composition and index of accumulation of macro and trace elements by *E. camaldulensis* (leaves and twigs) from flanking stream sediments at Racecourse Creek (Tibooburra). Index of accumulation is calculated at the ratio of macro and trace elements in plants to their concentration in adjacent stream sediments.

The elemental composition of the Racecourse Creek *E. camaldulensis* leaves and twigs (Figure 3.60) shows that leaves have higher concentrations of K, Mg, P, S, Mn, Fe, Al, Zn,

Cu, Ni, Co, As, Nd, La and Sm, compared to twigs, which have greater concentrations of Ca, Sr, Na, Ba, Cr, Sn, Au and Nb. Cobalt is only detectable within the leaves, and Nb is only detected in the twigs, which may reflect a preferential allocation of these elements within the *E. camaldulensis* organs.

In general, there is a decrease in concentrations for elements considered as macro>micro>beneficial>non-essential. The index of accumulation (Figure 3.60) illustrates that for both the <75 μ m and 75-300 μ m stream sediment size fractions, some elements are more bioavailable and more readily taken up by *E. camaldulensis* than others. The following summarises the index of bioaccumulation from both size fractions (<75 μ m and 75-300 μ m) for leaves and twigs:

- <75 μm size fraction (twigs): Ca, P, S, Sr and Au (high), K, Mg, Zn, Mn and Cu (medium), Sn, Ba, As and Cr (slight) and Na, Fe, Sm, Nd, Al, La and Nb (low);
- <75 μm size fraction (leaves): S, P and Ca (high), K, Mg, Sr, Zn, Mn, Cu, Ni and Au (medium), Sn, Ba, As and Co (slight) and Cr, Na, Fe, Sm, Nd, Al and La (low);
- 75-300 μm size fraction (twigs): S, P. Ca and Au (high), Mg, Zn, K, Mn, Cu, Ni, Sr and Sn (medium), As, Ba and Cr (slight) and Sm, Fe, Nd, Na, La, Al and Nb (low); and,
- 75-300 µm size fraction (leaves): S (very-high), P and Ca (high), Mg, Zn, K, Mn, Cu, Ni, Sr and Au (medium), Sn, As, Ba, Co and Cr (slight) and Sm, Fe, Nd, Na, La and Al (low).

Most of the essential elements tend to have high-medium biological absorption coefficients (index of accumulation) compared to the non-esential elements, these results are consistent with similar relationship found by Kovalevsky (cited in Brooks, *et al.*, 1995) and Timperley, *et al.*, (1970).

3.24 RACECOURSE CREEK TEMPORAL ELEMENTAL VARIABILITY WITHIN EUCALYPTUS CAMALDULENSIS

In general, Ba, Br, Ca, K, Zn, Cu, Mg, Mn, Nd, P, S and Sr are detectable in the leaves across all seasons for 2003 and 2004. Elements As, Fe, Au, La, Sm, Sc, Na, Al and Ni recorded below analytical detection limit concentrations for either one or more seasons. All of these elements, with the exceptions of As, Ba, Br, Au, La, Sm, Sc, Na, Al, Nd and Sr, are considered to be essential in higher plants. Table 3.30 and Figure 3.61 - Figure 3.66 presents the rainfall and temporal fluctuations in element concentrations for *E. camaldulensis* (leaves) at Racecourse Creek for all seasons for 2003 and 2004.

Table 3.30: Elemental composition of E. camaldulensis (leaves) sampled at Racecourse Creek across all seasons for 2003 and 2004. High
values and low values are for each calendar year. Green represents the season in which the lowest concentration was recorded e.g. 2003 (Zn
- 12 ppm; autumn), while yellow represents the season in which the highest concentration was recorded e.g. 2004 (Al - 79 ppm; winter &
spring). BDL denotes below detection limit.

Months	Autumn-03	Winter	Spring	Summer	Autumn-04	Winter	Spring	Summer	
As ppm	0.131	BDL	BDL	0.079	0.31	0.103	0.14	0.06	
Ba ppm	21.5	17.50	24.6	35	57.6	41.3	53	47	
Br ppm	15.22	11.8	10.9	11.2	18.4	11.6	11	14	
Ca ppm	9300	7360	12200	12700	15000	14000	15000	13000	
Fe ppm	106	BDL	52.3	76.5	68.3	100	100	BDL	
Au ppb	0.398	BDL	BDL	BDL	BDL	BDL	BDL	BDL	
La ppm	0.054	0.023	0.05	0.076	0.131	0.078	BDL	BDL	
K ppm	11202	7630	7760	6100	8620	5070	5000	7000	
Sm ppm	0.02	0.01	0.019	0.022	0.027	0.019	0.02	BDL	
Sc ppm	0.022	BDL	0.016	0.026	0.022	0.026	BDL	BDL	
Na ppm	28	BDL	16.4	21.5	1040	19.7	BDL	BDL	
Zn ppm	28.6	12.3	17	21	22	20	19	21	
Al ppm	72.2	BDL	43	102	56	79	79	111	
Cu ppm	6.8	5	6	6	8	4	4	5	
Mg ppm	2930.8	2101	2144	2026	2462	2241	2078	2217	
Mn ppm	150.6	96	140	129	344	167	208	192	
Nd ppm	0.062	0.02	0.04	0.09	0.11	0.07	0.08	0.08	
Ni ppm	30	20	BDL	30	30	BDL	BDL	BDL	
P ppm	1689.2	1160	1072	782	2032	819	814	951	
S ppm	1681	1190	1191	891	1080	1252	1344	1473	
Sr ppm	59.94	57.04	76.42	89.28	92.24	90.09	110.81	94.54	

The physical appearance of the *E. camaldulensis* sampled at Racecourse Creek across 2003 and 2004, was:

- 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.

Group A Elements (Periods of growth): more abundant during periods of growth. Spring and summer, are characterised by temperatures with an average maximum of 37.95°C and minimum of 19.62°C in 2003, and an average maximum of 33.53°C and minimum of 19.22°C in 2004. The average annual rainfall for these periods was 10.27 mm in 2003 and 9.97 mm in 2004. From September to February (spring and summer) 2003, Ba, Ca, La, Sm, Sc, Al, Nd and Sr and for the same period in 2004, S had a gradual increase in concentration, recording their highest concentrations in summer. Throughout the same period, Cu in 2003, and Nd and Ni in 2004 remained unchanged, with Au in 2003 and Fe, Au, La, Sm and Ni in 2004, recording below analytical detection limit values. Elements Ca and Sr in 2004 recorded their highest concentration in the spring. In contrast, during 2003, K, Mg, Mn, P and S and for the same period in 2004 As, Ba, Ca, Fe, Sm, Mn and Sr recorded a decrease in element concentration for the summer.

Group B Element (Periods of non-growth): reduced concentration levels during periods of non-growth. Autumn and winter are characterised by temperatures with an average maximum of 23.17°C and minimum of 9.6°C in 2003, and an average maximum of 23.65°C and minimum of 10.68°C in 2004. The average rainfall for these periods is 21.83 mm in 2003 and 15.33 mm in 2004. From March to August (autumn to winter) 2003, Ba, Ca, La, Sm, Zn, Cu, Mn, Nd, Ni and Sr and for the same period in 2004, Ba, Cu, Mn, Nd and Sr showed a gradual decrease in concentration, recording their lowest concentration in the winter, with As, Fe, Au, Sc, Na and Al in 2003 and Au and Ni in 2004, recorded below analytical detection limit values. While Ba, Cu, Mn, Nd and Sr in 2004 recorded their lowest concentration in the autumn.

The rainfall pattern for 2003 and 2004 appears to be quite consistent. There is, however, a difference of 5.62 mm in the average annual rainfall between 2003 and 2004. For 2004, As, Ba, Br, Ca, Fe, La, Na, Zn, Al, Mn, Nd, S and Sr recorded a higher concentration compared to 2003. In contrast, Au, K, Sc, Cu, Mg, Ni and P recorded a decrease in concentration compared to 2003.





Figure 3.62: Rainfall and the temporal fluctuations in Fe, Au, La and K for *E. camaldulensis* (leaves) at Racecourse Creek (Tibooburra). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.63: Rainfall and the temporal fluctuations in Sm, Sc, Na and Zn for *E. camaldulensis* (leaves) at Racecourse Creek (Tibooburra). ----- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.64: Rainfall and the temporal fluctuations in Al, Mg, Cu and Mn for *E. camaldulensis* (leaves) at Racecourse Creek (Tibooburra). ---- Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.65: Rainfall and the temporal fluctuations in Nd, Ni, P and S for *E. camaldulensis* (leaves) at Racecourse Creek (Tibooburra). -----Denotes detection limit. Standard error (± standard deviation for that element across the shown year)



Figure 3.66: Rainfall and the temporal fluctuations in Sr for *E. camaldulensis* (leaves) at Racecourse Creek (Tibooburra). ----- Denotes detection limit. Standard error (\pm standard deviation for that element across the shown year)

3.24.1 Racecourse Creek Elemental Variability

Table 3.31 shows the degree of element variability during periods of plant growth and periods of reduced plant growth for the Racecourse Creek *E. camaldulensis* during the 2003 and 2004 seasons.

Table 3.31: Shows the degree of elemental variation for the E. camaldulensis studied at Racecourse Creek (Tibooburra) between (2003 and
2004) periods of plant growth (G) shown by a green asterisk (*) and periods of reduced plant growth (RG) shown by a black asterisk (*) and
defines the optimal sampling period that should be utilised for selected elements. BDL = below detection limit.

Parameters	No seasonal			Slight seasonal			Low seasonal			Intermediate seasonal				High seasonal						
	variability			variability <30%			variability ~ 30%			variability ~ 50%				variability > 80%						
Years	2003 2004		2003 2004		4	2003 2004		4	2003 2004		4	2003		200	2004					
	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G	RG	G
As														*	*	*	*			
Ba					*	*	*	*												
Br					*	*		*			*									
Ca					*	*	*	*												
Au		BDL	BDL	BDL									*							
Fe										*	*		*			*				
La				*						*			*		*					
K						*		*	*						*					
Sm						*	*						*			*				
Sc				BDL			*			*							*			
Na				BDL		*											*		*	
Zn						*	*	*					*							
Al							*	*						*			*			
Cu		*			*			*							*					
Mg					*	*	*	*												
Mn						*		*	*						*					
Nd				*							*		*	*						
Ni				BDL					*									*	*	
Р						*		*	*						*					
S					*	*	*	*												
Sr					*	*	*	*												

The degree of concentration variability across 2003 and 2004 for the *E. camaldulensis* is mostly slight (< 30%) for Ba, Ca, Zn, Mg, S and Sr; slight – low (< 30% - ~ 30%) for Br, K and P; low – intermediate (~ 30 % - ~ 50%) for Al and Nd; intermediate – high (~ 50% - > 80%) for As, high (> 80 %) for Ni and variable for La, Sc, Na, Al, Cu and Mn with concentration variability within more than one parameter. The slight to intermediate variations suggest that seasonal variations are less important for many of the elements, with the exception of Ni, which suggests that the most appropriate sampling period for expressing higher contents is autumn.

3.25 INTRA-CELLULAR METAL DISTRIBUTION

The leaves of the E. camaldulensis (Figure 3.67) are isobilateral, consisting of:

- an adaxial epidermis with cuticle and hypodermis;
- four layers of columnar palisade parenchyma cells;
- a layer of sclerenchyma cells mixed with both major and minor veins;
- a further four layers of abaxial columnar palisade parenchyma cells; and,
- followed by the abaxial hypodermis, epidermis and cuticle.



Figure 3.67: A cross section of the internal structures of the Pine Creek (Barrier Pinnacles Mine) *E. camaldulensis*. Cut- (cuticle), Ep (epidermis), Fi (fibres), Ef (extraxylary fibres), X (xylem), P (phloem), Sf (sclerenchyma fibres), Pp (palisade parenchyma) and Og (oil gland) taken by the Nikon Eclipse TE300 Inverted Microscope. Sections A-B, C-D and E-F indicate where the cross section and accompanying illustration are derived from.

Results are shown as the average of the recorded counts per second, due to no internal standards being available to calibrate the results to standard concentrations. Figure 3.68 shows the counts per second of essential elements Si, Fe, S, Al, Mn, Zn, Sr Ca, Cu, Co and Ni and non-essential elements Pb, Sb, Ce, Ag, As, Cd, Ga, Au and In in the different cell types of the mature leaf of a *E. camaldulensis* from Pine Creek (Pinnacles Barrier mine).



Figure 3.68: Micrograph of an isobilateral *E. camaldulensis* leaf, from Pine Creek (Barrier Pinnacles Mine) graph and table showing the element compartmentation through the leaf, (C/S) Counts Per Second, E (epidermis), P (parenchyma), Sf (Sclerenchyma fibres), Ph (phloem) and X (xylem).

The results show that Pb, Fe, Al, Sb, Cu, Ce, Ag, As, Cd, Co, Ni and In are preferentially concentrated in the epidermis. In contrast, Si, S, Mn, Zn, Sr, Ca, Ga and Au accumulate in the parenchyma cells. The graph in Figure Figure 3.68 shows that the most abundant element in the epidermis was silica, from which the order of decreasing concentrations is: Pb > Fe > S > Al > Mn > Zn > Sr > Ca > Sb > Cu > Ce > Ag > As > Cd > Ga > Co > Ni > Au and In.