

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

**Karen A. Hulme, B.Env.Sc (Hons)**



**Geology and Geophysics**  
**School of Earth and Environmental Sciences**  
**The University of Adelaide**  
**April 2008**

## CHAPTER 5

### SYNTHESIS

Analysis of the composition of *E. camaldulensis* tissue can provide information for delineating local and regional geochemical dispersion patterns associated with mineralisation in regolith-dominated terrains. In order to make use of biogeochemistry in mineral exploration and environmental chemistry programs, the following discussion is presented within two themes: (i) the internal and external factors that characterize the biogeochemical composition of the *E. camaldulensis*; and, (ii) the application of *E. camaldulensis* biogeochemistry to assist in mineral exploration and environmental chemistry programs.

#### 5.1 CONTROLS & PROCESSES ON *E. CAMALDULENSIS* BIOGEOCHEMISTRY

The element composition of *E. camaldulensis* tissue across the Curnamona Province and adjacent areas in SE inland Australia is determined by a number of environmental factors such as: plant uptake (soil-plant transfer); organ tissue biogeochemistry (element translocation) strategies; bedrock (mineralised and non-mineralised) variations; regolith-landform settings (alluvial systems); and, temporal variations (temperature and water availability). These have been grouped into two sections:

1. intrinsic (*E. camaldulensis*) factors; and,
2. extrinsic (environmental) factors.

The uptake of elements by plants varies due to the overall nutritional requirement of the plant. In general, plants have the capacity to incorporate elements into their biomass as long as they are in a readily bioavailable form. There is an overall decrease in element concentration from elements classified as: “macro-nutrients,” such as Ca, K, Mg, S and P; “micro-nutrients” Cu, Zn, Ni and Mn; “beneficial,” Ni and Co; and, the “non-essential” elements La, Nb, Nd, Sm, As, Sn and Au. In general, this pattern is expressed at all 6 key orientation sites.

##### 5.1.1 Element Associations

Elements do not always occur in isolation, and they are more likely to be associated with a group of elements, which display similar chemical characteristics (Boyle, 1974). Due to the small data sets at the six individual study sites, a few patterns of possible inter-element (elements with similar chemical characteristics) associations are revealed, with some elements having relationships approaching a linear trend between leaves and twigs from the biogeochemical results across the Curnamona Province and adjacent areas in SE inland Australia (Chapter 3). However, at both Tibooburra and the Pinnacles, there are multiple patterns of inter-element associations.

There are groups of positive inter-element associations across both the Tibooburra and Pinnacles sites including: Ca-Mg-Sr-Ba (alkali earth metals), Mn-Zn, Co-Cu, Au-Cu and Zn-Cu (transition metals) and Al, Fe and Sc with La-Ce-Nd-Sm (lanthanide elements). These can be attributed to the valence charge of the cation, similar chemical properties in their hydrated form as they display equal ionic radii and charges such as: (alkali metals)  $\text{Na}^{1+}$  (0.4nm),  $\text{K}^{1+}$  (0.3 nm) and  $\text{Rb}^{1+}$  (0.3 nm); (alkali earth metals)  $\text{Ca}^{2+}$  (0.6 nm),  $\text{Mg}^{2+}$  (0.8nm),  $\text{Sr}^{2+}$  (0.5 nm) and  $\text{Ba}^{2+}$  (0.5 nm); (transition metals)  $\text{Zn}^{2+}$  (0.6 nm),  $\text{Co}^{2+}$  (0.6 nm),  $\text{Cu}^{2+}$  (0.6nm), Au (unknown) and  $\text{Zn}^{2+}$  (0.6 nm); (lanthanide elements)  $\text{La}^{3+}$  (0.9 nm),  $\text{Ce}^{3+}$  (0.9 nm),  $\text{Nd}^{3+}$  (0.9 nm)  $\text{Sm}^{3+}$  (0.9 nm) and,  $\text{Al}^{3+}$  (0.9 nm),  $\text{Fe}^{3+}$  (0.9 nm),  $\text{Sc}^{3+}$  (0.9 nm). These similarities make it possible for uptake interactions between individual elements to occur within *E. camaldulensis*.

In general, the chemical composition of the *E. camaldulensis* can be attributed to the relationship between the adjacent stream sediment, often referred to as soil-plant transfer (bioaccumulation). The extent that this relationship exists is variable. For example, the bioavailability of ions within the soil substrate and the presence of other ions with similar chemical characteristics may impact on the uptake of ions negatively (Stout, *et al.*, 1951), while other ions may result in the stimulation of element bioavailability (Hemphill, 1972). Similar elemental groups such as Ca-Mg-Sr-Ba (alkali earth metals); Mn-Zn, Co-Cu, Au-Cu and Zn-Cu (transition metals); and, Al, Fe and Sc with La-Ce-Nd-Sm (Lanthanide elements) for the *E. camaldulensis* at both Tibooburra and the Pinnacles.

These inter-element associations illustrate that plants have intrinsic uptake strategies that ultimately govern their overall elemental composition, such as:

- synergistic and antagonistic interactions; and,
- element translocation.

The current definitions of the above strategies have been taken from Kabata-Pendias & Pendias (1984), Brooks (1972) and are as follows:

- synergistic interactions occur when the combined physiological effect of two or more elements is greater than the sum of their independent effects;
- antagonistic interactions occur when the combined physiological effects of two or more elements is less than the sum of their independent effects; and,
- element translocation is generally in an upward direction towards the leaves. Garland (1981) also suggests that increases in evapotranspiration rates result in a greater movement of elements transported throughout the xylem and allocated to specific sites given their physiological role and the increase in cellular activity during the peak period of reproduction.

The ultimate concentration of a selected element, however, depends on the difference between the rate that it reaches a particular organ and the rate that the elements are consumed through biomass utilisation, such as loss via growth or energy production (Bargagli, 1998).

### 5.1.2 Synergistic and antagonistic interactions

In order to maintain a chemical balance, interactions between chemical elements may be synergistic, or antagonistic or both. The results show for the *E. camaldulensis* at both Tibooburra and the Pinnacles that no elements displayed antagonistic interactions, with only a

few elements within the *E. camaldulensis* showing evidence for synergistic interactions. The following (Table 5.1) highlights the synergistic interactions greater than or equal to 0.70 for essential to beneficial elements for both Tibooburra and the Pinnacles.

Table 5.1: Synergistic interactions between essential to beneficial elements observed across the study sites.

| Elements | Tibooburra             | Pinnacles                      |
|----------|------------------------|--------------------------------|
| Mg       | None                   | None                           |
| P        | None                   | None                           |
| S        | None                   | None                           |
| K        | None                   | None                           |
| Ca       | Sr, Ba                 | Sr, Ba                         |
| Fe       | Al, Th, La, Sm, Sc, Nd | Al, Cs, La, Nd, Pb, Pr, Sb, Si |
| Al       | Nd                     | Ce, Cs, Fe, La, Nd, Pr, Si     |
| Mn       | None                   | None                           |
| Ni       | None                   | None                           |
| Cu       | None                   | Pb, Sb                         |
| Zn       | None                   | Ag, Al, As, Cd, Pb, Sb, Th     |
| Na       | None                   | None                           |
| Co       | None                   | None                           |

Some researchers report on the interactions among essential to beneficial elements in plants the following (Table 5.2) modified after Dunn *et al.* (1995).

Table 5.2: Antagonistic and synergistic interactions between essential and trace elements in plants modified after Dunn *et al.*, (1995).

NOTE:  
This table is included on page 282 of the print copy of the thesis held in the University of Adelaide Library.

The *E. camaldulensis* results reveal that few of elements conform to the above table put forward by Dunn *et al.*, (1995), Table 5.2 highlights that there are very few synergistic interactions.

### 5.1.3 Environmental Controls

The landscape setting is one of the most important influences on the distribution of elements within the regolith substrate (Hill, 2004; Hill *et al.*, 2005). The ability of plants to biogeochemically express buried mineralisation potentially involves two mechanisms (Figure 5.1):

- root and associated biogeochemical ‘penetration’ of transported regolith to the underlying bedrock; or,
- root ‘amalgamation’ of stream sediments (and possibly hydrogeochemistry of shallow/perched aquifers) from within the transported regolith providing a chemical vector reflecting the underlying bedrock geochemistry.

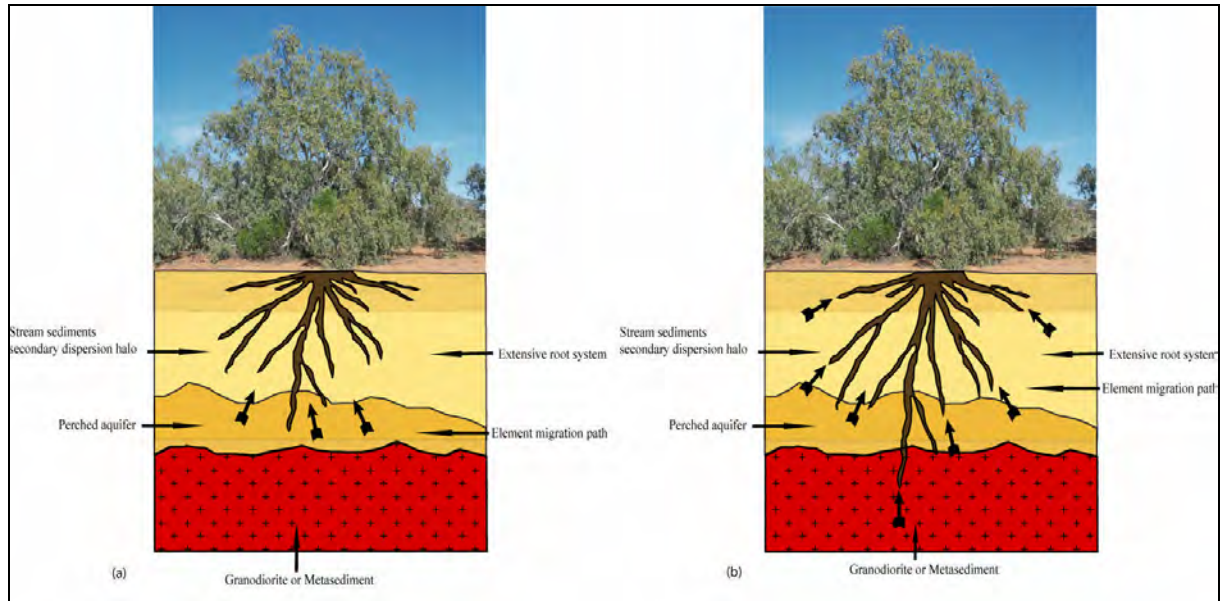


Figure 5.1: (a) Root and associated biogeochemical ‘amalgamation’ of stream sediments and possible hydrochemistry of perched aquifers, from within the transported regolith providing chemical vector reflecting the underlying bedrock chemistry, (b) root penetration to the underlying bedrock.

The overall geochemistry and characteristics of surrounding exposed bedrock in a given area will have either direct or indirect influences on the chemical composition of the vegetation. The competency of different bedrock types will lead to different degrees of weathering, and chemical input. Therefore, different degrees of weathering and chemical input will result in local variations in the chemical composition of the immediate regolith substrate and the overall chemical composition of plants.

In this study, comparisons of the whole rock geochemistry of the two main bedrock substrates with the biogeochemistry along the channel sampling transect (Tibooburra) revealed that the *E. camaldulensis* leaf chemical characteristics are more consistent with them being chemical ‘amalgamators’ of their regolith substrate, rather than chemical ‘penetrators’ to the underlying bedrock. For example, the metasediments generally have much higher As, Mg, K and Fe (> 10 times) contents than the granodiorite (Table 5.3), however the leaf chemistry from the plants growing over and adjacent to these two rock types revealed insignificant, or at the most very slightly higher concentrations overlying the metasediment (Figure 5.2). The results for As are an exception, with *Eucalyptus* adjacent to and growing on the granodiorite having higher concentrations than on the metasediment.

Table 5.3: Variations of selected metal concentration in oven dried tissue (leaves) of individual river red gums (RRG) across two bedrock substrates. Metal concentration in whole rock (WR) chemistry of the granodiorite and metasediment. Initial value represents the mean value  $\pm$  1sigma; values in brackets() are the range of values; and \* signifies values below detection limit. To calculate means, below detection limit values were taken as half the detection limit value. Values with a mean but no range recorded represent only one sample in that set. n= the number of samples recovered.

| Elements (ppm) | Granodiorite RRG Leaves (n=38) | Metasediment RRG Leaves (n=25) | Granodiorite WR | Metasediment WR | Stream sediment  |
|----------------|--------------------------------|--------------------------------|-----------------|-----------------|------------------|
| As             | 0.11 $\pm$ 0.07 (* - .31)      | 0.049 $\pm$ 0.027 (* - 0.098)  | 7               | 77              | 3.12 $\pm$ 0.72  |
| Fe             | 100 $\pm$ 20 (56 – 139)        | 119 $\pm$ 19 (88 – 147)        | 4364            | 56343           | 23700 $\pm$ 4265 |
| K              | 8847 $\pm$ 1119 (6161 – 10900) | 9158 $\pm$ 2192 (5520 – 13700) | 1618            | 36325           | 15050 $\pm$ 2521 |
| Mg             | 2496 $\pm$ 549 (1768 – 3925)   | 2731 $\pm$ 349 (1984 – 3554)   | 326             | 17029           | 4643 $\pm$ 1575  |

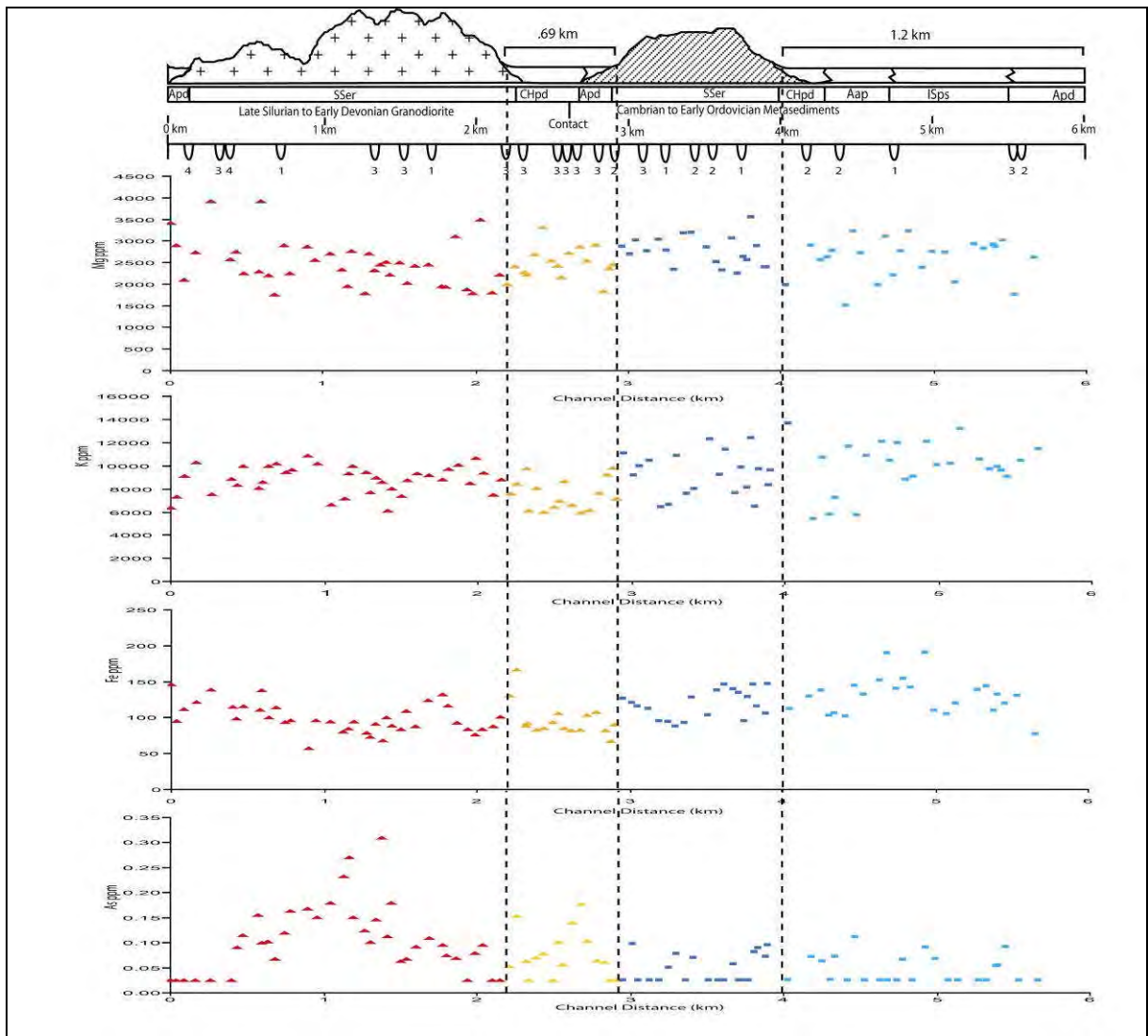


Figure 5.2: Mg, K, Fe and As abundance in oven dried tissue (leaves) of individual river red gums across two bed rock substrates.

The hypothesis that *E. camaldulensis* function more as regolith chemical ‘amalgamators’ rather than ‘penetrators’ is also consistent with associated studies of *E. camaldulensis* biogeochemistry in the Pine Creek – Pinnacles area (Chapter 4). *E. camaldulensis* expressed a chemical signature similar to that of Broken Hill type mineralisation such as Pb/Zn ratio of 3:2 and Ag/Pb 1:400. In addition, *E. camaldulensis* downstream of the Barrier-Pinnacles Mine, at the confluence of intersecting tributaries such as Gum Creek, draining from the area of the Broken Hill Line of Lode also expressed elevated Zn concentrations.

The elevated concentrations of Ag, Pb, Zn and As prompted the excavation of a trench around the *E. camaldulensis* at grid reference 531198 E; 6453879 N mN (Figure 5.3). This trench showed the interaction between the root system with the transported regolith, and the interface between the concealed mineralisation and perched water table. In general, the chemical composition of the *E. camaldulensis* tends to broadly reflect the contemporary landscape, such as the environmental chemistry (e.g. hydrochemistry and transported regolith), rather than strongly reflecting local lithological changes throughout the catchment, such as the underlying bedrock.

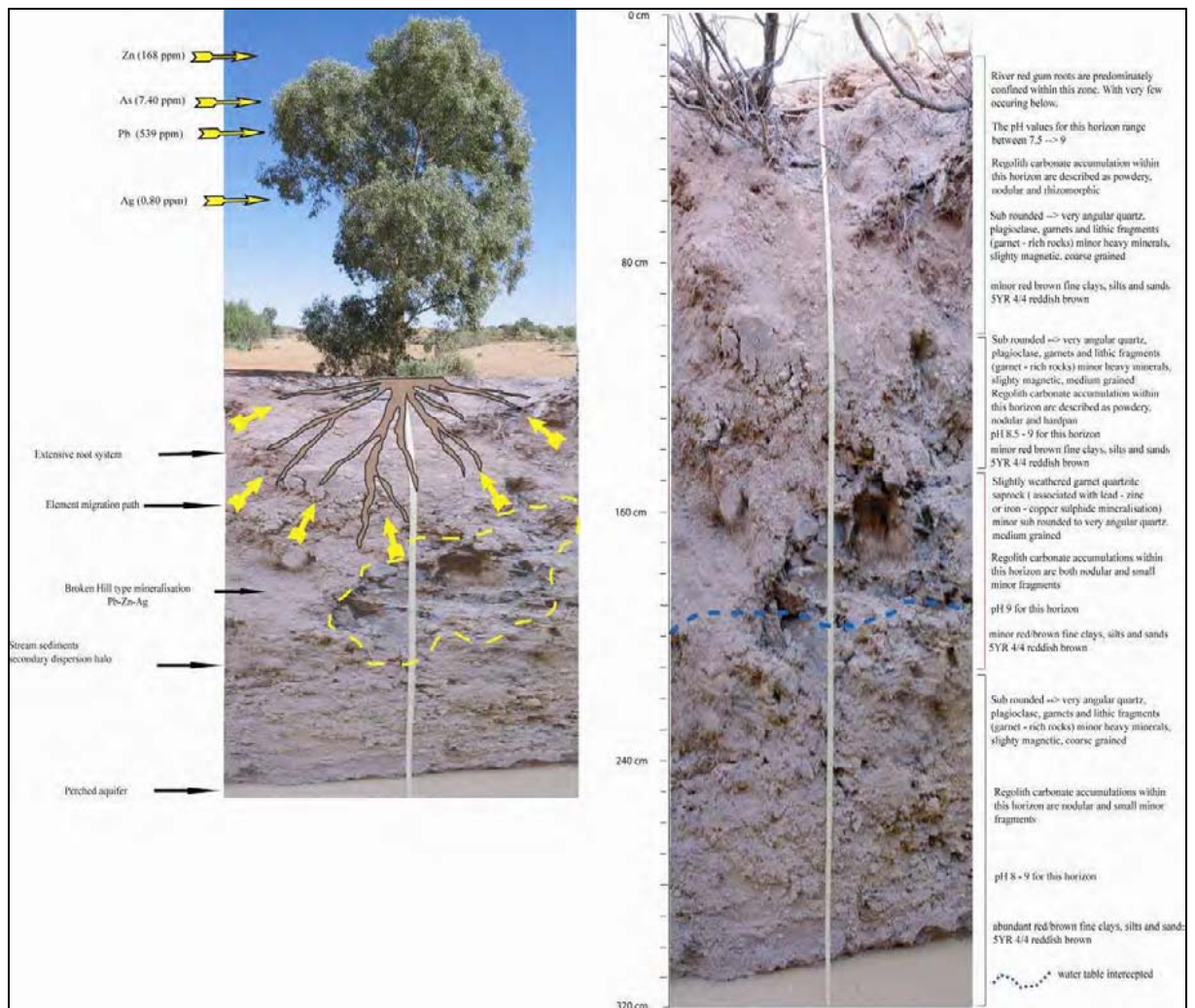


Figure 5.3: Elevated concentrations of Ag, Pb, Zn and As within the *E. camaldulensis*. The interaction between the root system with, the transported regolith, interface between the concealed mineralisation and perched water table.

#### 5.1.4 The contemporary landscape regolith-landforms

The regolith-landform settings for Tibooburra and the Pinnacles are shown by the regolith-landform maps (Figure 4.3 and Figure 4.26). The fluvial system in both regions is a process-response of the overall catchment that can be divided according to the overall relief of the surrounding landscape (e.g. low hills (slightly weathered bedrock), erosional rises (colluvial sediments), sandplains and longitudinal dunes (aeolian sediments) and areas of low lying relief (alluvial plains, alluvial drainage depressions and channel deposits).

The Tibooburra (Racecourse Creek) catchment is characterised by a 4<sup>th</sup> order, ephemeral sandy meandering to boulder braided, planar channel bed with a very low gradient of 0.14°, dominated by *E. camaldulensis*. The overall drainage pattern within the catchment is dendritic, expressing the channel crossing two homogenous bedrock substrates, however, in the upper reaches, the channel conforms to a rectangular pattern, expressing the jointing of the granodiorite. The overall channel width is irregular (e.g. widths of 6 – 8 m in the north and south, while in the lower sections of the granodiorite and neighbouring aeolian sandplains the channel width is 44 m).

The Pinnacles (Pine Creek catchment) area is characterised by a 4<sup>th</sup> order ephemeral, sandy meandering to gravel bar channel with a very low gradient of 0.19°, dominated by *E. camaldulensis*. In general the drainage pattern within the catchment is dendritic due to the channel flowing proximal to exposed bedrock, and associated subsurface bedrock having a similar weathering resistance. The channel width is irregular (e.g. widths of 25 m in the north and 40 m in the south, while in the mid-section of Pine Creek the channel width fluctuates between 60 - 95 m). Flanking the channel are approximately 300 m wide alluvial outwash plains.

Both drainage systems have similarities, such as there are several interfluves and tributaries entering the main channel, which when combine to promote intra-channel changes within the fluvial system. These intra-channel changes can be broadly subdivided into:

- free flow/erosion: predominately on the outer bends on the western side of Pine Creek and eastern side Racecourse Creek;
- floodout/deposition: point bars due to downstream migration of channel sediments, island side channels and aggradation at tributary confluences; and,
- constriction/barriers: exposed and shallow bedrock.

There are several spatial element patterns emerged from the biogeochemical results at both Racecourse Creek (Tibooburra) and Pine Creek (Barrier Pinnacles Mine) chapter 4.

### 5.1.5 Tibooburra

In general, the *E. camaldulensis* spatial chemical composition along Racecourse Creek show very little variability or distinct trends for Ca and Mg. However, several patterns emerge for the trees in the south (depositional 2) with elevated concentrations of Al, Fe, S, K, Sc, Zn, Br, La, Nd, Sm and Th, while P, As and Sr are less abundant. *E. camaldulensis* flanking bedrock exposures have higher concentrations Au, As, Zn, Rb, Cu, Ni, Mn and Br and lower concentrations in neighbouring deposition zones 1 and 2.

Racecourse Creek (Figure 5.4) outlines the general landscape settings that are influencing the chemical composition of the *E. camaldulensis*. The region includes 5 distinct zones as outlined in Table 4.9:

- northern section: Mesozoic palaeosurface and eastern tributary influence;
- granodiorite: bedrock constriction/barrier and tributary influence;
- depositional 1: influence of west and east tributaries;
- metasediment: primary influence; and,
- depositional 2: primary sink and tributary influence.

This spatial chemical composition strongly suggests an association between the contemporary landscape setting and the *E. camaldulensis* biogeochemistry.



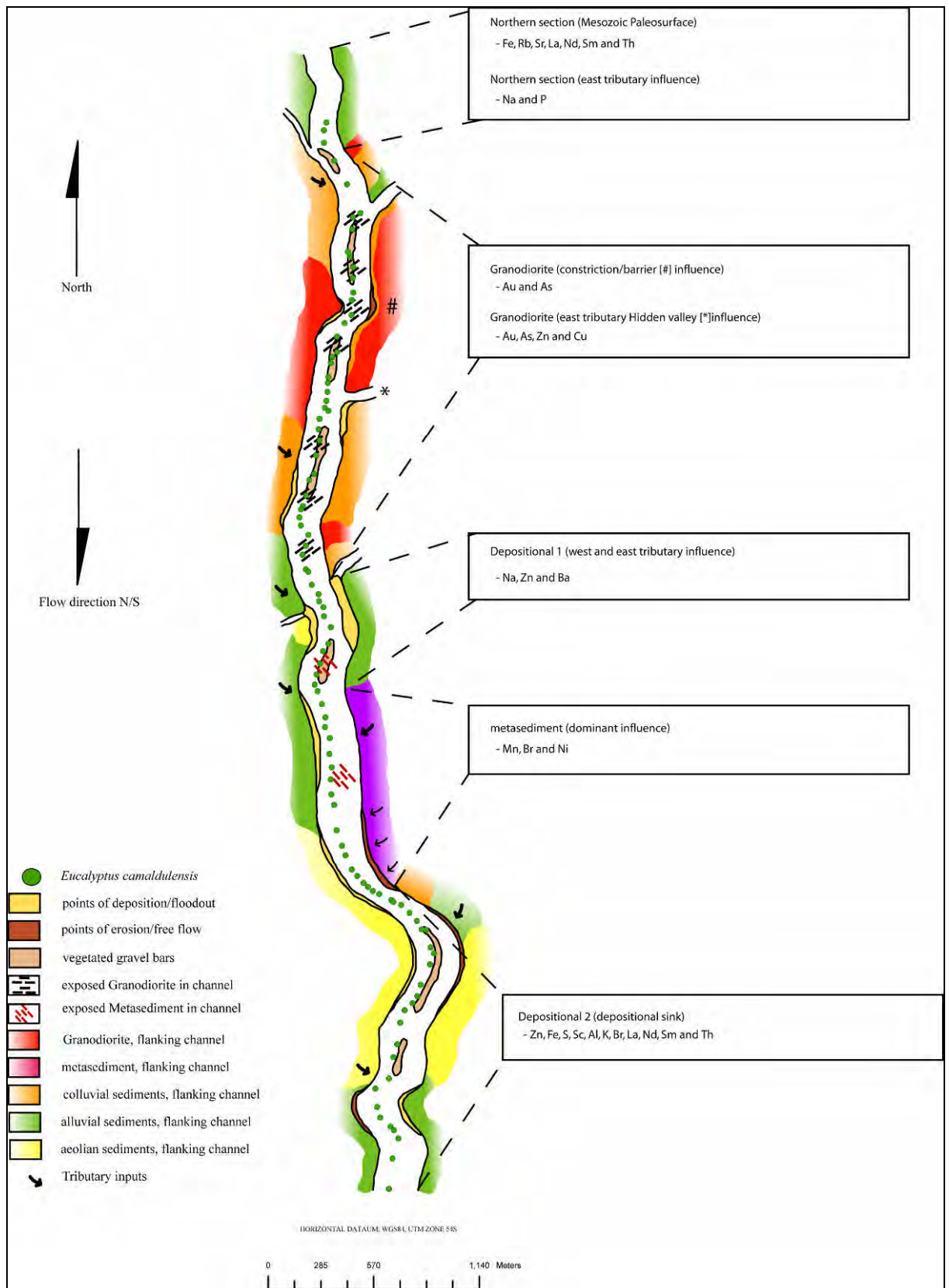


Figure 5.4: Sketch illustrating the morphology of Racecourse Creek, showing points of free flow/erosion, floodout/deposition and constriction/barriers. Regolith-landforms and exposed and subcropping bedrock geology within and flanking the main channel. Spatial variations of elevated element concentrations in *E. camaldulensis* at Racecourse Creek.

### 5.1.6 Palaeo-landscape control

An exhumed palaeo-surface flanks some of the margins of the granodiorite (exhuming palaeo-tors) and in particular forms a colluvial erosional rise that overlies the moderately weathered granodiorite at Quarry Hill (SSep<sub>1</sub>). *E. camaldulensis* associated with the palaeo-landsurface have elevated Fe, Rb, Sr, La, Nd, Sm and Th and relatively low concentrations of Al, Na, P, K, Cu Ni, and As. The landscape history of this palaeo-surface dates from prior to the Jurassic (Hill *et al.*, 2005; Chamberlain, 2001) after which it was buried by urassic-early Cretaceous Eromanga Basin sediments and has since been extensively eroded and reworked. Therefore the overall chemical composition of the *E. camaldulensis* in this region is therefore at least partly reflecting the geochemical composition of an ancient landscape, rather than that of the contemporary landscape.

### 5.1.7 Bedrock control

The local bedrock geology in the Racecourse Creek catchment both directly or indirectly influences *E. camaldulensis* trace element chemistry. The two most dominant bedrock exposures in the area are the granodiorite and metasediment, both of which have different chemical compositions, different weathering competencies and erosion potential.

The elevated Au, As, Zn and Cu concentrations in the *E. camaldulensis* (Table 5.4) at first appear to be associated with the weathered granodiorite, characterised by a well developed rectangular joint system, with cross cutting aplite and dacite dykes. Alexander (1976), however, reports that the only mineralisation to be associated with the granodiorite is minor cassiterite. Observations show that the dacite dyke associated with the granodiorite has inclusions of cubic voids that once hosted pyrite. It is possible that the elevated As, Zn and Cu are in part derived from the granodiorite its minor pyrite that may have inclusions of: As, Zn and Cu. In addition, *E. camaldulensis* samples from downstream of the constriction barrier defined by the flanking and partially exposed granodiorite also have increased concentrations of As, Zn and Cu. This area is dominated by sediment accretion, derived from the flanking granodiorite and the mechanical migration of upstream sediments. The accretion of sediments, is likely to be acting as an elemental sink and then being accessed by the *E. camaldulensis*.

Table 5.4: Variations of selected metal concentration in oven dried tissue (leaves) of individual river red gums adjacent to the granodiorite. Metal concentration of whole rock (WR) chemistry of the granodiorite. Initial value represents the mean; values in brackets () are the range of values; and \* signifies values below detection limit. To calculate means, below detection limit values were taken as half the detection limit value. n= the number of samples recovered.

| Elements (ppm) | Granodiorite RRG Leaves (n=38) | Granodiorite WR (n=1) |
|----------------|--------------------------------|-----------------------|
| As             | 0.016 (* - .31)                | 7                     |
| Cu             | 4 (2.00 – 8.00)                | 4                     |
| Zn             | 22 (11 – 38)                   | 38                    |

The elevated Au in *E. camaldulensis* (0.46 ppb), is from the confluence of an intersecting tributary (Hidden Valley) associated with the modern drainage system. The head waters of this modern alluvial drainage depression (tributary) can be traced back to the Mesozoic sediments and underlying palaeo-surface near Quarry Hill. An important sedimentary feature of the Quarry Hill sedimentary sequence is the basal gravels, which hosts detrital gold (Chamberlain, 2001). The gold within these basal gravels is irregularly distributed and does not appear to accumulate in channels or pockets (Barnes, 1975). Recoveries of crystalline

gold have also been reported to have been made (prospector, pers. comm., 2004) along this modern alluvial drainage depression. Therefore, the primary source for the Au expressed in the *E. camaldulensis* is most likely derived from the ancient basal conglomerates of Quarry Hill rather than directly from the granodiorite.

Several *E. camaldulensis* located slightly north of the metasediment have considerably reduced (average) concentrations of Ba, Fe, Mg, Mn and Ni and increased (average) concentrations of Ca, Na and P compared to the whole rock geochemistry (Table 5.5). The biochemical composition of these trees appears to reflect the geochemical composition of the alteration zone, especially the extensive depletion of the major elements (Ca > Mg > Mn > Na > Si > Fe > P) as outlined by Thalhammer (1991) in relation to the contact between the metasediment and granodiorite. The geochemistry of the alteration zone also reveals the relative enrichment of trace elements Cu > Zr > Rb > Y > Nd > Ba > Cr (Thalhammer, 1991). Trace element enrichment of Ba in *E. camaldulensis* slightly north of the metasediment compared other *E. camaldulensis* from along Racecourse Creek is possibly an indication of the *E. camaldulensis* taking up the available Ba, due to the reduced concentrations and unavailable Ca and Mg. In general Ca and Mg are considered antagonistic towards Ba, however, the Ca and Ba relationship for Tibooburra, is shown to be synergistic (Table 5.1).

In contrast, *E. camaldulensis* directly adjacent to the metasediment have increased concentrations of the (depleted) alteration/contact zone elements Ca, Mg, Mn, Na, Fe and P. In addition, several of the *E. camaldulensis* downstream from partially exposed bedrock and minor tributaries incising the metasediment have high concentrations of Mn, Ni and Br, which are indicative of the metasediment.

Table 5.5: Variations of selected metal concentration in oven dried tissue (leaves) of individual river red gums adjacent to the metasediment. Metal concentration of whole rock (WR) chemistry of the metasediment. Initial value represents the mean; values in brackets () are the range of values. To calculate means, below detection limit values were taken as half the detection limit value. n= the number of samples recovered.

| Elements (ppm) | Metasediment <i>E. camaldulensis</i><br>Leaves (n=25) | Metasediment Whole rock<br>(n=1) |
|----------------|---|----------------------------------|
| Ba             | 40 (17 – 89)  | 1240                             |
| Ca             | 12514 (7370 – 21100)                                  | 1708                             |
| Fe             | 119 (88 – 147)  | 56343                            |
| Na             | 214 (18 – 953)  | 438                              |
| Mg             | 2731 (1984 – 3554)                                    | 17029                            |
| Mn             | 207 (71 – 600)  | 519                              |
| Ni             | 3 (2 – 6)   | 30                               |
| P              | 978 (654 – 1574)                                      | 794                              |

### 5.1.8 Intersecting tributaries (alluvial drainage depressions)

The alluvial drainage depressions intersecting Racecourse Creek are associated with the NE/SW trending bedrock features of the granodiorite. In general, *E. camaldulensis* at tributary confluences have elevated concentrations of Na, P, S and Zn. Several of the alluvial drainage depressions have their upper reaches in the granodiorite. Whole-rock geochemistry (Table 5.6) shows that S and Zn with the exception of P and Na are higher in the metasediment; however, the *E. camaldulensis* adjacent to the metasediment have reduced concentrations of these elements. The metasediment is phyllitic and most elements are tightly bound within the lattice order. This suggests that the elevated Na, P, S and Zn are derived from the weathering of granodiorite, element mobility within the immediate landscape, the illuviation of water and associated soluble salts and the partially exposed Cretaceous bedrock in the intersecting drainage depressions.

Table 5.6: Metal concentration in whole rock (WR) chemistry of the granodiorite and metasediment. n= the number of samples recovered.

| Elements (ppm) | Granodiorite Whole rock (n=1) | Metasediment Whole rock (n=1) |
|----------------|-------------------------------|-------------------------------|
| Na             | 25350                         | 438                           |
| P              | 837                           | 794                           |
| S              | 248                           | 1490                          |
| Zn             | 55                            | 135                           |

### 5.1.9 Depositional Zone (southern margin)

There is an overall downstream increase in Zn, Fe, Al, S, Sc, K, Na, Br, La, Nd and Sm and reduced As concentration in *E. camaldulensis* tissues in the catchment. There are poor correlations between vegetation and the plant tissue-soil contamination markers (Chapter. 2) (Al, Fe and Ti), indicating that concentrations are not due to detrital contamination. The *E. camaldulensis* in the southern extent of channel occur predominately on the alluvial depositional plain. A characteristic of the alluvial depositional plain is the presence of light-brown to red-brown quartzose sands and micaceous silts. The chemical and physical property of the red-brown quartzose sands and micaceous silts is their small size, volume, surface area and cation exchange properties, making them a sink and source (Kabata-Pendias and Pendias, 1984) for the *E. camaldulensis*.

The downstream reduction in As content within the *E. camaldulensis* is indicative of the As-rich headwater granodiorite. Kabata-Pendias and Pendias (1984) propose that sediments derived from granites have a low affinity for the adsorption of As, making it relatively available for uptake. This is consistent with the *E. camaldulensis* associated with the granodiorite having elevated As concentrations.

### 5.1.10 Pinnacles

Pine Creek *E. camaldulensis* spatial chemical composition patterns indicate that Na and Cl show very little variability or distinct trends. However, *E. camaldulensis* in the north, adjacent to the Pinnacles Mine (Broken Hill Group) have anomalous concentrations of Ag, Pb, Zn, Cd, As, Fe, S, Cu, Sb, Al, Si, Ce, Cs and REE, while Mg, Ca, Sr, Ba, Rb, K, Mn and P are less abundant compared to the other *E. camaldulensis* assayed in the catchment. In contrast, the inverse is observed downstream from the Pinnacles Mine. The accumulation of Cl, K and Na dominate the lowest margins of Pine Creek.

Pine Creek (Figure 5.5) outlines the general landscape settings that are influencing the chemical composition of the *E. camaldulensis*. The region reveals 5 distinct zones as outlined in Figure 4.26 and Table 4.17, which include the following:

- Broken Hill Group (North): Barrier Pinnacles Mine (Ag-Pb-Zn mineralisation);
- Thackaring-Pinnacles schist zone: concealed by transported regolith ;
- Broken Hill Group (Central): concealed by transported regolith;
- Cainozoic rock units: concealed by transported regolith; and,
- Broken Hill Group (South): concealed by transported regolith.

This spatial chemical composition strongly suggests an association between the contemporary landscape setting and the *E. camaldulensis*.

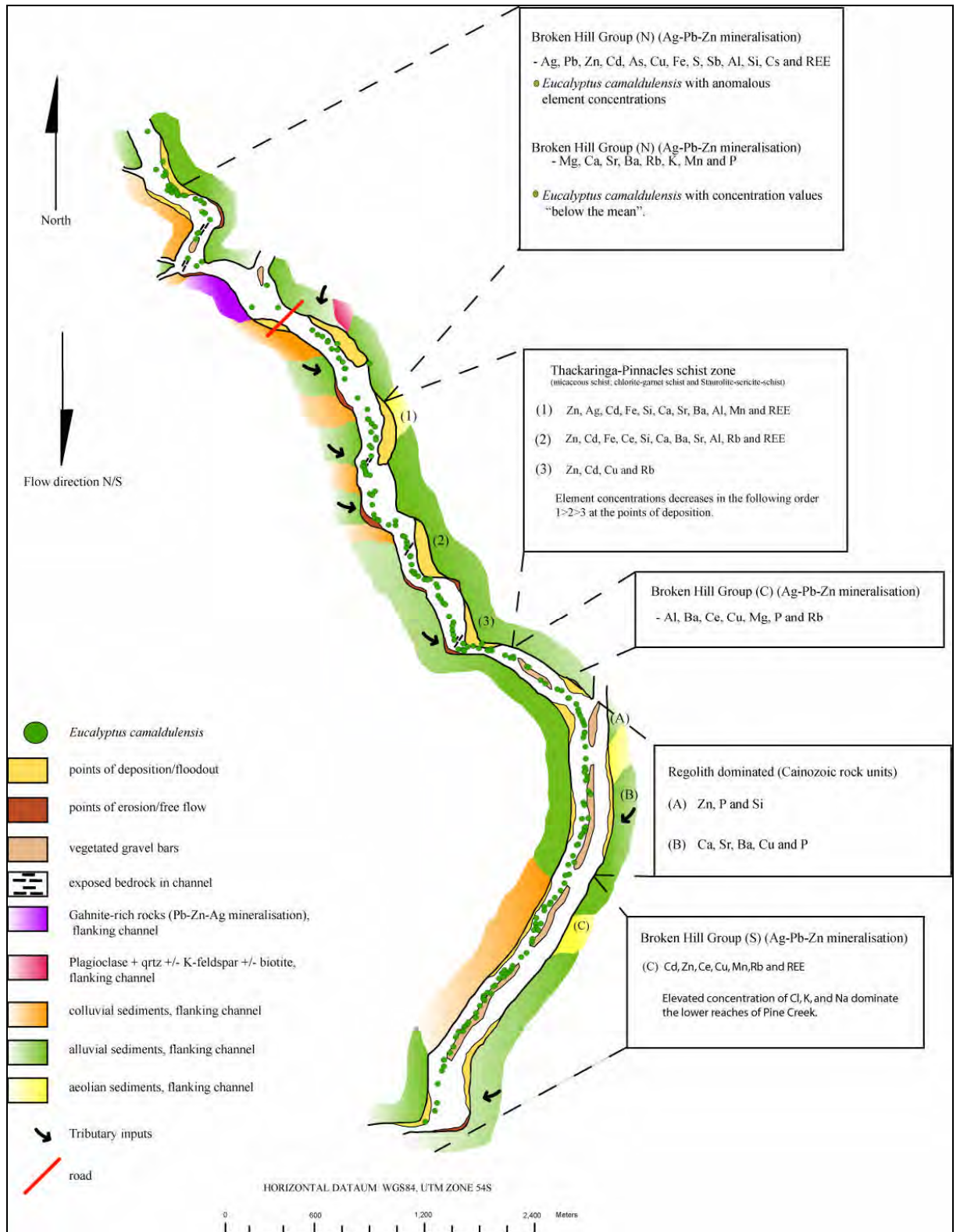


Figure 5.5: Sketch illustrating the morphology of Pine Creek, showing points of free flow/erosion, floodout/deposition and constriction/barriers. Regolith-landforms and exposed and subcropping bedrock geology within and flanking the main channel. Spatial variations of elevated element concentrations in *E. camaldulensis* at Pine Creek.

### 5.1.11 Bedrock control

The local bedrock geology in the Pine Creek catchment, especially in the north (Pinnacles Mine), directly and indirectly influences the chemical composition of the *E. camaldulensis*. The dominant landform flanking Pine Creek downstream of the Pinnacles Mine is alluvial outwash plains. There are also several partially exposed bedrock units in the lower reaches of the catchment setting (e.g. subcropping in and on the flanks on alluvial drainage depression) that may also influence the overall *E. camaldulensis* chemical composition.

### 5.1.12 Broken Hill Group (N) (Ag-Pb-Zn mineralisation)

The *E. camaldulensis* flanking the Barrier-Pinnacles Mine (Figure 5.5) have elevated Ag, Pb, Zn, Cd, As, Fe, S, Cu, Sb, Al, Si, Ce, Cs and REE concentrations and relatively low background concentrations of Mg, Ca, Sr, Ba, Rb, K, Mn and P. These samples with elevated concentrations have a strong association with the underlying Broken Hill Group (BHG) which is known to host Ag-Pb-Zn mineralisation (Figure 5.3). Rugless and Govett (1984) recognised a similar element association in drill core and surface rock samples, with the enrichment of Pb, Zn, Mn, Fe and (to lesser extent Cu and Ca) and the depleted Mg, Na, K, Rb, Sr and Ba that define narrow dispersion haloes associated with Pb-rich and Zn-rich mineralisation lode horizons, and adjacent metasedimentary rocks in this area. Specifically, several *E. camaldulensis* have a Pb/Zn ratio of 3:2, while the main lead lode is characterised by a Pb/Zn ratio between 2:1 and 4:1 and elevated Ag/Pb ratio of 45 g/t per 1% (~ 1:220), while Zn-rich mineralisation in the surrounding zone is generally characterised by a lower Pb/Zn and Ag/Pb ratios (Barnes, 1988). This suggests that the Pb/Zn ratio of 3:2 and Ag/Pb 1:400 is indicative of surrounding Zn-rich mineralisation.

### 5.1.13 Depositional zone (Thackaringa-Pinnacles schist zone)

Several individual trees immediately downstream have colonised point bars within the main channel, and have above background concentrations of elements that have a strong relationship with the Ag-Pb-Zn mineralisation (BHG) such as: Zn, Ag, Cd, Fe, Al, Si and REE. The chemical composition may indicate: (i) Ag-Pb-Zn mineralisation extending further down Pine Creek; (ii) an increase in transported regolith depth over mineralisation, resulting in the slightly above background concentrations; or, (iii) depositional features of the contemporary channel (Figure 5.5) acting as elemental sinks. The Pb/Zn and Ag/Pb ratios indicative of Ag-Pb-Zn mineralisation are not expressed in any of the *E. camaldulensis*. Consequently the above background chemical composition is a reflection of the contemporary landscape. This area is dominated by sediment accretion, derived from flanking colluvial, alluvial, aeolian and fluvial sediments, the mechanical migration of upstream sediments, and intersecting tributaries. The accreting sediments depositional points 1, 2 and 3 (Figure 5.5) correspond to elemental sinks that are accessed by the *E. camaldulensis*. In addition, the overall chemical composition of the *E. camaldulensis* within the depositional points 1, 2 and 3 decreases in concentration in the order of 1>2>3, further reflecting the overall mobility of the elements.

### 5.1.14 Regolith dominated (Cainozoic rock units)

In general, the chemical composition of the *E. camaldulensis* within the zone referred to as Cainozoic rock units (Brown, 1978) (Figure 5.5) have slightly high concentrations of Zn, P and Si (A) and Ca, Sr, Ba, Cu and P (B) compared to background concentrations (Table 5.7). A dominant feature of this region is the NE/SW longitudinal dune (Figure 4.26), resulting from the predominantly westerly winds and the local topographic interference of Stauroilite Ridge (SSer<sub>2</sub>) in the south. The slightly high Zn concentration at the confluence of Gum/Kelly Creek intersecting Pine Creek is possibly due to the high chemical mobility of Zn and that the upper reaches of Gum/Kelly Creek are proximal to the Ag-Pb-Zn Broken Hill type mineralisation such as the Main Line of Lode, White Leeds, Rising Sun and Rising Sun North. The *E. camaldulensis* with slightly high concentrations of Ca, Sr, Ba and (to a lesser extent Cu and P) are colonising an island sand bar. A possible source for the elevated elements are the exposed (SSer<sub>2</sub> and SSep<sub>1</sub>) slightly weathered bedrock units associated with hills, rises and erosional plains and alluvial drainage depression defined by (Brown, 1978) as amphibolites and cupriferous quartz lodes.

Table 5.7: Shows that of a number of *E. camaldulensis* within the regolith dominated (Cainozoic rock units) area have concentrations greater than the mean.

| Element (ppm) | Values below the mean | A (highest concentration) | B (highest concentration) | > than values below the mean |
|---------------|-----------------------|---------------------------|---------------------------|------------------------------|
| Zn            | 52                    | 116                       |                           | 2.2                          |
| P             | 1090(A)/1198(B)       | 1620                      | 1920                      | 1.4(A)/1.6(B)                |
| Si            | 910                   | 1510                      |                           | 1.6                          |
| Ca            | 9268                  |                           | 16800                     | 1.8                          |
| Sr            | 35                    |                           | 66                        | 1.8                          |
| Ba            | 15                    |                           | 24                        | 1.6                          |
| Cu            | 4.9                   |                           | 7                         | 1.4                          |

### 5.1.15 Depositional zone (Broken Hill Group (S) Ag-Pb-Zn mineralisation)

*E. camaldulensis* in the southern extent (Figure 5.5) of the study have above background concentrations of Zn, Cd, Ce, Cu, Mn Rb and REE (Table 5.8), and the Pb/Zn and Ag/Pb ratios indicative of mineralisation are not expressed in the assayed *E. camaldulensis*. Several of the elements however are associated with Ag-Pb-Zn Broken Hill type mineralisation such as Zn, Cd, Ce, Cu and REE. The chemical composition of the *E. camaldulensis* in the area express the proximal partially exposed and subcropping slightly weathered quartz-gahnite, amphibolite and pegmatites (Senior, 2000; Brown., 1978), which are flanking drainage depression to the south of the main channel (Figure 4.26). In particular, (Senior, 2000) reports that the dispersion pathway for elements associated with the bedrock in the area is predominately confined to the alluvial drainage depressions.

Table 5.8: Shows that of a number of *E. camaldulensis* within the depositional zone (Broken Hill Group (S) Ag-Pb-Zn mineralisation) area have concentrations greater than the mean.

| Element (ppm) | Values below the mean | C (highest concentration) | > than values below the mean |
|---------------|-----------------------|---------------------------|------------------------------|
| Zn            | 44                    | 70                        | 1.6                          |
| Cu            | 4.9                   | 7                         | 1.4                          |
| Cd            | 0.23                  | 0.59                      | 2.6                          |
| Ce            | 0.12                  | 0.38                      | 3.2                          |
| Mn            | 172                   | 361                       | 2.1                          |
| Rb            | 1.9                   | 5.3                       | 2.8                          |

The overall chemical composition of the *E. camaldulensis* for Tibooburra and the Pinnacles can be divided into the following major influences:

- their spatial relationship to their immediate landscape and regolith-landform settings (both contemporary and ancient);
- the geochemical composition of both exposed and buried bedrock;
- the interaction of their extensive root system and the interface between the perched water table and concealed bedrock/mineralisation;
- the relative mobility of the elements within the transported regolith;
- plant uptake and translocation strategies; and
- temporal influences.

## 5.2 PLANT PROCESS/ INTERNAL CONTROL AND ELEMENT PARTITIONING

The allocation of elements and the overall chemical composition of trees depends on element mobility, affinity to cell compartments (Ernst, 1990), the rate that it reaches the organ, and is consumed or lost to growth and energy production (Bargagli, 1998). Studies have shown that organs with high metabolic activity generally have the highest concentration of elements (Markert, 1989). Carlisle & Cleveland (1958) suggest that the element content of tree organs decrease in the following sequence: leaves; twigs; buds; bark and roots, however the results reveal that only a few elements conform to the suggested order of Carlisle & Cleveland (1958).

The partitioning and relative proportion of the elements within the organs of the *E. camaldulensis* at all six sites is heterogeneous (no clear patterns in tree element composition), however, the preferential partitioning and proportion of the same element throughout the *E. camaldulensis* organs is generally similar. The following (Table 5.9) summaries the partitioning of several elements ranging from their highest to lowest content throughout the *E. camaldulensis* organs.

Table 5.9: The preferential partitioning of elements throughout the *E. camaldulensis* organs observed at all six sites. BD = buds, L = leaves, T = twigs, BR = bark and R = root.   Elements that display a similar organ partitioning to that suggested by Carlisle & Cleveland (1958)

| Macro-elements | Organ partitioning | Micro-elements | Organ partitioning | Non-essential elements                  | Organ partitioning    |
|----------------|--------------------|----------------|--------------------|---|-----------------------|
| P              | BD>L>T>BR          | Mn             | L>BD>T>BR          | As                                      | L>BD>T                |
| K              | BD>L>T>BR          | Cu             | T>BD>L>BR          | Sc                                      | L>T>BD                |
| S              | BD>L>T>BR          | Zn             | T>L>BD>BR          | Au Williams Crk<br>Bindarraah<br>Teilta | BR>T>L<br>R<br>T>BR>L |
| Ca             | BR>T>BD>L          | Ni             |                    | Cd (Flying Doctor)                      | BD>T>L>BR             |
| Fe             | L>T>BD>BR          | Al             | L>T>BD>BR          | Br                                      | L>BD>BR>T             |
| Mg             | BD>L>BR>T          | Na             | BD>L>T>BR          | Sr                                      | BR>T>BD>L             |
|                |                    |                |                    | Ba                                      | BR>T>BD>L             |
|                |                    |                |                    | REE                                     | L>T>BD>BR             |

The transport of elements occurs predominately within the xylem, with subsequent re-translocation of elements via the phloem (Swanson, 1957). Element uptake, partitioning and the relative proportion of the elements within the *E. camaldulensis* organs is largely a reflection of the role of the organ, the element's physiological function and mobility within



the tree. It is also possible that the time of sampling (autumn), which is defined as a period of peak biomass (Huenneke *et al.*, 2001), has influenced the preferential partitioning of the elements throughout the organs.

The content of macro-elements P, K and S for different organs decreases in the following order buds>leaves>twigs>bark and to some extent Mg exhibited a similar partitioning buds>leaves followed by bark>twigs. The physiological roles of the elements outlined by (Kabata-Pendias & Pendias, 1991; Campbell, 1996; Marschner, 1997) include:

- P: nucleic acids, P-esters;
- K: major cytoplasmic cation, protein synthesis;
- S: cysteine, methionine, redox reactions; and,
- Mg: chlorophyll, protein and DNA synthesis.

The buds/inflorescence of the *E. camaldulensis* consists of a terminal bud containing cream-white flowers (stamen), stigma, style and ovary (reproduction organs). The preferential allocation of the elements to the buds is possibly a survival mechanism that will ensure the establishment and growth of seedlings in an otherwise nutrient poor substrate. Some organs, such as young leaves and buds, have an ability to withdraw these mobile elements from older organs via the phloem (Smith, 1962; Salisbury and Ross, 1992), such as from senescing leaves.

The partitioning and preferential allocation of Ca bark>twigs>buds>leaves is indicative of its physiological function, as it provides internal strength, and maintains membrane stability (Epstein, 1972). Elements with similar chemical characteristics (see section 5.1.1 element associations), such as Sr and Ba, exhibit similar partitioning. The initial uptake and allocation of Ca, and possibly to some extent Sr and Ba via the xylem, is preferentially towards organs that have low transpiration rates (Pilbeam & Morley, 2007), which supports the bark>twigs>buds>leaves partitioning observed. The physiological mobility of the alkaline earth elements, Ca, Sr and Br, is low (Dunn *et al.*, 1995) especially within the phloem where element re-translocation predominately occurs. Due to the structural role of Ca and possibly the related uptake of Sr and Ba in trees, such as *E. camaldulensis*, the decrease in element content appears to mirror the relative strength of the organs.

The partitioning of the micro-elements (Mn, Cu, Zn and Ni) and beneficial elements (Na and Al) appears to be independent of each other. These variations in allocation are reflective of the organ's nutritional requirement and the physiological function of the organ and element. For example, the preferential allocation of Mn in the leaves is due to its role in the activation of enzymes in respiration. The partitioning of Mn also reflects the decrease in photosynthesis ability of the organs leaves>buds>twigs>bark. In contrast the concentration of Al in the leaves compared to the twigs is above the suggested average for chemical dry-weight abundance for plants. The mobility of Al within trees is low (Miyasaka *et al.*, 2007), and it is possible therefore that the preferential partitioning to the leaves is a regulatory measure, as when the leaves senescence the re-translocation of Al is minimal.

The branches and stems/twigs may contain a large proportion of the nutrients in the tree and therefore act as elemental sinks (Grove *et al.*, 1996). This is reflected in the preferential allocation of Cu and Zn within the twigs. The physiological role of Cu and Zn is in the promotion of electron transfer during photosynthesis (Cu) and chlorophyll synthesis (Zn) within the leaves. The leaf concentration for both elements is within the suggested average

composition ranges of plant material, which may imply that the twigs are storing Cu and Zn, which will then be re-translocated to the leaves as both elements are utilised. This preferential allocation is a possible strategy for the efficient use of the elements that are either limited in bioavailability or that the immediate substrate is depleted in these elements.

In general, plants will accumulate elements without regard to the elements having an essential role in plant metabolism or physiology (Barker & Pilbeam, 2007). The compartmentation of the non-essential and toxic elements in their vacuoles is a detoxification strategy (Hall, 2002), and prevents them from interfering with the metabolically active organs and growth. The partitioning of the non-essential elements (As, Sc, Au-Williams Creek, Sr, Ba, Br and REE) is predominately towards organs that can be shed, such as leaves and bark, and through this redistribution the concentrations of these elements can be regulated.

In contrast, Cd (only detected at Flying Doctor) is partitioned preferentially to buds. The region hosts Ag-Pb-Zn mineralisation (Broken Hill type deposits), and Cd and Zn are known to have similar chemical properties. The allocation of Cd in the following organs buds>twigs>leaves>bark is possibly indicative of the reduced photosynthesis potential of the organs, as Cd typically inhibits photosynthesis and transpiration (Alloway, 1995).

The production of buds appears to have influenced the overall element allocation and mineral content across the *E. camaldulensis* organs, which needs to be considered when sampling and interpreting data. In addition to element uptake, the internal biochemical cycling of essential elements, with possibly the exception for Ca, Sr and Ba, is a major component of element re-translocation within eucalypts (Grove *et al.*, 1996).

### 5.3 SEASONAL VARIABILITY

The analytical results from individual trees were different over time (2 years) at all six sites. Variations appear to be irregular and do not follow systematic rainfall, temperature and seasonality patterns (autumn, winter, spring and summer). There is a systematic variation related to growth pattern characteristic, however, other variables (e.g. sampling representation and groundwater chemistry) are not fully constrained here and may also be important. These variations may be significant for mineral exploration and natural resource management programs, especially how they relate to biogeochemical thresholds/anomalies concentrations.

One study undertaken by Huenneke *et al.* (2001) in the Chihuahuan Desert of North America, proposes that vegetation in semi-arid terrains have highly variable compositional changes with time. These changes may be associated with the following annual growth cycle:

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

Two growth patterns were observed for all six study sites, based on the physical appearance of the *E. camaldulensis* over the 2 year period. They were defined as periods of growth and non-growth characterised by:

- period of growth: spring (initiation of flower bud production) and summer (increased bud, fruit and leaf production); and,

- period of non-growth: autumn (abundant fruit, buds and leaves) and winter (minor fruit and bud production).

In general, most of the elements recorded their highest concentration during periods of growth. The following summarises the elements at each study site that recorded their highest concentration during periods of growth and their lowest concentration during periods of non-growth for both 2003 and 2004:

- Winninnie Creek: Ba, Br, Ca, Ce, Na, Al, Cu, Mn, Ni, P, S and Sr;
- Cutana Creek: Ba, Br, Fe, Sc, Al, Cu, Ni, P, S and Sr
- Willawillyong Creek (Flying Doctor): As, Fe, Na, Al, Cu, Mn and S;
- Williams Creek: As, Ba, Ca, La, Na, Cu, Mn, P and Sr;
- Teilta Creek: Ba, Br, Ca, La, Na, Al, Cu, Mg, Mn, S and Sr; and,
- Racecourse Creek (Tibooburra): Ba, Al and Sr.

The higher concentrations of elements during periods of growth (spring and summer), corresponds with an increase in temperature, rainfall and extended periods of daylight, and therefore the potential for peak photosynthetic activity and evapotranspiration. For example, it is well known that Cu is important for the promotion of electron transfer during photosynthesis, so the higher concentrations of this element during periods of growth is indicative of the increased photosynthetic activity of the *E. camaldulensis*. The increase of element concentrations during periods of growth is also consistent with the suggestion of Garland *et al.* (1981) that the ultimate concentration of an element is related to the flux of transpiration through evapotranspiration and should be at its greatest during summer.

The decrease in element concentration during periods of non-growth (autumn and winter), for example Ca, Cu, and S, is indicative of the *E. camaldulensis* having peak biomass. The increase of cellulose and starches (biomass/plant tissue) produced during the growing period (spring and summer) results in a decrease in element concentration within the leaves due to dilution.

In contrast, at each of the study sites a few elements recorded their highest concentration during the periods of non-growth, such as at Winninnie Creek (K and Nd), Cutana Creek (K), Willawillyong Creek and Williams Creek (Br and K), Teilta Creek (K, Rb and Nb), and in particular at Racecourse Creek (As, Br, K, Sc, Na, Zn, Mg, P and S). Several of the elements are considered non-essential (As, Br, Sc, Na, Rb, Nb and Nd) with the exception of K, Zn, Mg, P and S. The higher concentration of the essential elements in the leaves is possibly a survival mechanism. For example, K is a major cytoplasmic cation and is required for protein synthesis (Kabata-Pendias & Pendias, 1991). To ensure that elements do not become a limiting factor during this relatively inactive period, the elements are possibly compartmentalised, into non-metabolic and inactive organs, and re-translocated when required.

In addition, during the period of non-growth, the *E. camaldulensis* and micro-organisms residing in the surrounding substrate are considered to be less biologically active. The higher concentration of the non-essential elements may be related to a substitution of one element for another. For example, As and P have similar chemical properties, where P is considered antagonistic towards As, and P will displace As in the competition for sorption within the soil environment (O'Neill, 1995). When the *E. camaldulensis* is less biologically active, potentially harmful elements may accumulate within the tree, and are less diluted by the reduced uptake and activity of the other elements.

Furthermore, there are subtle differences in the elemental composition of the *E. camaldulensis* between 2003 and 2004 for the same growth period, especially at Flying Doctor, Williams Creek, Teilta and to some extent Tibooburra. These variations may reflect other variables that are not fully constrained here and may also be important (e.g. groundwater chemistry and sample representation).

Fluctuations in surface temperature and soil moisture will influence the supply and overall chemical composition of *E. camaldulensis*. A feature of the *E. camaldulensis* is they have a dimorphic root system, consisting of two zones: (i) near the surface (lateral roots) to capture summer rains and take up nutrients; and, (ii) at depth (sinker roots) to utilise ground water (Knight, 1999). Mensforth *et al.* (1994) and Thorburn & Walker (1994) have shown that the *E. camaldulensis* is highly opportunistic in water sources, alternating between using shallow and deep water sources depending on availability.

For example, at Flying Doctor (Broken Hill) the rainfall pattern was consistent for 2003 and rather erratic for 2004. The elemental compositions of the *E. camaldulensis* for periods of non-growth (2003 and 2004) are comparable, allowing for the significant reduction in rainfall (28.4 mm) during the transition from the period of growth (spring-summer) in 2003, to the period of non-growth (autumn-winter) in 2004. This suggests that the rainfall for September-December (2003) may have been sufficient enough to provide a soil/pore water nutrient-rich source that was accessed by the *E. camaldulensis* (Figure 5.6) during periods of reduced rainfall in March-June 2004.

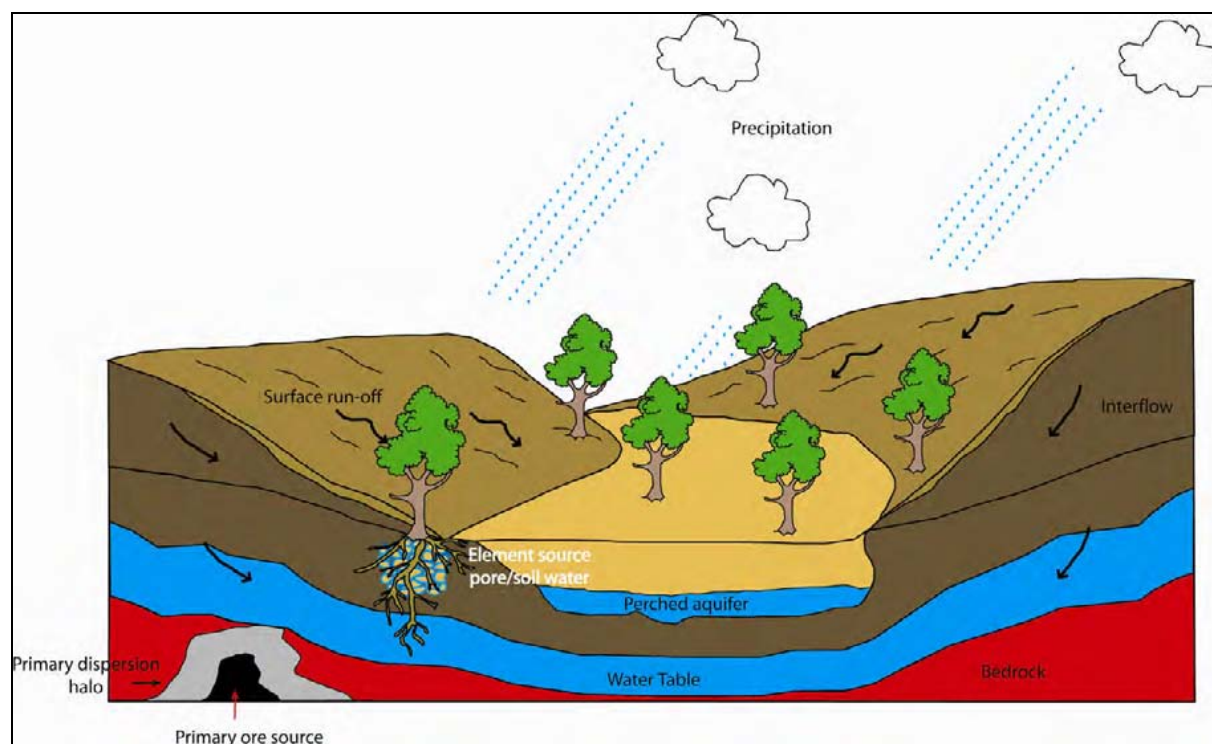


Figure 5.6: Cartoon illustrating the *E. camaldulensis* accessing the nutrient rich soil/pore waters supplied by the (spring-summer) 2003 that the *E. camaldulensis* is further accessing during a period of reduced rainfall (autumn-winter) 2004.

The rainfall for the periods of growth (spring-summer) for 2003 and 2004 was consistent, however, the elemental composition of the *E. camaldulensis* was significantly different such that As, Ca, Fe, La, K, Sm, Sc, Zn, Al, Mg, Nd, Ni, P, Sn and Sr are reduced during (spring-summer) 2004 compared to September-December (spring-summer) 2003. This possibly indicates that the *E. camaldulensis* has utilised all of the bio-available elements from within

the pore/soil surface zone, and the extensive dimorphic root system is accessing the water table (Figure 5.7), which is either deficient in these elements or that they are not in a readily available form.

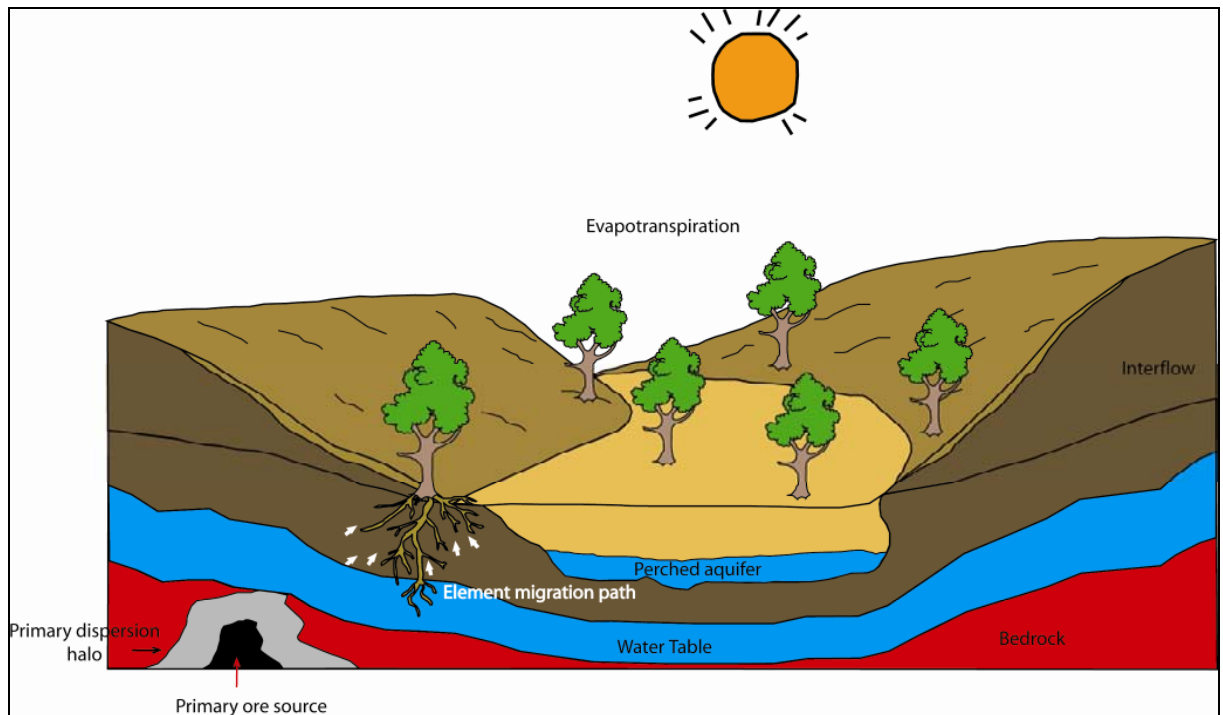


Figure 5.7: Cartoon illustrating the *E. camaldulensis* accessing the water table directly after a period of reduced rainfall (autumn-winter) 2004 to maintain high transpiration rates and growth during spring and summer 2004.

The variations in concentrations for the different growth periods are the first step in constraining the influences of temporal variability on the *E. camaldulensis*. In general, the concentration values between the two periods were within a few ppm of each other, with the exception of P, K, Ca, Mg and S with concentration values differing as much as 100s to 1000s (e.g. Flying Doctor non-growth Ca – 8750 ppm and growth 11750 ppm). For mineral exploration the degree of variability is important, as this refers to the amount of fluctuation that an element may experience between seasons, in this case growth patterns. The estimation of the degree of variability between the two growth periods for all six sites is shown in chapter 3, and was established by  $(\max_{(\text{conc})} - \min_{(\text{conc})}) = X; X/\max_{(\text{conc})} (x) 100 = \%$ . Examination of the elemental concentration of *E. camaldulensis* coupled with the defined categories of seasonal variation in element concentrations as outlined by Markert & Weckert (1989) are summarized in Table 5.10.

Table 5.10: The degree of elemental variation between (2003 and 2004) across the six study sites. Highlighting which elements have a variation >80% therefore sampling time needs to be considered when undertaking a mineral exploration program.

|  | <b>Winnininnie Creek</b>                           | <b>Cutana Creek</b>                           | <b>Willawillyong Creek</b>                | <b>Williams Creek</b>                  | <b>Teilta Creek</b>                        | <b>Racecourse Creek</b>  |
|--|--|---|---|--|--|--------------------------|
| No seasonal variability                |  |   |   |  |  |                          |
| Slight seasonal variability <30%       | Ba, Br, Ca, K, Sm, Na, Zn, Cu, Mg, Mn, P, S and Sr | Br, Ca, K, Sm Na, Sc, Mg, Mn, Ni, P, S and Sr | Ba, La, K, Sm Na, Zn, Cu, Mg, P, S and Sr | Ba, K, Sm, Na, Zn, Cu, Mg, Mn, P and S | Ba, Br, Ca, Sm Na, Zn, Mg, Mn, P, S and Sr | Ba, Ca, Zn, Mg, S and Sr |
| Low seasonal variability ~30%          | La and Sc  | Ba, Fe, Zn, Cu and Nd                         | Ca, Sc and Mn                             | Br, Ca, La, Sc and Sr                  |  | Br, K and P              |
| Intermediate seasonal variability ~50% | Fe   |   | As  | As                                     | Ni   | Ni and Al                |
| High seasonal variability >80%         | Ni   |   | Fe  | Ni                                     |  | Ni                       |

A few elements showed concentration variability within more than one parameter (slight, low and intermediate). These variations occurred at Flying Doctor, Williams Creek, Teilta and Tiboburra (see chapter 3), which is possibly a further reflection of the extensive dimorphic root system alternating between using shallow and deep water sources depending on availability. In general, the slight to intermediate variation for many of the elements (Table 5.10) at the six study sites suggests that seasonal variations are less important. Elements that have a high seasonal variability need to be considered as the most appropriate sampling period for mineral exploration, and for the elements shown here the following sampling periods have been recommended:

- Winnininnie Creek – Ni (autumn);
- Willawillyong Creek – Fe (summer);
- Williams Creek – Ni (summer); and,
- Racecourse Creek – Ni (summer).

The high seasonal variability recorded for Au, would largely represent the patchy nature of the element in the substrate environment, and with concentrations only been detected through the sub-division of the *E. camaldulensis* (see section 2.2.2) when sampling.

#### **5.4 APPLICATIONS FOR MINERAL EXPLORATION AND NATURAL RESOURCE MANAGEMENT**

The biogeochemical applications for mineral exploration and natural resource management programs can be interchangeable. In both programs trees and shrubs can be utilised, as either a biomonitoring or geochemical perspective, where plants provide surface extensions or expressions of the underlying soils, perched aquifers, and concealed bedrock. The advantages of using *E. camaldulensis* as a sampling medium in either mineral exploration or natural resource management programs outlined from this research include:

- a widespread distribution and in some locations abundant cover across the landscape;
- convenient access to sample sites and organs
- a tendency to colonise areas of transported regolith (where bedrock related information is less readily available);
- an extensive root system that may penetrate transported cover and provide an homogenised expression of heterogeneous transported cover;

- the ability to select and accumulate a range of elements;
- retention of many plant organs throughout the year; and,
- sample collection is environmentally passive, with little to no site disturbance and no need for remediation.

A part of an applied objective and implication for this study, the following sub-section provides a guide for taking *E. camaldulensis* samples within the landscape as part of a mineral exploration program; however the suitability of each step with respect to the specific objectives may vary on a case by case basis. This outline has been developed as a direct result of the research outcomes in this study.

#### 5.4.1 Sampling within the landscape

There is an increasing need from mineral explorers for innovative methods to ‘see through’ transported cover. To date, mineral explorers are now considering the advantages of taking plant samples in mineral exploration programs to explore this transported cover. Biogeochemical studies, such as those undertaken by Warren & Delavault (1952; 1970), Cole (1970; 1991), Brooks (1972), Lintern (1997), and Arne (1999) have demonstrated the effectiveness of biogeochemistry at detecting local and regional geochemical dispersion patterns in regions either densely vegetated and/or dominated by regolith. As shown in Table 5.11, the use of biogeochemical media, such as *E. camaldulensis* organs, has the potential for many advantages over other more traditionally used sampling media such as: low sampling cost; regional and local dispersion pathways depending on elements assayed; a relatively homogeneous sampling medium for a given site; an easily obtained medium across a wide area; and, no remediation costs following sampling.

Table 5.11: Some features of various sample media for regolith-dominated terrains.

|                              | <b>Stream Sediments</b> | <b>Hydrogeochemistry</b> | <b>Soils</b> | <b>Bedrock Drilling</b> | <b>Biogeochemistry <i>Eucalyptus camaldulensis</i></b> |
|------------------------------|-------------------------|--------------------------|--------------|-------------------------|--|
| Relative Sampling Cost       | Moderate                | Expensive                | Moderate     | Very Expensive          | Low to moderate  |
| Dispersion pathways          | Local - Regional        | Variable                 | Local        | Very Local              | Variable   |
| Chemical heterogeneity       | Large                   | Low                      | Large        | Large                   | Moderate   |
| Accessibility - Availability | Good                    | Poor to variable         | Good         | Variable                | Good to Variable                                       |
| Remediation Costs            | None                    | None                     | Variable     | High                    | None   |
| Knowledge Base               | Good                    | Variable to Good         | Good         | Very Good               | Moderate   |

#### 5.4.2 Sample strategy

The considerations for the allocation of the biogeochemical sampling sites and distribution may be no different than that employed for any type of mineral exploration program (e.g. stream sediments, soils, hydrogeochemistry and bedrock drilling). The general parameters for reconnaissance biogeochemical surveys outlined by Dunn *et al.* (1995) are as follows:

- Low density (1 sample per 10 km<sup>2</sup> or more);
- Moderate density (1 samples per 1-10 km<sup>2</sup>);
- Semi-detailed (1 sample per 0.25-1 km<sup>2</sup>); and,

- Detailed (1 sample every 200 m).

To further understand the application of different biogeochemical survey densities (e.g. low-density to detailed surveys), and the ideal sample density, the results from the Barrier-Pinnacles Mine (Pine Creek) have been used. The following survey scales were considered for the 13km (transect) of sampling that was undertaken along Pine Creek:

- Low density (5 samples ) 1 sample every 2.6 km;
- Moderate density (10 samples) 1 sample every 1.3 km;
- Semi-detailed (64 samples) 1 sample every 200 m; and,
- Detailed (214 samples) 1 sample every 60 m.

### Low-density (1 sample every 2.6 km)

If the area selected to host a biogeochemical survey has received little or no previous exploration, a low-density (1 sample per 10 km<sup>2</sup> or more) sampling strategy is recommended. This approach can enable the delineation of geological provinces and base metal dispersion within a catchment. Table 5.12 outlines a range of lithologies and their elemental associations, and pathfinder elements associated with possible base-metal deposits.

Table 5.12: Selected geochemical associations of minor and trace elements. Compiled from Levinson 1974 and AMDEL (2003).

| Geological occurrence       | Elemental association                            | Pathfinder elements       | Base-metal deposits                    |
|-----------------------------|--|---------------------------|--|
| Plutonic associations       |  | As                        | Au, Ag; vein-type                      |
| Ultramafic                  | Cr-Co-Ni-Cu                                      | As                        | Au-Ag-Cu-Co-Zn; complex sulphide ores  |
| Mafic rocks                 | Ti-V-Sc  | B                         | W-Be-Zn-Mo-Cu-Pb; skarns               |
| Alkaline rocks              | Ti-Nb-Ta-Zr-RE-F-P                               | B                         | Sn-W-Be; veins or greisens             |
| Granitic rocks              | Ba-Li-W-Mo-Sn-Zr-Hf-U-Th-Ti                      | Hg                        | Pb-Zn-Ag; complex sulphides            |
|                             |  | Mo                        | W-Sn; contact metamorphism deposits    |
| Hydrothermal sulphides      |  | Mn                        | Ba-Ag; vein deposits; porphyry copper  |
| Ores                        |  |                           |  |
| General associations        | Cu-Pb-Zn-Mo-Au-Ag-As-Hg-Sb-Se-Te-Co-Ni-U-V-Bi-Cd | Se, V, Mo                 | U; sandstone-type                      |
| Porphyry copper deposits    | Co-Mo-Re-Te-Au                                   | Cu, Bi, As, Co, Mo, Ni, U | Vein-type                              |
| Complex sulphides           | Hg-As-Sb-Se-Ag-Zn-Cd-Pb                          | Mo, Te, Au                | porphyry copper                        |
| Base metal deposits         | Pb-Zn-Cd-Ba                                      | Pd, Cr, Cu, Ni, Co        | Platinum in ultramafic rocks           |
| Precious metals             | Au-Ag-Cu-Co-As/Au-Ag-Te-Hg                       | Zn                        | Ag-Pb-Zn; sulphide deposits in general |
| Associated with mafic rocks | Ni-Cu-Pt-Co                                      | Zn, Cu                    | Cu-Pb-Zn; sulphide deposits in general |
|                             |  | Rn                        | U; all types of occurrences            |
|                             |  | SO <sub>4</sub>           | Sulphide deposits of all types         |

Low-density surveys will not necessarily delineate areas of mineralisation; however they have the capability of providing a broad geochemical signature, and highlighting areas of further exploration interest, which can form the foundation for a more detailed survey.

The results of the low-density survey (5 samples taken one every 2.6km) (Figure 5.8 - Figure 5.9), show that the *E. camaldulensis* within the 13km transect area sampled for Pb and Zn and to some extent Cd recorded concentrations greater than their detection limit, while pathfinder elements As and Ag recorded concentrations below their analytical detection limits. The implications of this sample density highlights two areas warranting further exploration investigation: 1, the northern margin of Pine Creek, with Pb concentrations 5 times greater than the plant average (1 ppm); and, 2. the southern margin of Pine Creek, with Zn concentrations being slightly higher than the plant average (50 ppm) and Cd concentrations approximately 8 times higher than the plant average (0.05 ppm).



The low-density map also highlights regolith-landform units that possibly provide a basis to rank results higher compared to other units, such as floodout areas and depositional plains that possibly preferentially accumulate heavy minerals.

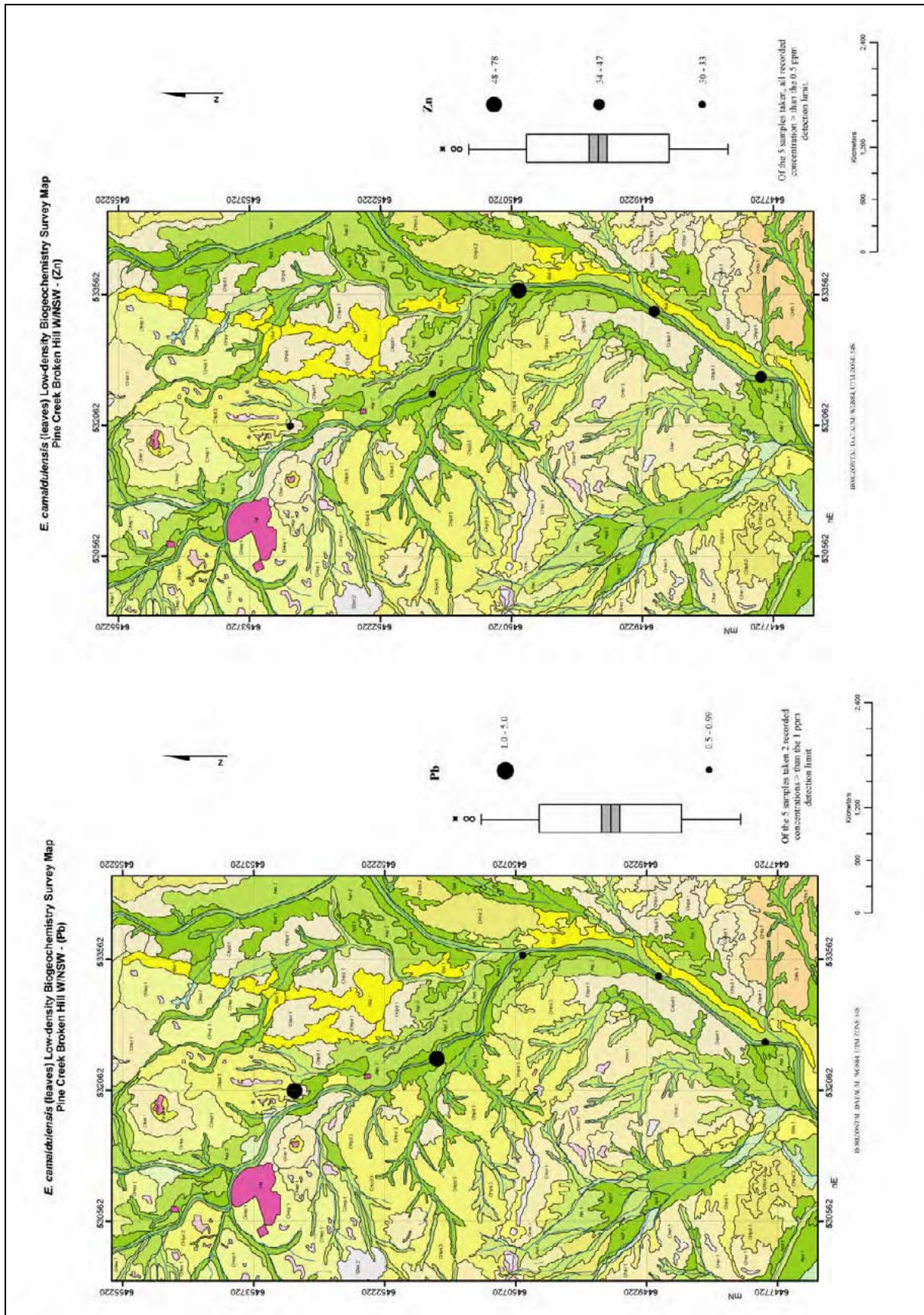


Figure 5.8: Low-density survey (5 samples taken one every 2.6km) at Pine Creek (Pinnacles), showing concentrations of Pb and Zn in *E. camaldulensis* leaves.

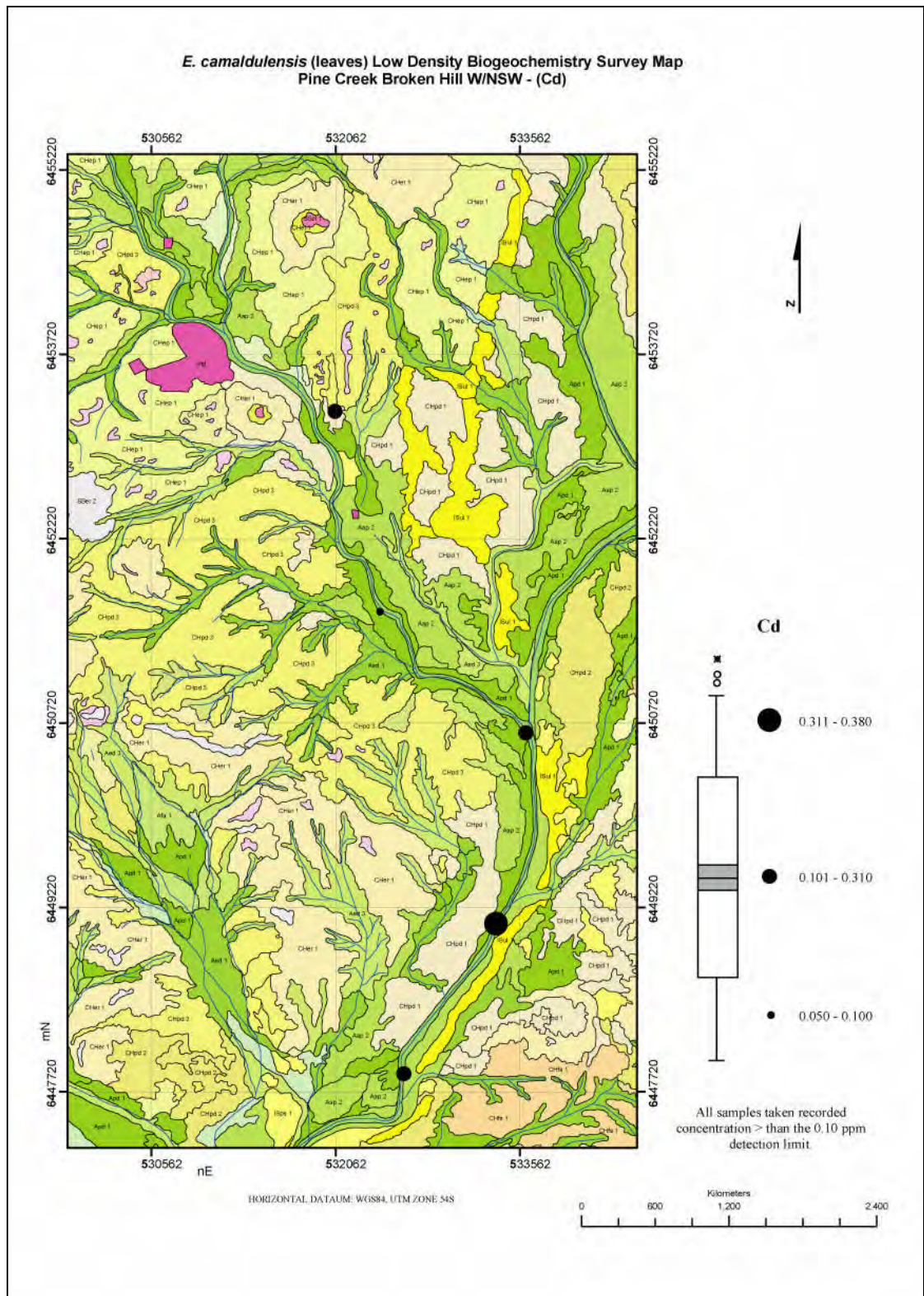


Figure 5.9: Low-density survey (5 samples taken one every 2.6km) at Pine Creek (Pinnacles), showing concentrations of Cd in *E. camaldulensis* leaves.

### Moderate density (1 sample every 1.3 km)

The moderate-density survey compilation of results includes 10 samples, at a spacing of one every 1.3km, (Figure 5.10 - Figure 5.12). This shows that of the 10 *E. camaldulensis* included for Zn, 4 had concentrations greater than the plant average of 48 ppm and for Cd 5 had concentrations greater than the plant average of (0.24 ppm), further highlighting the possible economical potential of the chosen study area. In particular, one *E. camaldulensis* in the north had concentrations 1.4 (Cd), 1.5 (Zn), 4.8 (Pb) and 8.8 (Ag) times greater than the plant average. The same *E. camaldulensis* had As concentrations of 0.9 ppm, which is 9 times greater than the plant average (0.1 ppm). This area of enrichment corresponding to this tree defines the approximate location of the Ag-Pb-Zn Barrier-Pinnacles Mine. The following (Table 5.13) shows that As:Ag, Pb:Ag, and Pb:As have very strong correlations (> than 0.90); Zn:Ag, Zn:As, Zn:Cd and Zn:Pb have moderate correlations (0.7 – 0.9); and, Cd:Ag, Cd:As and Pb:Cd have weak to low correlations (0.2 – 0.4).

|           | <b>Ag</b> | <b>As</b> | <b>Cd</b> | <b>Pb</b> | <b>Zn</b> |
|-----------|-----------|-----------|-----------|-----------|-----------|
| <b>Ag</b> | 1         |           |           |           |           |
| <b>As</b> | 0.97      | 1         |           |           |           |
| <b>Cd</b> | 0.28      | 0.35      | 1         |           |           |
| <b>Pb</b> | 0.99      | 0.98      | 0.27      | 1         |           |
| <b>Zn</b> | 0.46      | 0.55      | 0.56      | 0.45      | 1         |

Table 5.13: Correlation co-efficients the moderate-density (1 sample every 1.3 km) for polymetallic elements indicative of the Barrier Pinnacles Mine.

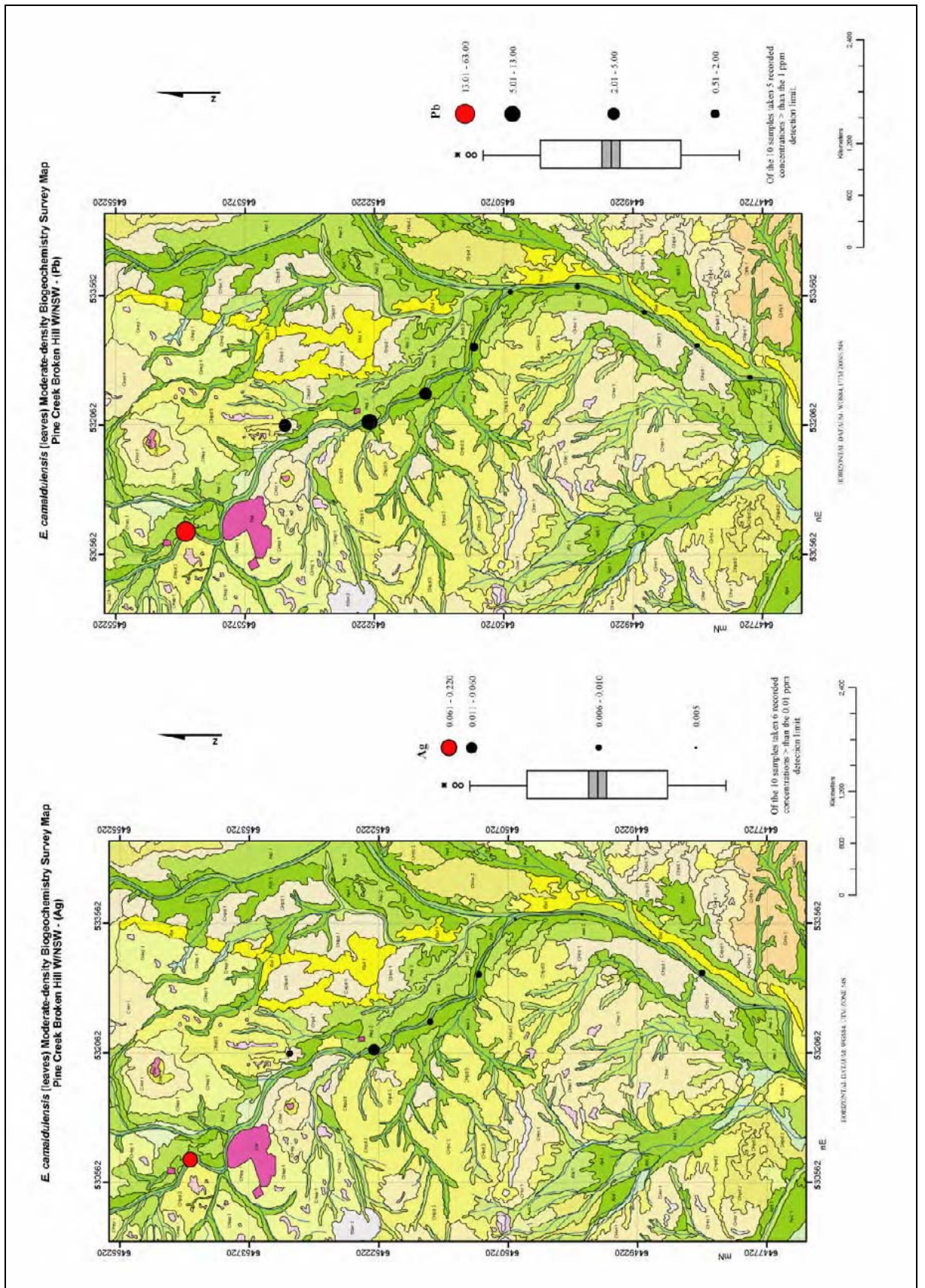


Figure 5.10: Moderate-density survey (10 sample taken one every 1.3km) at Pine Creek (Pinnacles), showing concentrations of Ag and Pb in *E. camaldulensis* leaves.

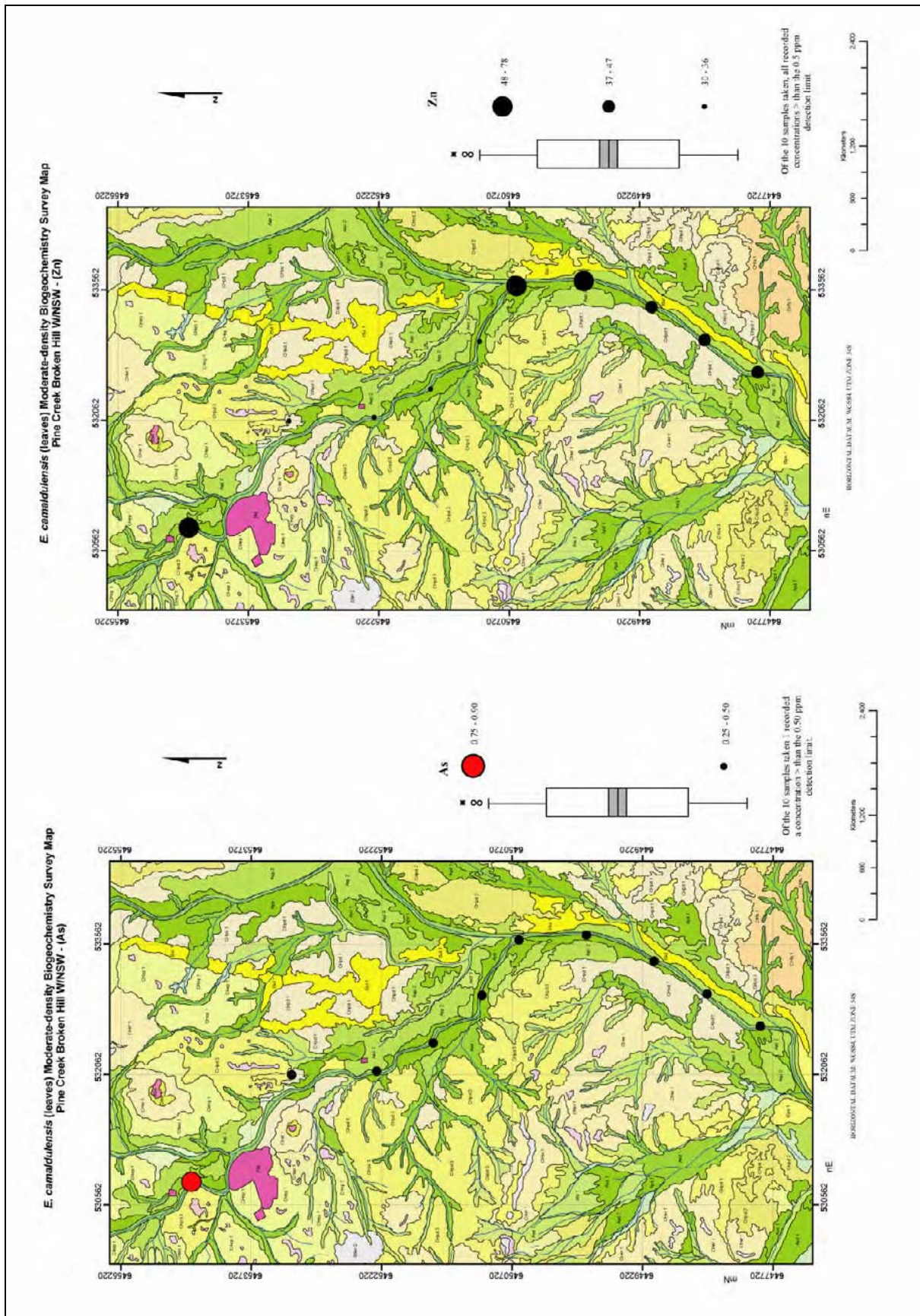


Figure 5.11: Moderate-density survey (10 samples taken one every 1.3km) at Pine Creek (Pinnacles), showing concentrations of As and Zn in *E. camaldulensis* leaves.

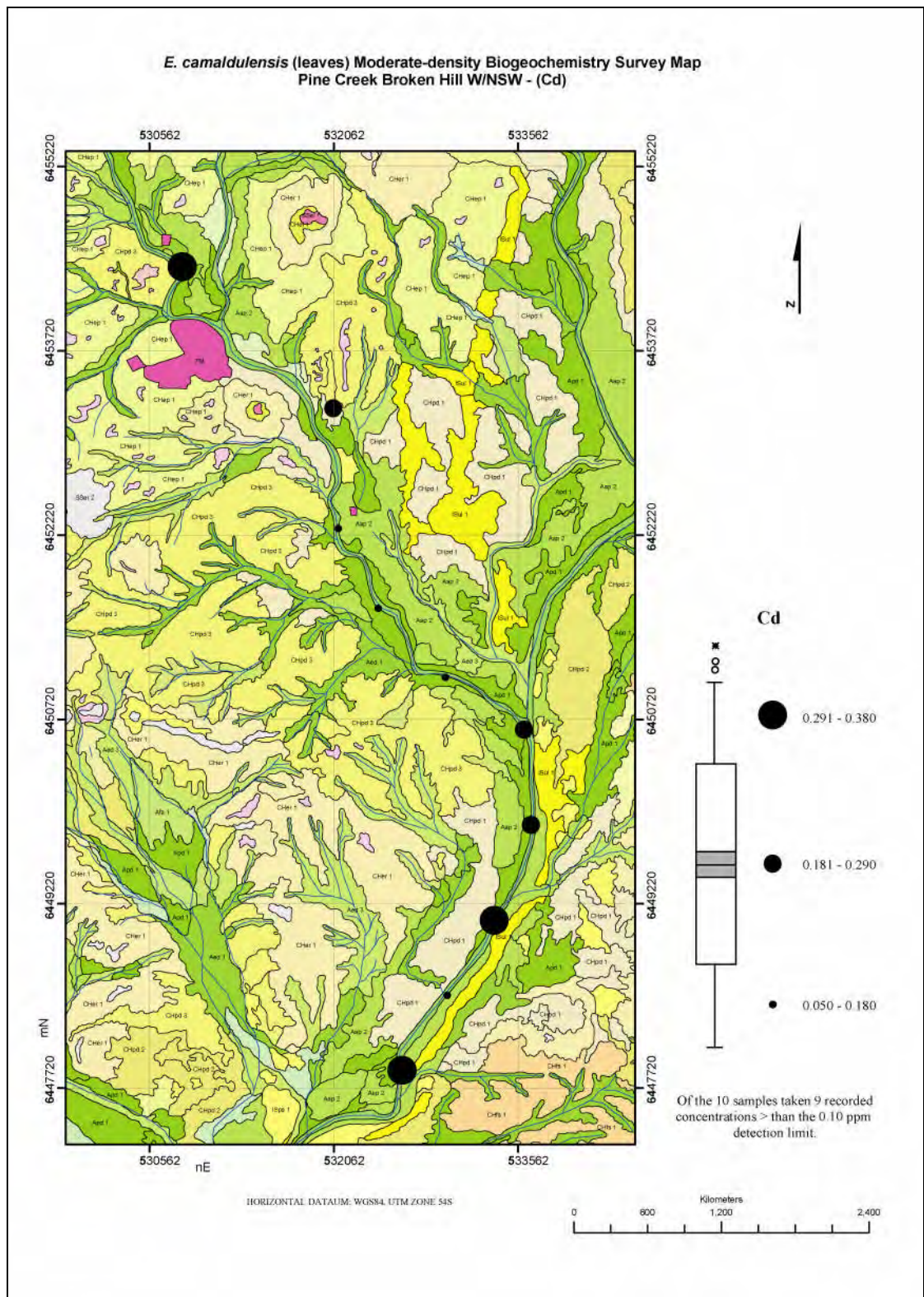


Figure 5.12: Moderate-density survey (10 samples taken one every 1.3km) at Pine Creek (Pinnacles), showing concentrations of Cd in *E. camaldulensis* leaves.

### Semi-detailed (1 sample every 200 m)

For the semi-detailed density survey (64 samples taken at 200 m spacing), the *E. camaldulensis* in the north of the 13 km transect Pine Creek study area (Figure 5.13 – Figure 5.15) show significantly elevated concentrations of Ag, Pb, Zn, As and Cd. The *E. camaldulensis* have concentrations 30 (Ag), 15 (Pb), 5 (Zn), 2.7 (As) and 10 (Cd) times greater than the calculated plant average. The results for Zn and Cd also reveal the possibility of a zone of enrichment to the south, down stream of the confluence tributary Gum Creek. In addition, the following (Table 5.14) shows that As:Ag, As:Pb, and Pb:Ag have very strong correlations ( $> 0.90$ ), while Cd:Ag, Cd:As, Pb:Cd, Zn:Ag, Zn:As, Zn:Cd and Zn:Pb have strong to high correlations (0.7 – 0.9).

|    | Ag   | As   | Cd   | Pb   | Zn |
|----|------|------|------|------|----|
| Ag | 1    |      |      |      |    |
| As | 0.98 | 1    |      |      |    |
| Cd | 0.78 | 0.75 | 1    |      |    |
| Pb | 0.97 | 0.99 | 0.70 | 1    |    |
| Zn | 0.87 | 0.85 | 0.88 | 0.82 | 1  |

Table 5.14: Correlation co-efficients the semi-detailed (1 sample taken every 200 m) for polymetallic elements indicative of the Barrier Pinnacles Mine.

The semi-detailed survey also outlines the approximate boundary of the Barrier-Pinnacles Mine. For concentrations defined as outliers (determined from accompanying boxplots) the following geochemical footprint sizes were recognised near the mine: As (0.29 km), Pb (0.79 km), Ag (0.86 km). The results for Zn and Cd suggest sub-division of the broad zone near the Barrier-Pinnacles Mine into two geochemical footprints: one in the north (Zn 0.6 km and Cd 1.2 km); and, one in the south (Zn 0.07 km and Cd 1.7 km).



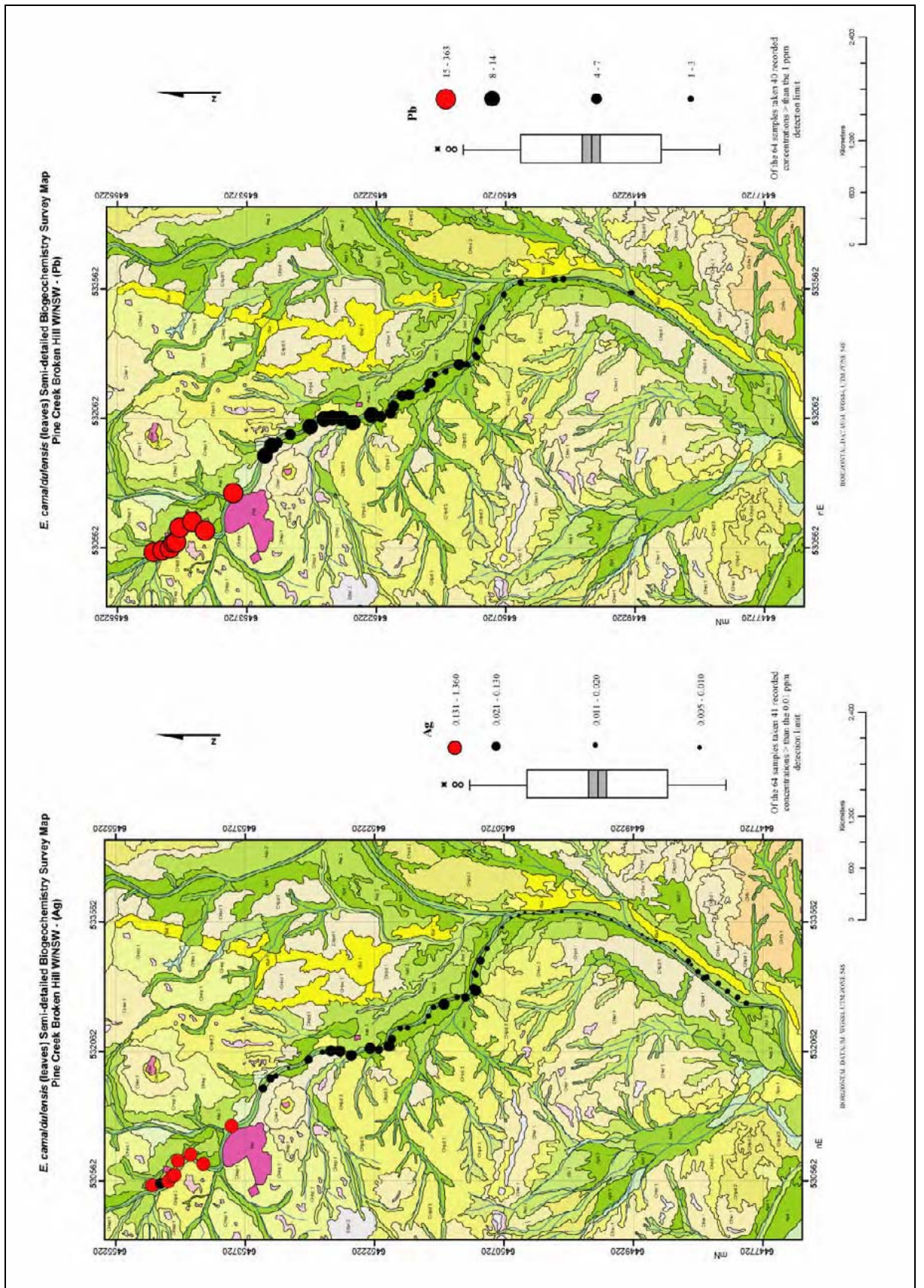


Figure 5.13: Semi-detailed survey (64 samples taken one every 200m) at Pine Creek (Pinnacles), showing concentrations of Ag and Pb in *E. camaldulensis* leaves.

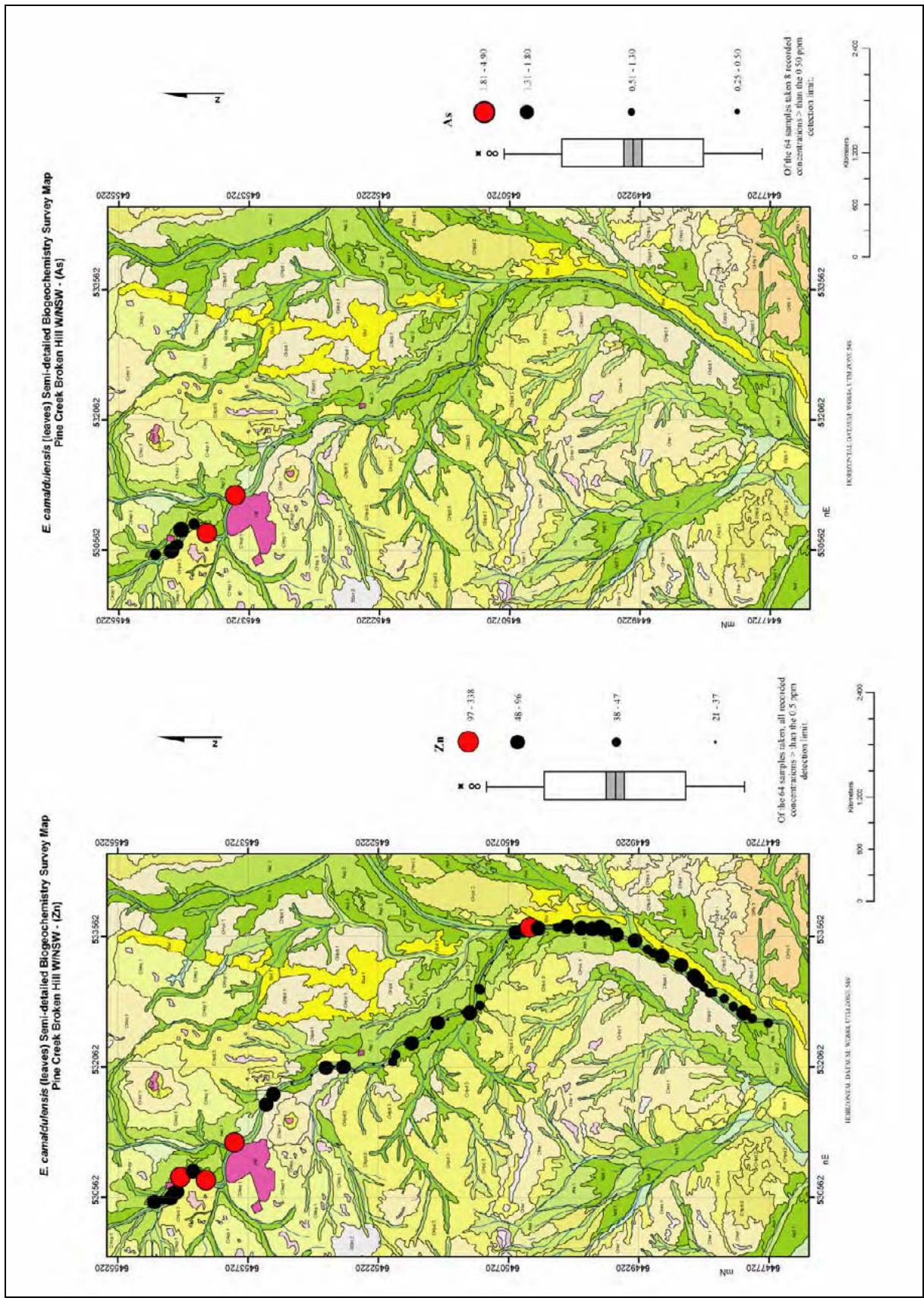


Figure 5.14: Semi-detailed survey (64 samples taken one every 200m) at Pine Creek (Pinnacles), showing concentrations of Zn and As in *E. camaldulensis* leaves.

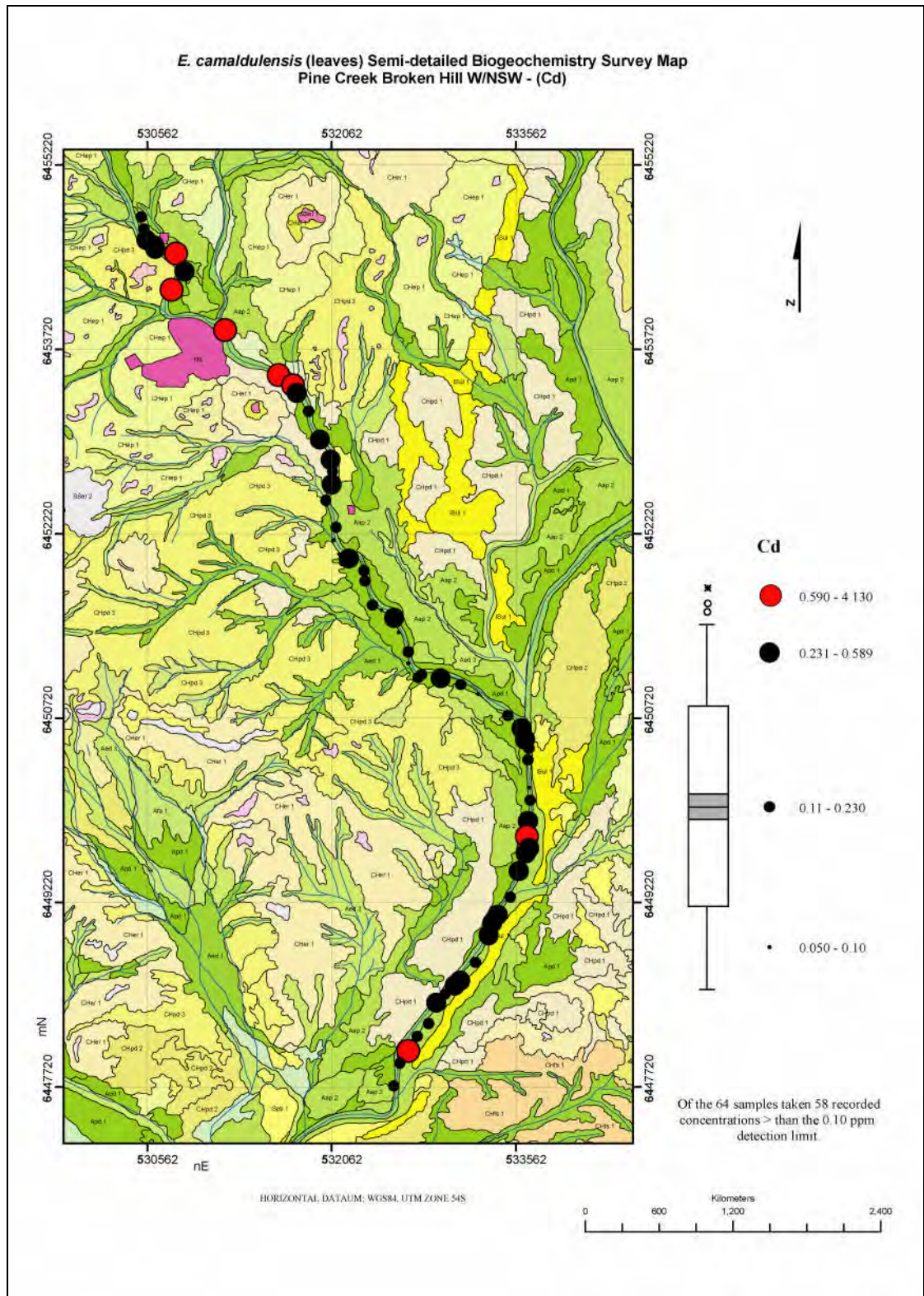


Figure 5.15: Semi-detailed survey (64 samples taken one every 200m) at Pine Creek (Pinnacles), showing concentrations of Cd in *E. camaldulensis* leaves.

**Detailed survey (1 sample every 60 m).**

Detailed surveys can be conducted in the attempt to closely delineate the extent of mineralisation, prior to drilling and/or other more costly methods of exploration. The results of the detailed survey (214 samples taken one every 60m), (Figure 5.16 - Figure 5.18) show that the *E. camaldulensis* had concentrations greater than the plant average values by factors of 30 (Ag), 15 (Pb), 5 (Zn), 2.8 (As) and 10 (Cd). In addition, the results suggest that the high Zn and Cd concentrations may indicate a second region of mineralisation. The following (Table 5.15) shows that As:Ag, Pb:Ag and Pb:As have very strong correlations (> 0.90), while Zn:Ag, Zn:As, Zn:Cd and Zn:Pb have strong to high correlations (0.7 – 0.9).

|           | <b>Ag</b> | <b>As</b> | <b>Cd</b> | <b>Pb</b> | <b>Zn</b> |
|-----------|-----------|-----------|-----------|-----------|-----------|
| <b>Ag</b> | 1         |           |           |           |           |
| <b>As</b> | 0.98      | 1         |           |           |           |
| <b>Cd</b> | 0.70      | 0.68      | 1         |           |           |
| <b>Pb</b> | 0.98      | 0.99      | 0.66      | 1         |           |
| <b>Zn</b> | 0.86      | 0.84      | 0.82      | 0.84      | 1         |

Table 5.15: Correlation co-efficients the detailed survey (1 sample every 60 m) for polymetallic elements indicative of the Barrier Pinnacles Mine.

The *E. camaldulensis* detailed survey constrains the extent of the Barrier-Pinnacles Mine. For concentrations defined as outliers (determined from accompanying boxplots), the following geochemical footprints were recognised; As (0.9 km), Pb (1.3 km), Ag (0.96 km). With Zn and Cd possibly suggesting two geochemical footprints one in the north Zn (0.5 km) and Cd (2.5 km) and one in the south Zn (0.04 km) and Cd (0.06 km).

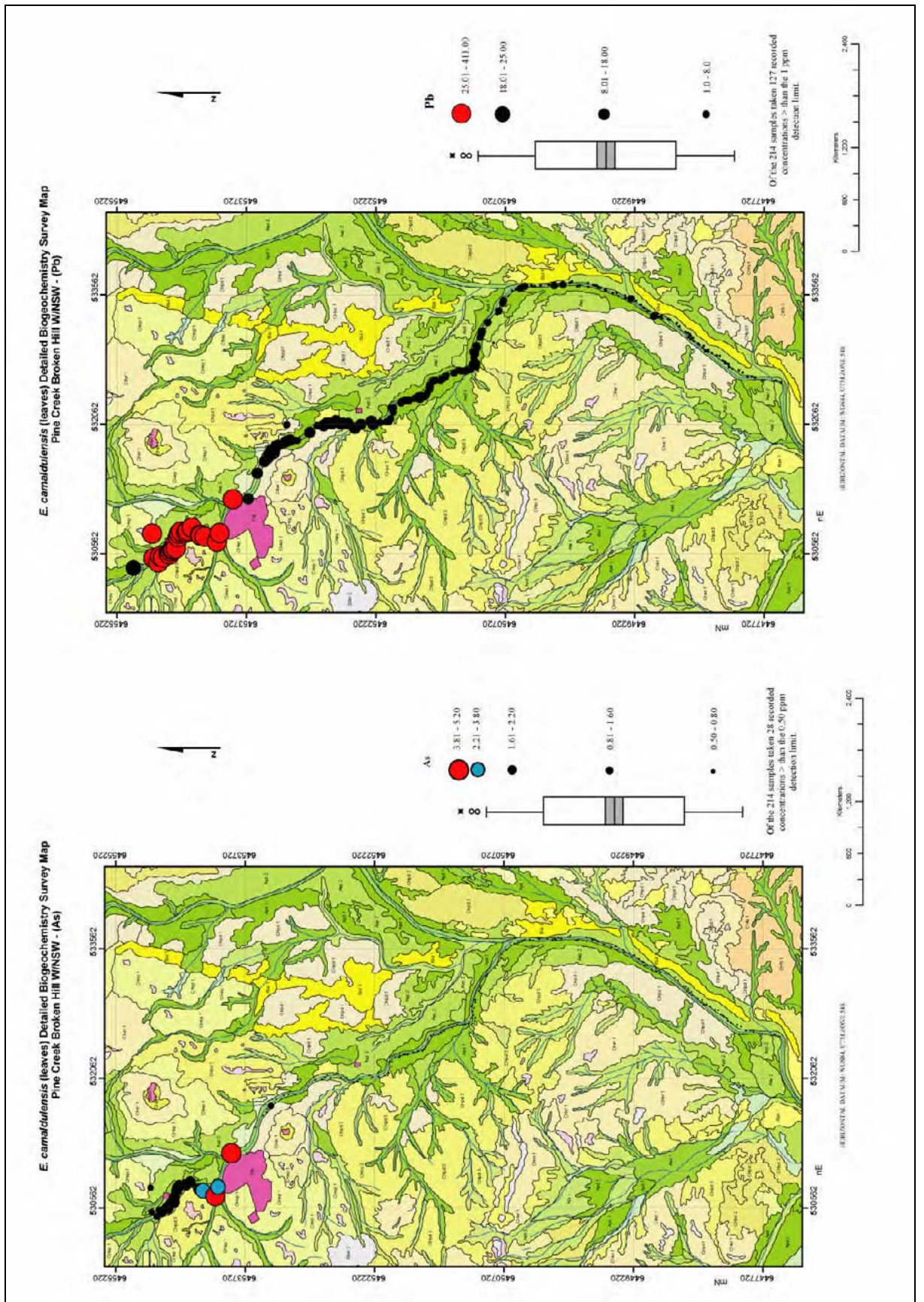


Figure 5.16: Detailed survey (214 samples taken one every 60m) at Pine Creek (Pinnacles), showing concentrations of Ag and Pb in *E. camaldulensis* leaves.

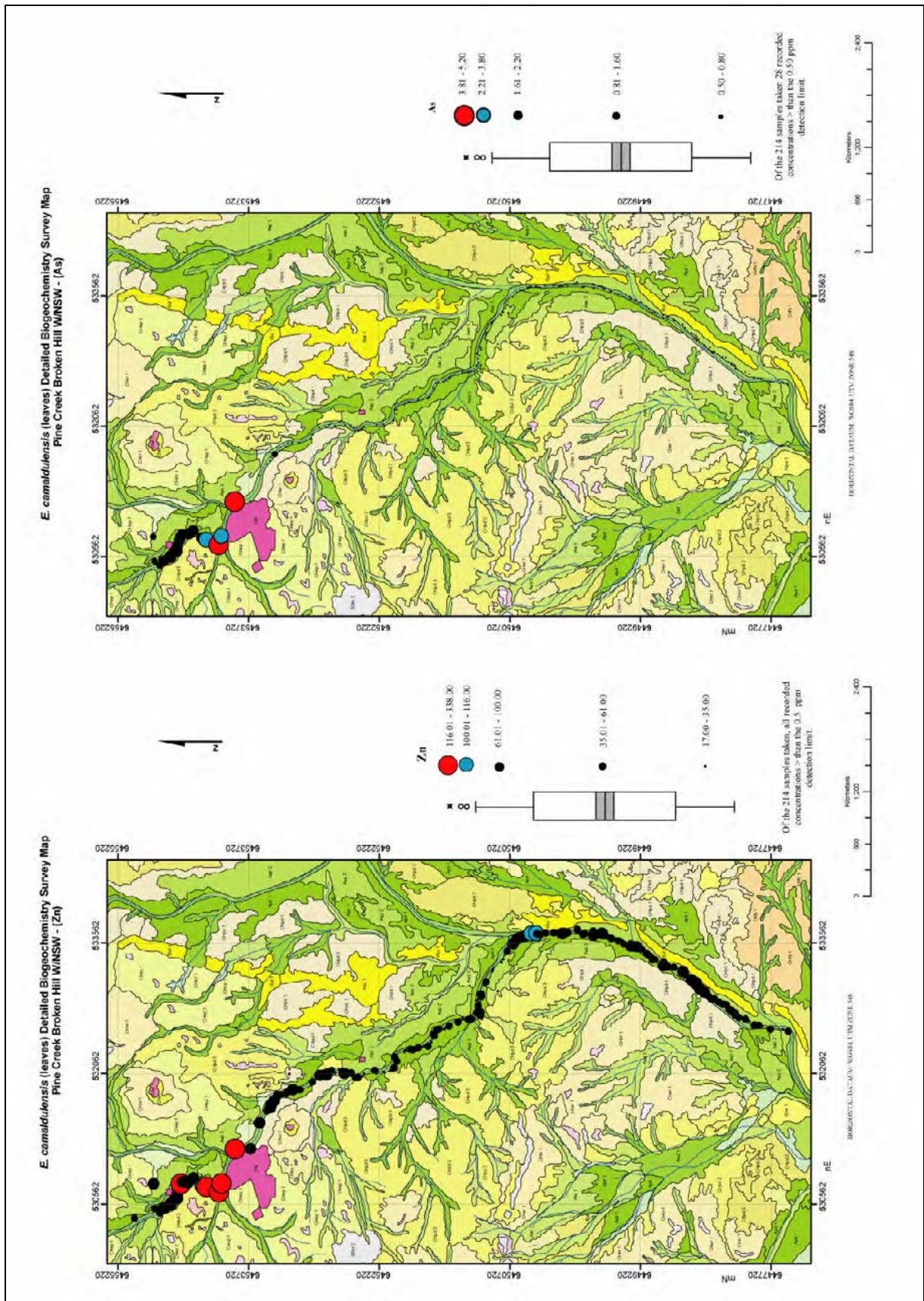


Figure 5.17: Detailed survey (214 samples taken one every 60m) at Pine Creek (Pinnacles), showing concentrations of Zn and As in *E. camaldulensis* leaves.

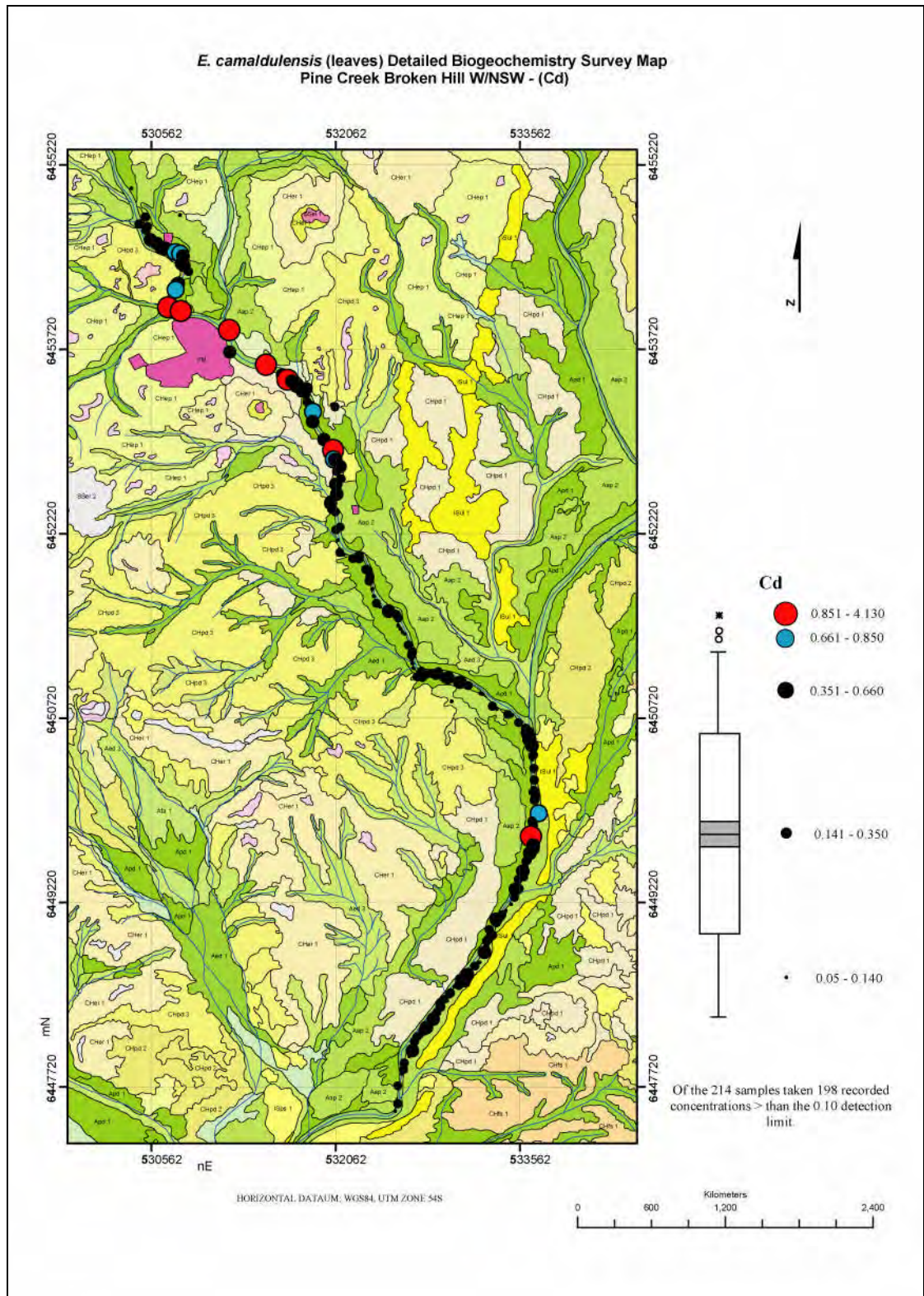


Figure 5.18: Detailed survey (214 samples taken one every 60m) at Pine Creek (Pinnacles), showing concentrations of Cd in *E. camaldulensis* leaves.

## 5.5 OVERVIEW OF SURVEYS

The following (Table 5.16) summarises the results of the different *E. camaldulensis* survey densities obtained through the distillation of the biogeochemical survey performed at the Barrier Pinnacles Mine.

Table 5.16: Outlines the different *E. camaldulensis* survey density, the sample size of each survey, the geochemical footprint of the chosen elements and the approximate cost of each survey for preparation and analysis only. Cost is based on available prices given per sample for analysis as of time of writing (Dec, 2007).

| Scale            | Sample #                   | Geochemical footprint  | Cost (ICP-MS) |
|------------------|----------------------------|--|---------------|
| Low-density      | 5 samples one every 2.6km  | N/A  | \$165         |
| Moderate-density | 10 samples one every 1.3km | N/A  | \$330         |
| Semi-detailed    | 64 samples one every 200m  | As (0.29 km), Pb (0.79 km),<br>Ag (0.86 km)<br><br>North Zn (0.6 km), Cd (1.2 km) and south Zn (0.07 km),<br>Cd (1.7 km) | \$2673        |
| Detailed         | 214 samples one every 60m  | As (0.9 km), Pb (1.3 km),<br>Ag (0.96 km)<br><br>North Zn (0.5 km), Cd (2.5 km) and south Zn (0.04 km),<br>Cd (0.06 km)  | \$7062        |

Biogeochemical surveys can be carried out over different densities. The chosen survey density will depend on the scope of the study, the degree of available knowledge (local geology, and whether the region has mineralisation or not), the size of the target mineral system, and a number of survey factors such as the time frame and funds available.

If the scope of the study is to highlight areas of potential economical interest, moderate-density survey (1 sample approximately every 1.3 km) would be effective and efficient (at a cost of approximately \$330.00). A limitation of this survey density would have been its inability to specifically delineate areas of mineralisation. Instead the preferred survey density to undertake in order to delineate the zone of mineralisation would have been either a semi-detailed or detailed survey. The choice here would more than likely be determined on the time-frame available for the survey to be conducted and the available budget.



## 5.6 OVERVIEW OF RECOMMENDED SAMPLING PROGRAM

The knowledge developed in this study can be used to develop a recommended sampling procedure and methodology for *Eucalyptus camaldulensis* trees. Although this study was based in the area of the Curnamona Province and adjacent areas, preliminary observations of the growth forms and habitat of this tree species growing elsewhere in Australia suggest that the recommendations from this study should be transferable elsewhere. Some important initial considerations include:

- applicability of this study results for *E.camaldulensis* in different landscape, regolith and geological settings;
- ensure that *E.camaldulensis* is the most widespread and abundant plant species in the study area as this will ensure that results are accurate and comparable;
- sample a consistent plant organ (e.g. leaves, twigs of similar diameter, bark, fruit, flowers and roots) as there are substantial differences in elemental composition between different organs. From this study, leaves were found to be the most convenient to sample and prepare, had minimal detrital inputs and provided a biogeochemical contrast between sites overlying buried mineralisation and non-mineralised settings;
- be aware of the potential significance of temporal variations (time of year with respect to seasons and/or rainfall events especially in semi-arid and arid regions), which can have a significant impact on the variability of biogeochemical results. The elemental composition of plant tissues/organs can vary considerably as a plant grows. Sampling is ideally within a short time frame, and care is needed in comparing results from samples taken at different times of the year and in different climatic conditions; and;
- to ensure quality assurance/quality control the inclusion of blind duplicates and international standard reference material are essential. The number of duplicates and international standards submitted will depend on the total number of samples collected. A general rule of thumb is 1 blind duplicate every 10 samples, followed by the inclusion of 1 international standard every 20 samples.

### 5.6.1 Sample site recording

Once the sampling program objectives, potential target size and therefore plant sample spacing has been selected, the GPS coordinates of trees to be sampled are recorded and brown paper sample bags labelled. In addition, descriptive notes of the tree's immediate surroundings are included noting attributes such as:

- potential contaminants particularly anthropogenic (such as the distance that the selected plant species is from a main road);
- landform setting (e.g. setting of the plant relative to the upper catchment head waters or lower in the catchment system);
- regolith materials (including if they are heterogeneous or homogenous in composition);
- surface expression (e.g. erosional landforms, depositional landforms, fans, plains or depressions);
- what possible external factors could impact on the plant species; and,
- what other dominant plant species are present.

## 5.6.2 Quality control

To reduce the risk of contamination during sampling the following must be considered:

- remove all jewellery and other metallic objects;
- hands washed and air dried if sunscreen has been applied (hats and the shade of the trees provide temporary sunscreen while sampling);
- Non-powdered, latex gloves are to be worn on at least one of the sampling hands (gloves are to be changed between samples); and,
- For twigs sampling, use Teflon-coated clippers.

## 5.6.3 Plant organ sampling (pre-digestion)

The objective is to collect homogeneous and therefore comparable samples between the population of *E. camaldulensis* trees. The following are some general thoughts that need to be considered before sampling begins:

- immediately prior to sampling, make sure that potential leaf and twig samples are healthy and mature, (not carrying fungal growth and/or faecal deposits);
- twigs can be removed by using Teflon-coated clippers. Twigs can be sampled along with the leaves by separating them by tearing leaves at their stalk base;
- this procedure allows for the additional collection of fruit and flowering buds;
- bark can be recovered by using a hatchet and peeled away; and,
- root sampling depends largely upon the landscape setting (e.g. within alluvial plains). The collection involves digging for the roots, while samples from major drainage channels typically have some of their roots exposed, and therefore allow for simple collection with the aid a hatchet.

All samples collected are taken from approximately chest height, and taken from around the circumference of the *E. camaldulensis*. At times this method of sampling is not practical as sections of the *E. camaldulensis* canopy will be out of reach, however, were possible canopy circumference sampling maintains a level of representative consistency.

## 5.6.4 Sample storage

Brown paper lunch bags are recommended for the storage and transport of the collected *E. camaldulensis* organs. Brown paper lunch bags allow the sample to breathe, reducing the rate of respiration which may lead to organic breakdown. Baddfield & Bould (1963, cited in Allen, 1974) and Hill (2002; 2004) have suggested that plant organ storage in paper bags for up to 4 days will result in minimal changes to biogeochemical composition. The method of storage to be employed includes:

- all samples collected are to be placed in individual brown paper bags (235 mm x 200 mm);
- the bags are sealed by folding over the top; and,
- samples are then stored in a well-ventilated and dry area for the duration of the sampling period.

### 5.6.5 Biogeochemical Assay

To ensure a successful outcome for a biogeochemical exploration survey, the selection of an appropriate sample preparation is paramount. One of the greatest concerns for biogeochemical exploration surveys in semi-arid and arid regions is the likelihood of detrital contaminations, from wind-borne, non-mineralised and mineralised dust. It is important to have a good understanding of the leaf external morphological features such as having waxy rods or trichomes (hairs), as this will determine the first step to be undertaken in your sample preparation (pre-digestion). *E. camaldulensis* has epicuticular wax that can appear platey or tube like, or a combination of both.

The following methods of sample preparation, analytical techniques and analytical suite were employed during the research of *E. camaldulensis* as a biogeochemical sampling medium, however it is only a guide and the suitability of each step should be evaluated with respect to chosen target species and the objectives of the program.

### 5.6.6 Sample preparation

Whether to wash samples or not is a controversial decision for biogeochemical researchers. The main intention of sample washing is to remove surface contaminants, such as detrital particles derived from proximal dusty roads and mining operations. Washing samples can involve using the locally derived waters (stream); however this method can lead to sample contamination as these waters will contain dissolved minerals due to its interaction with outcropping/subcropping bedrock and migration across the dominant surface regolith. Another method involves washing your sample in a bath of de-ionised water for a period of time (generally for approximately 1 hour). Both methods also have the potential to leach a number of highly soluble elements, which can be significant. Other disadvantages of washing plant samples are the variable degrees of washing effectiveness, and potential contamination from further laboratory handling and washing solutions.

The external morphological features of the *E. camaldulensis*, such as their large, smooth, waxy leaves appear to hold minimal detrital material see section (2.4 Detrital contamination) making them a valuable biogeochemical sampling medium.

### 5.6.7 Drying

No ideal temperature or drying time is universally recommended. Drying samples stops plant decomposition and enables long-term storage. Drying procedures should be chosen according to the elements assayed. Studies have shown that high temperature drying (ashing) of samples may promote the significant losses of moisture, which is further likely to result in the loss of volatile and in some cases important pathfinder elements, such as Se, Hg and As.

This research opted for a drying time of 48 hrs at 60°C in accordance with Hill (2002), as this drying time minimises the loss of valuable volatile elements and important pathfinder elements.

### 5.6.8 Homogenisation

The type of sample preparation (homogenisation) employed will depend on the analytical technique performed. To ensure that the sample to be assayed is a true representative of the original larger sample (homogenised), this research used a stainless steel ‘coffee-n-spice’ grinder. The following method of homogenisation is suitable for most vegetation media:

- Thoroughly clean your mill using a combination of high purity ethanol (ethanol 100%, undenatured; C<sub>2</sub>H<sub>5</sub>OH; density 0.79g/ml), paper towel and compressed air. To minimise contamination it is important to adopt the same level of care employed in the field, such as wearing non-powdered latex or nitrile gloves;
- Pre-contamination of the mill further ensures a reduction in contamination; by using a short milling time. Add a small amount of the sample to the mill, pulse the sample and then discard this preliminary material before milling the main body of the sample;
- The homogenised sample should resemble a fine powder (a typical consistency would be approaching that of talcum-powder); however the consistency will be dependent on the target species selected. The sample is then placed/stored in labelled, snap-lock plastic bags; and,
- Repeat steps 1-3 with all other samples.

### 5.6.9 Sample Digestion and Analytical techniques

Trace elements in plants can be measured by a range of different methods such as X-Ray Fluorescence (XRF), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Optical Emission Spectrometry (ICP-OES) and Instrumental Neutron Activation Analysis (INAA).

The analytical technique employed must provide a measure of both precision and accuracy within a framework that reflects the objectives of the study. Ideally the technique is relatively easy, quick, reliable and inexpensive. Throughout this research, to obtain a large elemental assay suite, several analytical techniques were employed owing to the different strengths, weakness and best detection limits for each technique. Table 5.17 outlines the detection limits for each analytical technique and assay concentrations for several elements from the Barrier-Pinnacles Mine.

Table 5.17: Comparisons of the detection limits for ICP-MS, ICP-OES, INAA and XRF analysis. Average element concentrations for the *E. camaldulensis* (leaves) adjacent to mineralisation and background. Concentrations are in ppm unless otherwise shown. n= the number of *E. camaldulensis* sampled.

| Elements<br>(ppm<br>unless<br>shown) | ICP-MS | ICP-OES | INAA | XRF  | Average <i>E. camaldulensis</i><br>concentration (Barrier<br>Pinnacles Mine (Ag-Pb-Zn)<br>N=42 | Average <i>E. camaldulensis</i><br>concentration (values below<br>the mean) N=172 |
|--------------------------------------|--------|---------|------|------|--|---|
| Ag                                   | 0.01   |         | 0.10 |      | 0.27   | 0.034   |
| As                                   | 0.50   |         | 0.05 |      | 1.83   | 0.90  |
| Au ppb                               |        |         | 0.50 |      | 0.5  | N/A   |
| Ca                                   |        |         | 500  | 14   | 10117  | 9671  |
| Cd                                   | 0.05   |         | 2    |      | 0.67   | 0.24  |
| Cu                                   |        | 1       |      | 0.80 | 6.74   | 5.14  |
| Fe                                   |        |         | 20   | 14   | 144  | 94  |
| Mg                                   |        | 20      |      | 24   | 1544   | 1402  |
| Mn                                   |        | 1       |      | 7    | 148  | 159   |
| Ni                                   |        | 1       |      | 1.3  | 3.23   | 2.96  |
| P                                    |        | 20      |      | 4    | 1116   | 1140  |
| Pb                                   | 2      |         |      | 0.50 | 78   | 9   |
| S                                    |        | 10      |      | 4    | 1103   | 1030  |
| Sb                                   | 0.01   |         | 0.02 |      | 0.51   | 0.20  |
| Zn                                   |        | 1       |      | 0.50 | 82   | 44  |

#### 5.6.10 Analytical suite

The selection of an analytical suite is largely dependant on the available geological, geochemical and hydro-geochemical knowledge of the study area. If the chosen site has received little previous exploration, or past work has only concentrated on small sections of the study area (as was the situation for both Tibooburra and the Pinnacles) a multi-element assay suite was performed as this procedure highlighted lithological boundaries and constrained elemental associations. Table 5.12 outlines rock type and/or occurrences and their element associations in mineral deposits, and possible pathfinder elements used in mineral exploration programs.

#### 5.6.11 Data presentation and interpretation

The construction of both regolith and biogeochemical maps provides an efficient and convenient method for illustrating the spatial distribution of detectable elements within the *E. camaldulensis* in a regolith-landform context. The maps were constructed using ArcGis 9 software package, while the statistical analysis and information accompanying the maps such as, box-plots, histograms and cumulative fraction plots were performed using DataDesk 6.1 software package.

#### 5.6.12 Regolith-Landform maps

Regolith-landform maps represent the distribution and setting of regolith material in the landscape, such as weathered rock, colluvial and alluvial sediments. Two 1:10 000 scale regolith maps produced as part of this thesis show the distribution of *in situ* and transported regolith and their association with the immediate landscape. They also provide an important framework for the delineation of chemical and physical dispersion mechanisms, and

pathways, further aiding in the understanding of the chemical composition of *E. camaldulensis*, within both highly weathered mineralised and non-mineralised landscape settings.

A further application of regolith-landform maps is that they highlight the distribution of specific sampling media for example: *E. camaldulensis* colonise the main contemporary channels, *Maireana sedifolia* colonise areas generally indicative of regolith carbonate accumulations. Geochemical dispersion pathways and areas with similar geochemical thresholds can also be derived (Hill, 2000). In addition landowners and pastoralists may also find these maps useful for developing and implementing land management practices.

### **5.6.13 Statistics (boxplots, histograms and cumulative frequency plots)**

Statistical analysis allows for large volumes of data to be compressed into manageable representative values that describe the data population (Dunn *et al.*, 1992). All biogeochemical maps produced from this research are accompanied by box plots, histograms, cumulative frequency plots and summary statistics, as they further characterise the data.

The data that was collected was firstly analysed by the Student's T-test which is a statistical method that assesses whether the means of two groups are statistically similar or different from each other. In addition through application of the Student's T-test a null hypotheses can be adopted.

In order to better define the two populations, the data was subjected to further statistical analysis through the application of Principal components analysis.

Principal component analysis is a statistical approach that can be used to analyse interrelationships among a large number of variables and to explain these variables in terms of their common underlying dimensions (factors).

The interpretation of biogeochemical data and the construction of biogeochemical maps start with quality assurance and the analytical precision. For each element assayed (see section 2.3 chemical analysis), elements with poor quality assurance are removed from the data set. All analytical laboratories have fixed detection limits (Table 5.17). Throughout this thesis the handling of data that recorded below the detection limit values were converted to half of the detection limit, especially for the purposes of boxplot construction. For example, the detection limit for arsenic (As) determined by INAA of 0.05 ppm is replaced with 0.025 ppm. All elements with below detection limits are removed prior to the generation of histogram, cumulative frequency plots and summary statistics, which minimises the introduction of bias.

Boxplots are widely used for the characterisation of data, such as the distribution and the range of concentrations within a single element. The boxplot also identifies the number of classes within a population. These populations were then assigned symbols (Figure 2.7) and spatially displayed on biogeochemical maps (chapter 4).

Histograms graphically summarise the overall distribution of the data, identify the centre of the data, overall spread of the data, skewness, the mode of the data and the presence of outliers.

Cumulative frequency plots highlight inflections or breaks within the data, indicating the presence of multiple populations and emphasise outliers and their distance from the main body of data.

The statistics summary provides a concise description of the data (*E. camaldulensis*) population for individual elements, the following summaries are provided with each biogeochemical map, the following definitions are adopted from (Rollinson, 1993; Data Desk 6.0):

- count: the number of *E. camaldulensis* that recorded concentrations above the detection limit for that given element (e.g. Cd ppm 214 *E. camaldulensis* total cases of which 16 recorded below detection limit);
- max: the highest recorded value for the *E. camaldulensis* for a given element (e.g. Pb 411 ppm);
- min: the lowest recorded value for the *E. camaldulensis* for a given element (e.g. Pb 1 ppm);
- mean: the arithmetic average of a set of values (e.g. the sum of the observations, divided by the number of observations);
- median: the absolute middle value (e.g. half of the numbers in the population are  $\leq$  to the median and half are  $\geq$  to it);
- standard deviation: measures the spread of the data from its mean, the greater the spread the higher the deviation;
- range: the absolute difference between the highest and lowest recorded values; and,
- detection limit: the lowest concentration that can be determined to be statistically different from a blank (99 % confidence).

The combined statistics add strength to the overall interpretation of the data. The identification of outliers from background concentrations, allows for a better graphical representation of the data within the framework of the constructed biogeochemical maps

#### **5.6.14 Biogeochemical maps**

The biogeochemical maps are a visual representation of the spatial distribution of *in situ*, transported regolith and detectable elements within the *E. camaldulensis*. A total of 51 biogeochemical maps were constructed in this thesis and each map consists of two individual maps and supportive statistics, including: (i) individual element concentration (raw data) of *E. camaldulensis* at each point sampled; and, (ii) EDA (exploratory data analysis) map.

Biogeochemical maps within this thesis (chapter 4) are multi-purpose, as they are able to accommodate the needs of several different end users such as, mineral exploration and mining companies, environmental agencies (NRM), landowners and geologists. The biogeochemical maps within this thesis have shown that there is a strong association between the contemporary landscape setting and the chemical composition of the *E. camaldulensis* and in addition have highlighted several areas of importance such as: area of potential economic interest through defining the geochemical footprint for Ag, Pb, Zn, As, Cd (Pinnacles) and Au and As (Tibooburra); areas susceptible to potential contamination e.g. perched water table and the geochemical footprint for Ag, Pb, Zn, As, Cd (Pinnacles) and the dispersion potential of these heavy metals within the contemporary landscape, and areas at risk to element

accumulation (Na and Cl); areas of potential resource, such as areas of ground water recharge and discharge (Pinnacles). The location of many dams corresponds closely with regolith-landform patterns indicative of an areas hydrology (Hill, 2000); and, concealed lithological boundaries such as the granodiorite and metasediment (Tibooburra), geochemical signatures (Barrier Pinnacles Mine) the enrichment of Pb, Zn, Mn, Fe and (to lesser extent Cu and Ca) and the depleted Mg, Na, K, Rb, Sr and Ba associated with mineralisation lode horizons, and adjacent metasedimentary rocks.

### 5.6.15 Ranking

Ranking data places a measure of preference on one location over another. In order to highlight areas of greater potential interest the pathfinder elements Ag, As, Au, Cd, Co, Cr, Hg, Ni, Mo, Pb, Sb, Sc, Se, U and Zn, can be normalised by elements Al, Fe and Ti. The data can then be numerically ranked, and plotted as a cumulative frequency plot, to define areas that warrant a further biogeochemical investigation. A limitation of ranking the data is that it does not reflect the overall magnitude of the enrichment, or indicate whether the enrichment is sourced locally or regionally. The ranking of data was not performed within this thesis.

## 5.7 A SUMMARISED BIOGEOCHEMICAL SAMPLING DESIGN

Throughout this research, and working and liaising with colleagues in Canada the application of biogeochemistry in Australian and in particular the *E. camaldulensis* has been developed through modifying methods which are applicable in cool environments (Canada) to the more arid – semi arid Australian environment. Table 5.18, outlines the basic rules to be applied when undertaking a biogeochemical sampling survey, either for mineral exploration or natural resource management programs in Australia, especially within semi-arid to arid regions.

| <b>Australia</b>   | <b>Reasons</b>  |
|--|---|
| Subdivide the tree into 8 equal sectors (Reconnaissance) or sample around the circumference of each tree   | To determine preferential translocation throughout the tree to allow for well developed conducting systems                                |
| Collect same species   | Every species has different chemical composition, trace element tolerances and nutrient requirements                                      |
| Use non-powdered latex or nitrile gloves   | Reduce contamination; also if survey is environmentally based, perspiration can induce elevated sodium concentrations                     |
| Collect same plant organ   | Each plant organ has different nutritional requirements and capacity to store trace elements  |
| Collect same amount (age) of growth, from the same area of the tree (at chest height)  | Chemical variations (twig: wood ratio) see Dunn et al 1995, to ensure homogeneous sampling should be taken from around the entire species |
| Collect samples of similar age and appearance, and don't mix live with dead tissue   | This ensures that all samples are repeatable, comparable and representative.  |
| Collection of living material should be undertaken at the same time of the year (over a 2-3 week period); otherwise normalization of data to a common datum is required. | Significant temporal variations in plant chemistry may be observed.   |
| Do not return to same tree previously sampled and expect to obtain exactly the same analysis   | This is unrealistic in view of the heterogeneity of element distributions and seasonal variations in composition.                         |

Table 5.18: The basic rules to be applied at each sampling site when undertaking a biogeochemical survey.





## CHAPTER 6

### SUMMARY AND CONCLUSIONS

This is the first study to characterise the detailed and regional biogeochemical attributes of Australia's most widespread and dominant tree species – *E. camaldulensis*. After developing a methodology for effectively and efficiently sampling this tree, six individual trees at key sites across the Curnamona Province and adjacent regions were characterised.

The results showed many of the elements have a detectable chemical heterogeneity between the *E. camaldulensis* major organs (leaves, twigs, fruit, bark and roots) and different sampling sites. Although there is a difference in element concentration between the major organs, the overall biogeochemical profiles are very similar, especially for leaves, twigs and fruit (chapter 3). The following conclusions are from investigating organ chemical heterogeneity:

- Leaves are readily available all year round and can be pulled straight from their branches;
- Twigs required some effort, in particular in obtaining twigs of the same diameter (ensuring a consistent bark to wood ratio) for sampling;
- Bark sampling created visible scarring to the tree and was more difficult to grind during the sample preparation stage, and the chemical content for most elements was not as high as for the leaves;
- Fruit sampling took a longer time to collect an adequate sampling weight (300 gm) as they could only be picked in clusters, and are only available during the growth period (spring and summer); and,
- Root sampling in general required digging and roots were typically coated by the surrounding regolith substrate (contaminated).

An assessment of the chemical characterisation between the major organs identified that the leaves are a more convenient, reproducible and comparable sampling media.

The spatial biogeochemical results within the *E. camaldulensis* sampled at each individual site (chapter 3) showed that there is very little difference between the sectors sampled for the same sampling media. In general the distribution of the essential elements throughout the *E. camaldulensis* is uniform (Figure 6.1).

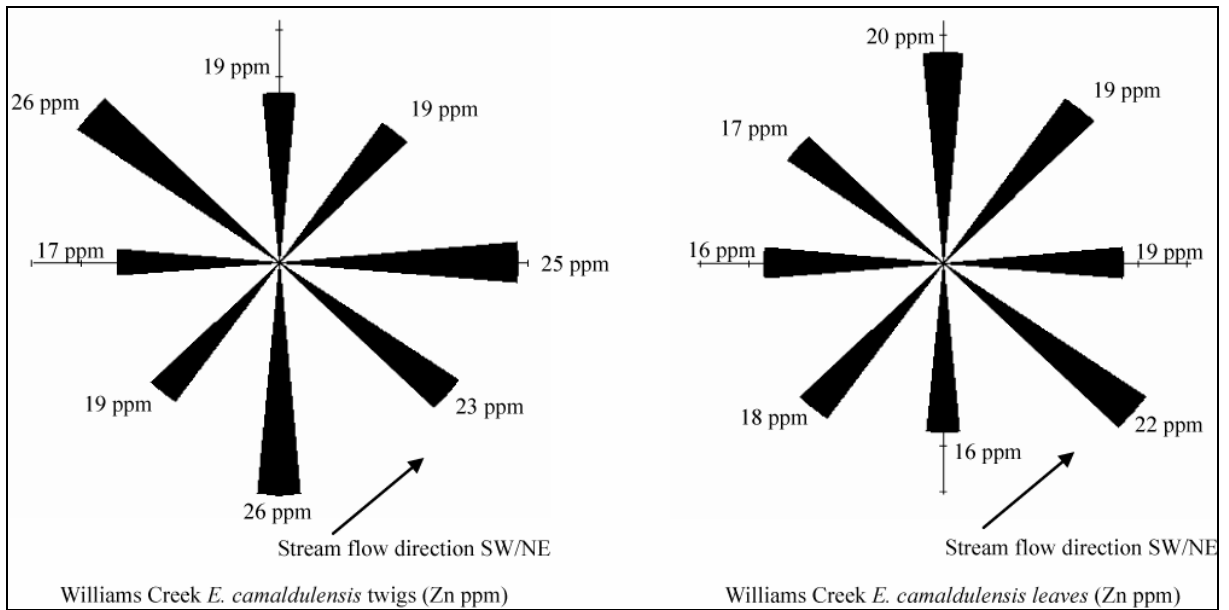


Figure 6.1: The uniform distribution and concentration of the essential element Zn through out the *E. camaldulensis* sampled at Williams Creek.

In contrast the distribution of the non-essential elements is predominately irregular (Figure 6.2).

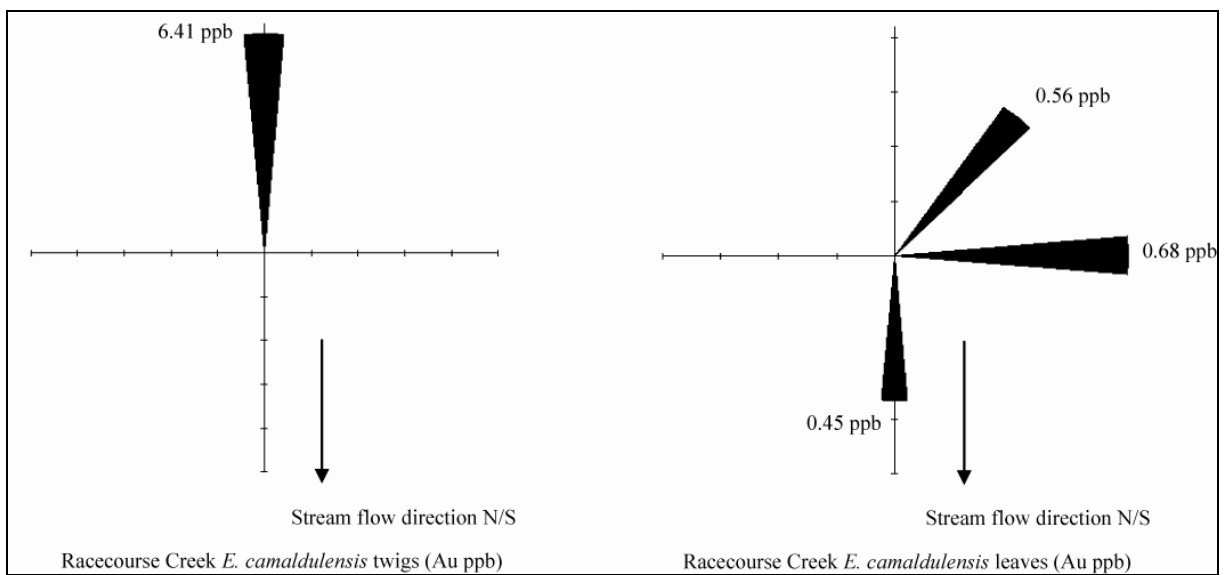


Figure 6.2: The irregular distribution and concentration of the non-essential element Au through out the *E. camaldulensis* sampled at Racecourse Creek (Tibooburra).

The results sector sampling illustrated by the rose diagram (Figure 6.2) substantiate that it is paramount for any biogeochemical and/or environmental sampling program circumference sampling will ensure that all collected samples are representative (an estimate of the trees overall chemical composition), and that all results are accurate and analogous.

In addition identifying that chemical variations within the *E. camaldulensis* (leaves) do not follow systematic rainfall, temperature and seasonal patterns, but rather are indicative of two distinct growth periods, and the slight to intermediate degree of variation between these two growth periods for the detectable elements has constrained the optimal sampling period to be (spring-summer). As these periods especially in western New South Wales experiences increases in temperature and daylight lengths. These factors will contribute to an increase in

evapotranspiration rates (Garland 1981), resulting in a greater movement of elements being transported throughout the xylem and being allocated to specific sites given their physiological role and the increase in cellular activity during the (spring-summer) period.

Following these observations, catchment-scale biogeochemical surveys were undertaken at Racecourse Creek (Tibooburra) and Pine Creek (Pinnacles Barrier Mine). The studies at these sites showed that the optimal sampling space in these areas is 1 sample every 200 m (semi-detailed survey). By visual inspection of the spatial survey density maps (Chapter 5) it can be seen that the semi-detailed survey defined the broad pattern of regional variations related the local geology; furthermore the local variation between background to anomalous concentrations characteristic of the gahnite-rich bedrock (associated with Ag-Pb-Zn sulphide mineralisation) and host rock (quartzo-feldspathic gneisses) geochemistry were identified.

The environmental setting was characterised through the construction and production of two regolith-landform maps. The maps provided a framework that allowed for a greater understanding of the chemical and physical dispersion of trace elements within both catchments. The integration of biogeochemical datasets defined background versus anomalous values, and *in-situ* anomalies were distinguished from transported anomalies (Chapter 5). In addition the regolith-landform maps can aid in the development of more effective biogeochemical and geochemical exploration strategies, in particular in terrains dominated by extensive transported regolith cover.

The characteristics of *E. camaldulensis* are consistent with the criteria required of a biogeochemical sampling medium as outlined by Dunn *et al.*, (1992) and Hill, (2002). These include:

- an easy to identify plant species;
- a locally dominant and widespread distribution (Chapter 1);
- a tendency to colonise areas of regolith cover (where bedrock related information is less readily available);
- an extensive root system that may penetrate transported cover and possibly also provide a homogenised expression of heterogeneous transported cover (Chapter 5);
- an ability to retain many plant organs throughout the year; and,
- large, smooth and waxy leaves that shed detrital surface contaminants (Chapter 2).

The prevalence of *E. camaldulensis* in regolith-dominated terrains, in particular the basin margins flanking highly prospective bedrock-dominated uplands, provides mineral explorers with a new sampling medium that can be employed along with more traditional sampling media, resulting in more effective mineral exploration through transported cover. In addition the employment of biogeochemistry, in particular *E. camaldulensis*, as a sampling medium, is its non-destructive application to the environment.

This study has shown that *E. camaldulensis* has the ability to tolerate, accumulate and translocate heavy metals such as Pb, Zn, Ag, Cd and As to their organs (leaves), which reflect their immediate environment (Barrier Pinnacles Mine). Thus they can also be recommended as a potential biomonitoring (medium) in the determination of direct and indirect points of pollution levels (anthropogenic) within the environment.

An immediate implication of this approach for mineral exploration was that an ore body extension to the Barrier Pinnacles Mine was discovered. This included the identification of several *E. camaldulensis* proximal to the Barrier Pinnacles Mine having polymetallic (Ag, Pb,

Zn, Cd and As) concentrations between 3 and 150 times greater than background concentrations, and Pb/Zn ratio of 3:2 and Ag/Pb 1:400 indicative of zinc mineralisation. These results lead to the excavation of a trench around an *E. camaldulensis* resulting in the discovery of a previously unknown Zn-lode. This approach is now “industry ready” for application to other *E. camaldulensis* dominated channels in the region.

## CHAPTER 7

### FUTURE RESEARCH

Mineral exploration sampling surveys have relied heavily on traditional sampling methods such as; stream sediments, groundwater, soils or drilling to the underlying bedrock. Isotopic analysis has been used successful in the study of ore deposits. The isotopic analysis of *E. camaldulensis*, and in particular the Pb, Zn and S isotopes, may further aid in constraining *in-situ* anomalies from transported anomalies. The Broken Hill region would be an ideal area to examine this as there is extensive knowledge of the sulphur isotopic composition of the sulphides within the garnet-rich rocks and high grade ore showing range values of -3.3 to +6.7 mil (Spry, 1987). With the recent advancement of analytical techniques, such as the development of the multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS), this further research would be timely.

A 3-dimensional sampling program would further characterise the overall chemical composition of the *E. camaldulensis*. In addition it would further constrain variables such as: shade versus sunlight, temporal summer versus winter, and the influence of annual growth cycle (i) spring – reproduction begins, (ii) summer – summer rains give rise to peak production, (iii) autumn – peak biomass, and (iv) winter – stage of dormancy. The following diagram (Figure 7.1) outlines a possible sampling strategy.

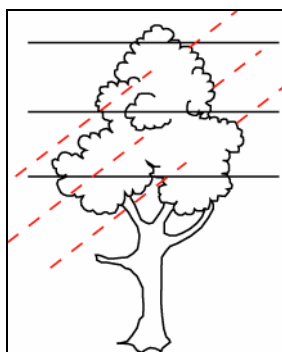


Figure 7.1: A possible sampling strategy, for the *E. camaldulensis* with leaves, twigs, fruit and buds to be sampled at each circumference level (3-D).

The additional characterisation of the *E. camaldulensis* (twigs) such as the spatial variations in the chemical composition of the twig wood to twig bark concentrations and the degree of variability. This additional knowledge would further enhance the employment of *E. camaldulensis* as a biogeochemical exploration medium, especially in times of extreme drought when *E. camaldulensis* may have shed all lower available leaves leaving behind only the twigs. Studies in Canada (Dunn, 2007) suggest that variations in U concentrations in dry black spruce twigs are possibly because of the changing ratio of twig wood to twig bark as the tree grows.

## REFERENCE

- Adams, M.A. and Attiwill, P.M., 1986. Nutrient cycling and nitrogen mineralization in eucalypt forests of southeastern Australia II. Indices of nitrogen mineralization. *Plant Soil* **92**: pp. 341–362.
- Akçay, M., Lermi, A., Van, A. (1998). Biogeochemical exploration for massive sulphide deposits in areas of dense vegetation: an orientation survey around the Kanköy Deposit (Trabzon, NE Turkey). *Journal of Geochemical Exploration* **63**: 173-187.
- Albarède, F. (2003). *Geochemistry: An introduction*. The press syndicate of the University of Cambridge. Cambridge, United Kingdom.
- Alexander, P. (1976). Whim Creek Consolidated N.L. Report on E.L. 861 Tibooburra District. Whim Creek Consolidated N.L. *Geological Survey of New South Wales*, Report: GS1976/205 (unpublished).
- Allen, S.E., Grimshaw, H.M., Parkinson, J.A. and Quarmby, C. (1974). *Chemical analysis of ecological materials*. Blackwell Scientific Publications, Oxford.
- Allen, S.E. (1989). *Chemical analysis of ecological material, 2<sup>nd</sup> Edition*. Blackwell Scientific Publications, Oxford.
- Alley, N.F. (1998). Cainozoic stratigraphy, palaeoenvironments and geological evolution of the Lake Eyre Basin. *Palaeogeography, Palaeoclimatology, Palaeoecology*, **144**: 239-263.
- Alloway, B.J. (1995). *Heavy metals in soils*. Blackie Academic & Professional. London.
- Alloway, B.J. (1995). Cadmium. In: Alloway, B.J., Editor, 1995. *Heavy Metals in Soils*, Blackie Academic & Professional, London, pp. 122–151
- AMDEL, (2003). Mineral service price guide: Analytical chemistry; mineralogy and mineral processing. (unpublished report)
- Andrews, E.C. (1922). Geology of the Broken Hill district. *Geological Survey of New South Wales*, Memoir 8.
- Arne, D.C., Stott, J.E. and Waldron, H.M. (1999). Biogeochemistry of the Ballarat east goldfield, Victoria, Australia. *Journal of Geochemical Exploration*. **67**: 1-14.
- Ashton, L.W and Riese, W.C. (1989). Seasonal variation of gold and arsenic in biogeochemical samples from a disseminated gold deposit in the Northern Cordillera. *Journal of Geochemical Exploration*. **31**:171-184.
- Aspandiar, F.M., Anand, R & Gray, D., 2006. Mechanisms of metal dispersion through transported cover: A review. CRC LEME Report 20.
- Atkins, P.W. (1940). *Chemistry: molecules, matter and change*. – 3<sup>rd</sup> ed. Peter. W. Atkins, Loretta L. Jones. pp 886.

Ayres, D.E. (1962). The Mineralogy of the Pinnacles Mine, Broken Hill, New South Wales. University of Adelaide-M.Sc. Thesis (unpublished).

Bargagli, R. (1998). Trace elements in terrestrial plants: *an ecophysiological approach to biomonitoring and biorecovery*, Springer, New York.

Barker, A.V. and Pilbeam, D.J. (2007). *Introduction. In: Handbook of Plant Nutrition.* (eds) Barker, A.V. and Pilbeam, D.J. CRC Press, Florida.

Barnes, R.G. (1974). Tibooburra-Wonominta Block. In: Markham, N.L. and Baseden, H. Eds. The Mineral deposits of New South Wales. *Geological Survey of New South Wales*. Department of Mines. Sydney, Australia, 92-101.

Barnes, R.G. (1988). 2. Mineral deposits of the Southwestern Broken Hill Block. In: Metallogenic studies of the Broken Hill and Euriovie Blocks, New South Wales. Department of Mineral Resources. *Geological Survey of New South Wales*, Bulletin **32** (1,2).

Beadle N. C. W. (1968) Some aspects of ecology and physiology of Australian xeromorphic plants. *Australian Journal of Science*, Vol, **30**: p.348-55.

Beadle, N.C.W. (1981). *The Vegetation of Australia*, Cambridge University Press, Cambridge.

Bhimaya, C.P. and Kaul, R.N. (1966). Leaves of Macro- and Micro-elements in *Eucalyptus camaldulensis* Dehn. (*E. rostrata* Schlecht). *Nature* 212. 319-320.

Bureau of Meteorology (2005a). Average for Yunta.  
[http://www.bom.gov.au/climate/averages/tables/cw\\_020026.shtml](http://www.bom.gov.au/climate/averages/tables/cw_020026.shtml)

Bureau of Meteorology (2005b). Average for Bindarra.  
[http://www.bom.gov.au/climate/averages/tables/cw\\_020026.shtml](http://www.bom.gov.au/climate/averages/tables/cw_020026.shtml)

Bureau of Meteorology (2005c). Averages for Flying Doctor: Stephens Creek Reservoir.  
[http://www.bom.gov.au/climate/averages/tables/cw\\_047031.shtml](http://www.bom.gov.au/climate/averages/tables/cw_047031.shtml).

Bureau of Meteorology (2005d). Average for White Cliffs.  
[http://www.bom.gov.au/climate/averages/tables/cw\\_046042.shtml](http://www.bom.gov.au/climate/averages/tables/cw_046042.shtml)

Bureau of Meteorology (2005e). Average for Tibooburra (Tibooburra Post Office).  
[http://www.bom.gov.au/climate/averages/tables/cw\\_046037.shtml](http://www.bom.gov.au/climate/averages/tables/cw_046037.shtml)

Bierlein, F.P., Ashley, P.M. and Plimer, I.R. (1995). Sulphide mineralisation in the Olary Block, South Australia: evidence for syn-tectonic to late-stage mobilisation. *Mineral. Deposita*, **30**: 424-438.

Bogoch, R. and Brenner, I.B. (1984). A biogeochemical orientation survey in an arid rocky desert. *Journal of Geochemical Exploration*. 20:311-321.



- Bounessah, M. and Atkin, B.P. (2003). An application of exploratory data analysis (EDA) as a robust non-parametric technique for geochemical mapping in a semi-arid climate. *Applied Geochemistry*. **18**: 1185-1195.
- Boyle, R.W. (1967). Geochemical prospecting-retrospect and prospect. *Geological Survey of Canada*. Paper 66-54, 30-43.
- Boyle, R.W. (1974). Elemental association in mineral deposits and indicator elements of interest in geochemical prospecting (revised). *Geological Survey of Canada Paper*. 74-45: 1-40.
- Bradley, G.M. (1984). Mount Gipps 1:25 000 Geological Sheet 7234-III-S. *Geological Survey of New South Wales*, Sydney.
- Bradley, G.M. (1980). Stratigraphic interpretation of the Mount Gipps-Rockwell area. In: Stevens, B.P.J. ed. A guide to the stratigraphy and mineralisation in the Broken Hill Block, New South Wales. *Geological Survey of New South Wales*. Records 20(1), 87-96.
- Brakel, A.T. and Totterdell, J.M. (1993). The Sakmarian–Kungurian palaeogeography of Australia, In: R.H. Findlay, R. Unrug, M.R. Banks, J.J. Veevers (Eds.), *Eighth Gondwana Symposium*, Balkema, Rotterdam, pp. 385–396.
- Briat, J.F. and Lebrun, M. (1998). Plant response to metal toxicity. *Comptes Rendus de l'Académie des Sciences - Series III - Sciences de la Vie*, Volume 322, Issue 1, Pages 43-54.
- Brooks, R.R. (1972). *Geobotany and Biogeochemistry in Mineral Exploration*. Harper & Row, pp 231.
- Brooks, R.R. (1973). Biogeochemical Parameters and Their Significant for Mineral Exploration. *Journal of Applied Ecology*. **10**: 825-836.
- Brooks, R.R. (1998). *Plants that hyperaccumulate heavy metals: Their role in phytoremediation, microbiology, archaeology, mineral exploration, and phytomining*, CAB International, New York.
- Brooks, R.R., Baker, A.J.M., Ramakrishna, R.S. and Ryan, D.E. (1985). Botanical and geochemical exploration studies at the Seruwila copper-magnetite prospect in Sri Lanka. *Journal of Geochemical Exploration*. **24**: 223-235.
- Brooks, R.R, Dunn, C.E. and Hall, G.E.M. (1995). *Biological Systems in Mineral Exploration and Processing*. Published in 1995, Ellis Horwood (New York), pp. 538.
- Brown, R.E. (1978). The geology of the Pinnacles 1:25 000 Sheet area, Broken Hill, New South Wales, Department of Mineral Resources, *Geological Survey of New South Wales*, Report No: GS 1978/057.
- Brown, R.E. (1984). Pinnacles 1:25 000 Geological Sheet, 7133-I-N, *New South Wales Geological Survey*, Sydney.

Brunker, R.L., Offenber, A.C. and Rose, G. (1967). Explanatory notes 1:3,000,000 Geological Map of New South Wales. *NSW Mines Department - Geological Survey*.

Buckley, P.M. (2000). The regional context of copper and gold mineralisation at Grasmere, the Koonenberry Belt's best kept secret. In: Peljo, M., (compiled), 2000. *Broken Hill Exploration Initiative: Abstracts of Papers Presented at the May 2000 Conference in Broken Hill*. Australian Geological survey Organisation, Record 2000/10, 8-11.

Burton, G.R. (1994). Metallogenic studies of the Broken Hill and Euriowie Blocks, New South Wales. 3. Mineral deposits of the South Eastern Broken Hill Block. *Geological Survey of New South Wales*, Bulletin 32, 100 pp.

Busche, F. (1989). Using plants as an exploration tool for gold. *Journal of Geochemical Exploration*. **32**: 199-209.

Callen, R.A., Alley, N.F. and Greenwood, D.R. (1995). Lake Eyre Basin. In: Drexel, J.F., Preiss, W.V. (Eds), *The Geology of South Australia. Volume 2. The Phanerozoic. South Australia Geological Survey Bulletin*, 54, pp. 188-194.

Campana, B. and King, D. (1958). Regional geology and Mineral resources of the Olary Province. *South Australia. Geological Survey*. Bulletin 34.

Campbell, N.A. (1996). *Biology*. Benjamin-Cummings Publishing Company California. U.S.A.

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

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

Carlisle, D. and Cleveland, G.B. (1958). Plants as a guide to mineralisation: California Div. Mines Geology Spec. Rept. 50, 31 pp.

Chamberlain, T. (2001). Regolith Geology and Landscape Evolution of the Tibooburra Inlier, north-west New South Wales. University of Canberra B. App. Sc (Hons) Thesis (unpublished).

Chamberlain, T. and Hill, S.M. (2002). Tibooburra Inlier regolith-landform map (1:25 000). *CRC LEME*, Perth.

Cohen, D.R., Shen, X.C., Dunlop, A.C. and Rutherford, N.F. (1998). A comparison of selective extraction soil geochemistry and biogeochemistry in the Cobar area, NSW. *Journal of Geochemical Exploration*. **61**: 173-190.

Cohen, D.R., Silva-Santisteban, C.M., Rutherford, N.F., Garnett, D.L. and Waldron, H.M. (1999). Comparison of vegetation and stream sediment geochemical patterns in northeastern New South Wales. *Journal of Geochemical Exploration*, Volume 66, Issue 3, 469-489.

- Cole, M.M. (1965). The use of vegetation in mineral exploration in Australia. *Eight Commonwealth Mining Metallurgical Congress Australia and New Zealand*. Volume 6, pp1429-1458.
- Cole M.M. (1970). The importance of environment in biogeographical/geobotanical and biogeochemical investigations. *Geochemical Exploration: proceedings of the 3rd International Symposium, Toronto, Special volume 11*. Canadian Institute of Mining and Metallurgy, Montreal, pp 414 – 425.
- Cole, M.M. (1973) Geobotanical and biogeochemical investigations in the sclerophyllous woodland and shrub associations of the Eastern Goldfields area of Western Australia, with particular reference to the role of *Hybanthus floribundus* (Lindl.) F. Muell. as a nickel indicator and accumulator plant. *Journal of Applied Ecology*. **10**: 269-320.
- Cole, M.M. (1991) Remote sensing, geobotany and biogeochemistry in detection of Thalanga zinc-lead-copper deposit near Charters Towers, Queensland, Australia. *Transactions of the Institute of Mining and Metallurgy Section B*. 100: 1-8.
- Cooper, P.F. (1975). Explanatory notes on the Broken Hill 1:250 000 geological sheet SH5415. Department of New South Wales. *New South Wales Geological Survey*. Explanatory (R00050788).
- Correll, R.L. and Taylor, R.G. (1974). Occurrence of *Polcarpaea spirostylis* at Daisy Bell copper mine, Emuford, north Queensland, Australia. *Transactions of the Institute of Mining and Metallurgy Section B*. **83**: 30-34.
- Cramsie, J.N. and Hawke, J.M. (1984). 1. Introduction: Structural subdivision of the Great Australian Basin in New South Wales. In: J.M. Hawke and J.N. Cramsie (eds), *Contributions to the geology of the Great Australian Basin in New South Wales*, New South Wales Department of Mineral Resources Bulletin, **31**: 1-22.
- Crisci, G.M., De Vivo, B., Lafratta, R., La Valva, V and Lima, A. (1982). Metal response in plants to sulfide mineralisation in the Longobucco area (Calabria, Southern Italy). *Journal of Geochemical Exploration*. **17**: 187-204.
- Cruikshank, B.I. and Pyke, J.G. (1986) Biogeochemistry and soil geochemistry of the Ranger One, Number 3 Orebody, Australia. *Uranium* **3**: 1-26.
- Dann, R. (2001). Hydrogeochemistry and Biogeochemistry in the Stephens Creek Catchment, Broken Hill, NSW. Honours Thesis Unpublished. University of Canberra.
- Davies, N. (1953). Investigations on the soil and water relations of the river red gum forests. Final Report Murray Management Survey. *Forestry Commission of New South Wales, Resources Branch*, Report No. R.124.
- Day. F.P. (1983). Effects of flooding on leaf litter decomposition in microcosms. *Oecologia* **56**: 180-184.
- De Caritat P. & Kirste D. 2004. Teilta Regolith Project: groundwater geochemistry. *CRC LEME Open File Report* 158.

Dexter, B.D. (1967). Flooding and regeneration of river red gum, *Eucalyptus camaldulensis*. Dehn. Bull. *For Comm. Vic.* 20: 35pp.

Dickson, K.J. (1972). Mining history of the silver lead zinc and copper mines of the Broken Hill district to 1939, excluding the Main Line of Lode: *New South Wales Geological Survey Bulletin*, No. 21, 96pp.

Drexel, J.F. and Preiss, W.V (Eds), (1995). The geology of South Australia. Vol. 2, The Phanerozoic. *South Australia. Geological Survey. Bulletin*, 54.

Dunkerly, D.L. and Brown, K.J. (1995). Runoff and runoff areas in a patterned chenopod shrubland, arid western New South Wales, Australia: characteristics and origin. *Journal of Arid Environments*. **30**: 41-55.

Dunn, C.E. (1981). The biogeochemical expression of deeply buried uranium mineralisation in Saskatchewan, Canada. *Journal of Geochemical Exploration*. **15**: 437-452.

Dunn, C.E. (1983). Biogeochemical investigations in northern Saskatchewan: preliminary data on tungsten, gold, platinum, rare-earths and uranium. In: Summary of investigations 1983. *Saskatchewan Geological Survey, Miscellaneous Report 83-4*: 106-122.

Dunn, C.E. (1984). Biogeochemical method and surveys, southern La Ronge Belt. In Summary of Investigations 1984. *Saskatchewan Geological Survey, Miscellaneous Report 84-4*: 95-103.

Dunn, C.E. (1993). Diamondiferous kimberlite in Saskatchewan, Canada-a biogeochemical study. *Journal of Geochemical Exploration*. **47**: 131-141.

Dunn, C.E., Erdman, J., Hall, G. and Smith, C. (1992). Short course 'notes' for conducting an effective biogeochemical exploration survey. (unpublished).

Dunn, C.E., Scagel, R., Hall, G.E.M., Cohen, D., Catt, P. and Lintern, M. (1995). *Applied biogeochemistry in mineral exploration and environmental studies* (short course), The Associations of Exploration Geochemists, 25<sup>th</sup> Anniversary: 1970-1995.

Dunn, C.E., Brooks, R.R., Edmondson, J., Leblanc, M., Reeves, R.D. (1996). Biogeochemical studies of metal-tolerant plants from Southern Morocco. *Journal of Geochemical Exploration*. **56**: 13-22.

Dunn, C.E., (2007). Handbook of Exploration and Environmental Geochemistry series (M. Hale, series editor), Volume 9. Amsterdam, Elsevier.

Dury, G.H. (1966). Pediment slope and particle size at Middle Pinnacle, near Broken Hill, New South Wales. *Australian Geographical Studies*. **4**: 1-17.

Dury, G.H. and Langford-Smith, T. (1964). The use of the term peneplain in descriptions of Australian landscapes. *Australian Journal of Science*. **27**: 171-175.

- El Shazly, E.M., Barakat, N., Eissa, E.A., Emara, H.H., Ali, I.S., Shaltout, S. and Sharaf, F.S. (1970). The use of Acacia trees in biogeochemical prospecting. *Can. Inst. Min. Metall., Spec. Vol.*, 11: 426-434.
- Ernst, W.H.O. (1990). Element allocation and (re)translocation in plants and its impact on representative sampling. In: H. Lieth and B. Markert, Editors, *Element Concentration Cadasters in Ecosystems. Methods of Assessment and Evaluation*, VCH Publ. Inc, New York, pp. 17–40.
- Ernst, W.H.O. (1995). Sampling of plant material for chemical analysis. *The Science of the Total Environment*. Vol. 176: 15 – 24 pp.
- Fabris, A.J, Sheard, M.J, Keeling, J.L, Hill, S.M, McQueen, K.G, Conor, C.C.H and de Caritat, P, 2008. Guide For Mineral Exploration Through The Regolith In The Curnamona Province, South Australia. 1. Regolith. 2. Mineral exploration. 3. Geomorphology. 4. Geochemistry.
- Facelli, J.M. and Pickett, S.T.A. (1991). Plant Litter: Its dynamics and effects on Plant Community Structure. *Botanical review*, Vol. 57, No. 1, pp. 1-32.
- Fanning, P.C. (1999). Recent landscape history in arid western New South Wales, Australia: a model for regional change. *Geomorphology*, **29**: 191-209.
- Feeny, P.P. (1970). Seasonal changes in oak leaf tannins and nutrients as a cause of spring feeding by winter moth caterpillars. *Ecology* **51**: 565-581.
- Field, J.B. & Little, D. 2008. Biota and the Regolith. Ch 8 in Scott, K and Pain, C. (eds) *Regolith Science*, CSIRO Pub, Melb.
- Flemming, G.D. (1995). Preliminary Koonenberry 1:500 000 sheet mineral deposit compilation. Summary notes. Geological Survey of New South Wales, Department Mineral Resources Report: GS1995/212.
- Flint, D.J. and Parker, A.J. (1993). Willyama Inliers. In: Drexel, J.F., Preiss, W.V. and Parker, A.J. (Eds), *The Geology of South Australia*. Vol. 1, The Precambrian. South Australia. Geological Survey. Bulletin, **54**: 82-93.
- Flint, R.B., Ambrose, G.J. and Campbell, K.S.W. (1980). Fossiliferous Lower Devonian boulders in Cretaceous sediments of the Great Australian Basin. *Transactions of the Royal Society of South Australia* 104, 57-66.
- Forbes, B.G. (1991). OLARY, South Australia. Sheet SI/54-02, International Index. 1:250 000 Geological Series - Explanatory Notes. Geological Survey of South Australia.
- Forbes, B.G. and Preiss, W.V. (1987). Stratigraphy of the Burra Group. In: *The Adelaide Geosyncline – Late Proterozoic stratigraphy, sedimentation, palaeontology and tectonics*. South Australia Geological Survey, Bulletin 53.
- Forbes, B.G. (1991). *Olary, South Australia, Explanatory Notes. 1:250 000 Geological Series*. Geological Survey of South Australia, Canberra, Australian Capital Territory.

Fortescue, J. A. C. and Hornbrook, E. H. W. (1969) - Part II A brief survey of progress made in biogeochemical prospecting research at the Geological survey of Canada 1962-65 (1969) 111 pp.

Gallo, M.E., Porrás-Alfaro, A., Odenbach, K.J. and Sinsabaugh, R.L. (2009). Photoacceleration of plant litter decomposition in an arid environment. *Soil Biology & Biochemistry* **41**: 1433-1441.

Garland T.R., Cataldo A. and Wildung R.E. (1981). Absorption, transport, and chemical fate of plutonium in soyabean plants. *Journal Agricultural Food Chemistry* **29**: 915-920.

Gerritsen, J. (1981). Tibooburra-Corner Country. Tibooburra Press, Gympie, Queensland, Australia. 149pp.

Gibson, D.L. and Wilford, J.R. (1996). Broken Hill 1:50 000 regolith-landforms map. CRC LEME, Perth.

Groves, T.S., Thomson, B.D. and Malajczuk, N. (1996). Nutritional physiology of Eucalyptus: Uptake, distribution and utilization. In: Attiwill, P.M. and Adams, M.A, (eds), Nutrition of Eucalyptus, CSIRO, Victoria. 440pp.

Hair, J.F., Anderson, R.E., Tatham, R.L. and Black, W.C. (1992) *Multivariate data analysis* (3rd ed.). New York: Macmillan.

Hall, J.L. (2002). Cellular mechanisms for heavy metal detoxification and tolerance. *Journal of Experimental Botany*, Vol. 53, No. 366, pp. 1-11.

Hall, J.S. (1971). A comparative biogeochemical investigation in the semi arid/arid zone of West Australia. Unpublished honours thesis, University of Adelaide pp. 22.

Hanna, W.J. and Grant, C.L. (1962). Spectrochemical analysis of the foliage of certain trees and ornamentals for 23 elements. *Bulletin of the Torrey Botanical Club*. No 5, pp. 293-302.

Hatton, O.; Snodin, S.; Walker, R.N.; Michael, S.S.; Mackee, G. and Mann, S. (2006). Unlocking South Australia's Mineral and Energy Potential - A Plan for Accelerating Exploration. Theme 2 (drilling partnerships with PIRSA and industry): Year 2 partnership no. 34, Drew Hill JV area Curnamona Group base metal mineral prospects. Project final report. South Australia. Department of Primary Industries and Resources. Open file Envelope, 11108.

Hemphill, D.D. (1972) Availability of trace elements to plants with respect to soil-plant interaction. *Annals of the New York Academy of Sciences* 199 (1), 46-61

Hill, L.J. (2002). Branching out into biogeochemical surveys: a guide to vegetation sampling. In: ROACH I.C. ed. Regolith and Landforms in Eastern Australia. CRC LEME, 50-53.

Hill, L.J. (2004). Geochemical and biogeochemical dispersion and residence in landscapes of western New South Wales, p. 376. Australian National University, Ph.D. (unpublished).

- Hill, S.M. (1995). Regolith Mapping: What Do We Think We Are Doing? (and are We Really Doing It?). In McQueen K.G. & Craig M.A. ed. *Developments and new approaches in regolith mapping*. pp. 17-24.
- Hill, S.M. (1999). Mesozoic regolith and palaeolandscape features in southeastern Australia: significance for interpretations of denudation and highland evolution. *Australian Journal of Earth Sciences*, **46**: 217-232.
- Hill, S.M. (2000). The Regolith and Landscape Evolution of the Broken Hill Block, western New South Wales, Australia. Ph.D Thesis. Australian National University, Canberra. Unpublished. 476pp.
- Hill, S.M. (2001). Broken Hill Domain Regolith-Landforms (1:100 000 map). CRC LEME, Canberra/Perth.
- Hill, S.M. (2003). Exploration without hitting rock bottom: A brief guide to recent developments in exploration in regolith-dominated terrains of the Curnamona Craton and adjoining areas. *Broken Hill Exploration Initiative: Abstracts of papers presented at the July 2003 conference in Broken Hill*. Geoscience Australia Records: 2003/13.
- Hill, S.M. (2005). Teilta, Western New South Wales. In: R.R. Anard and P. de Broekert (Editors), *Regolith Landscape Evolution Across Australia*. CRC LEME, Perth. pp. 110-117.
- Hill, S.M. (2005). Regolith and Landscape Evolution of Far Western New South Wales. In: R.R. Anard and P. de Broekert (Editors), *Regolith Landscape Evolution Across Australia*. CRC LEME, Perth. pp. 130-145.
- Hill, S.M. and Hill, L.J. (2003). Some important plant characteristics and assay overviews for biogeochemical surveys in western New South Wales. In: ROACH I.C. ed. *Advances in Regolith*, pp. 187-192.
- Hill, S.M., Chamberlain, T. and Hill, L.J. (2005). Tibooburra, New South Wales. In: R.R. Anard and P. de Broekert (Editors), *Regolith Landscape Evolution Across Australia: A compilation of regolith landscape case studies with regolith landscape evolution models*. CRC LEME, Perth. pp. 118-122.
- Hill, S.M., Thomas, K.E. and Foster, K.A. (2005). Flying Doctor Ag-Pb-Zn Prospect, Northern Leases, Broken Hill, NSW. In: Butt C.R.M., Cornelius, M., Scott, K.M. and Robertson, I.D.M. eds. *Regolith Expression of Australian Ore Systems: A compilation of geochemical case histories and conceptual models*. CRC LEME Monographs, Perth.
- Hill, S.M., West, D.S., Shirtliff, G., Senior, A.B., Maly, B.E.R., Jones, G.L., Holzapfel, M., Foster, K.A., Debenham, S.C., Dann, R. and Brachmanis, J. (2005). Southern Barrier Ranges-Northern Murray Basin, New South Wales. In: R.R. Anand and P. de Broekert (Editors), *Regolith Landscape Evolution Across Australia: A compilation of regolith landscape case studies with regolith landscape evolution models*. CRC LEME, Perth. pp. 104-109.
- Hill, SM, Greenfield, JE, Gilmore, PG and Reid, WJ, 2008. Guide for mineral exploration through and within the regolith in the southwestern Thomson Orogen, New South Wales. 1. Regolith. 2. Mineral exploration. 3. Geomorphology. 4. Geochemistry.

Huenneke L.F., Clason D and Muldavin E. (2001). Spatial heterogeneity in Chihuahuan Desert vegetation: implications for sampling methods in semi-arid ecosystems. *Journal of Arid Environments* 47, 257-270.

Hulme K.A., and Hill S.M. (2003). River red gums as a biogeochemical sampling medium in mineral exploration and environmental chemistry programs in the Curnamona Craton and adjacent regions of NSW and SA. In: Roach I.C. ed. *Advances in Regolith*. CRC LEME, pp. 205-210.

Hulme K.A., and Hill S.M. (2004). Seasonal element variations of *Eucalyptus camaldulensis* biogeochemistry and implications for mineral exploration: An example from Teilita, Curnamona Province, western NSW. In: Roach I.C. ed *Regolith 2004*. CRC LEME, pp. 151 – 156.

Hulme, K.A., Dunn, C.E. and Hill, S.M. (2006). Biogeochemistry for mineral exploration in Canada & Australia: a comparison based on international collaboration. In: R.W. Fitzpatrick and P. Shand eds. *Regolith 2006- Consolidation and Dispersion of Ideas*, CRC LEME, Perth, Western Australia, pp. 161-165.

Horn, C.M. and Morris, B.J. (1988). Review of Lead-Zinc mineralisation in South Australia-Willyama Inlier and Curnamona Cratonic nucleus. Department of Mines and Energy, South Australia, Rept. Bk. No. 88/75.

Hornbrook, E.H.W. (1970b), Biogeochemical investigations in the Perch Lake area, Chalk River, Ontario, Geological Survey of Canada, Paper 70-43.

Jordan, C.F. (1983). Productivity of tropical rain forest ecosystems and the implications for their use as future wood and energy sources. In. F.B. Golley, (ed.) *Tropical Rainforest Ecosystems. Structure and Function*. Amsterdam, Netherlands, Elsevier Science Publishers. 14A of 'Ecosystems of the World': 117-136.

Kabata-Pendias, A. and Pendias, H. (1984). Trace elements in soils and plants. CRC Press, U.S.A.

Kabata-Pendias, A. and Pendias, H. (1991). Trace elements in soils and plants 2<sup>nd</sup> edition. CRC Press, U.S.A.

Keller, W.D. and Frederickson, A.F. (1952). Role of plants and colloidal acids in the mechanism of weathering. *American Journal of Science*, Vol. 250, August 1952, P.594-608

Kenny, E.J. (1934). West Darling District. New South Wales Geological Survey-Mineral Resources, 36, 180 pp.

Knapp, A.K. and Seastedt, T.R. (1986). Detritus accumulation limits productivity of tallgrass prairie. *BioScience* 36: 622-668.

Knight, J.H. (1999). Root distributions and water uptake patterns in Eucalypts and other species. In: *The Way Trees Use Water* (Ed J. Landsberg) *Water and Salinity Trends in Agroforestry* no. 5, RIRDC Publication no. 99-37, 66-102.



- Kovalevskii, A.L. (1979). Biogeochemical Exploration for Mineral Deposits. Oxonian Press, New Delhi, 136 pp.
- Kovalevskii, A.L. (1987). Biogeochemical exploration for mineral deposits: 2<sup>nd</sup> edition (revised and supplemented) / A.L. Kovalevsky; transl. [from the Russian] by M.B Rosenberg; technical ed. R.R Brooks.-Utrecht: VNU Science Press.-III. pp 224.
- Krieg, G.W. and Rogers, P.A. (1995). Eromanga basin. Stratigraphy-marine succession. In: Drexel, J.F. and Preiss, W.V. (eds), The geology of South Australia. South Australia Geological Survey Bulletin, 54, 112-123.
- Laclau JP, Deleporte P, Ranger J, Bouillet JP, Kazotti. 2003. Nutrient Dynamics throughout the Rotation of *Eucalyptus* Clonal Stands in Congo. *Annals of Botany* **91**: 879–892.
- Larson, F. and Whitman, W. (1942). A comparison of used and unused grassland mesas in the badlands of South Dakota. *Ecology* **23**: 438-445.
- Laut, P., Heyligers, P.C., Keig, G., Löffler, E., Margules, C., Scott, R.M. and Sullivan, M.E. (1977). Environments of South Australia, Province 5 Eastern Pastoral and Province 6 Flinders Ranges. Division of Land Use Research Commonwealth Scientific and Industrial Research Organisation Canberra, Australia. Pp. 219.
- Lehy, W. (2003). Pinnacles Mining Lease. Eaglehawk Geological Consulting Pty. Ltd. In: Extracts Due Diligence Report (2000). 43pp.
- Lehy, W.R. & Conor, C.H.H. (2000). Stratigraphically controlled metallogenic zonation associated with the regional redox boundary of the Willyama Supergroup – Economic implications for the Southern Curnamona Province. MESA Journal (Quarterly Earth Resources Journal of Primary Industries and Resources South Australia), **16**: 39-47.
- Levinson, A.A. (1980). Introduction to exploration geochemistry 2<sup>nd</sup> ed. Applied Pub. Wilmette.
- Lewis, P.C. (1976). Exploration report EL 824 Nuntherungie-Wertago area. Esso Exploration and Production Australia Inc. Geological Survey of New South Wales Unpublished Open File Report GS1976/146.
- Lieth, H. (1975). Primary production of the major vegetation units of the world. In: H Lieth and R.H. Whittaker, (eds.) Primary Productivity of the Biosphere. New York, Springer-Verlag: 96-163.
- Likens, G.E., Tartowski, S.L., Berger, T.W., Richey, D.G., Driscoll, C.T., Frank, H.G. and Klein, A. (1997). Transport and fate of trifluoroacetate in upland forest and wetland ecosystems. *Proceedings of the National Academy of Sciences of the United States of America* **94**: 4499-4503.
- Lintern, M.J., Butt, C.R.M., Scott, K.M. (1997). Gold in vegetation and soil-three case studies from the gold fields of southern Western Australia. *Journal of Geochemical Exploration*. **58**: 1-14.

Lopes, D.; Whitehead, S. and Webb, J.E. (1970). Olary area. Progress reports to licence expiry for the period 1/7/1968 to 30/6/1970. South Australia. Department of Primary Industries and Resources. Open file Envelope, 01343.

McCallum, W.S. (1997). Review of open file company exploration data from the early 1980s to mid-1997, over the Yunta, Winnininnie, Anabama and Oakvale 1:100 000 map sheets, OLARY 1:250 000 map sheet, South Australia. South Australia. Department of Mines and Energy Resources. Report Book, 98/00022.

Mc Innes, I.A., Dunn C.E., Cameron E.M., Kameko, L. (1996). Biogeochemical exploration for gold in tropical rain forest regions of Papua New Guinea *Journal of Geochemical Exploration*. **57**: 227-243.

McKinney, A.L. (1929). Effects of forest litter on soil temperature and soil freezing in autumn and winter. *Ecology* **10**: 312-321.

Malyuga, D.P. (1964). Biogeochemical methods of prospecting. Consultants Bureau. New York. (Translation from the Russian).

Markert, B. and Weckert, V. (1989). Fluctuations of element concentration during the growing season of *Polytrichum formosum* (hedw.). *Water, Air and soil Pollution*. **43**,177-189.

Marschner, H. (1986). *Mineral Nutrition of Higher Plants*. Academic Press Limited. London.

Marschner, H. (1995). *Mineral Nutrition of Higher Plants*. Academic Press Limited. London.

Memon, A.R., Aktoprakligil, A., Özdemir, A. and Vertii, A. (2001). Heavy metal accumulation and detoxification mechanisms in plants. *Turkish Journal of Botany*, **25**: 111-121.

Mensforth, L.J., Thornburn, P.J., Tyerman, S.D. and Walker, G.R. (1994). Sources of water used by riparian *Eucalyptus camaldulensis* overlying highly saline groundwater. *Oecologia*, **100**: 21-28.

Mills, K.J. (2002). Explanatory Notes to accompany Kayrunnera 1:100 000 Geological Sheet 7436, Koonenberry Region, far Western New South Wales. Geological Survey Report No: GS2002/752.

Mills, K.J. and Hicks, M.G. (2001). Kayrunnera 1:100 000 Geological Sheet 7436. First Edition. Geological Survey of New South Wales, Sydney.

Miyasaka, S.C., Hue, N.V. and Dunn, M.A. (2007). Aluminium. In: Handbook of Plant Nutrition. (eds) Barker, A.V. and Pilbeam, D.J. CRC Press, Florida.

Morton, J.G.G. (1982). *The Mesozoic-Cainozoic stratigraphy and faunas of the Tibooburra-Milparinka area*. University of New South Wales Master Thesis (unpublished).

Nicholls, O.W., Provan, D.M., Cole, M.M. and Tooms, J.S. (1966). Geobotany and geochemistry in mineral exploration in the Dugald River area, Cloncurry District, Australia

(Discussions and contributions). *Transactions of the Institute of Mining and Metallurgy Section B*. **75**: 168-171.

Noy-Meir, I. (1985). Desert ecosystem structure and function. Pages 93-104 in M. Evenari, I. Noy-Meir & D.W. Woodall (eds.), *Hot deserts and shrublands*. Elsevier, New York.

Ollier, C.D. (1986). Early Landform Evolution. In: Jeans D. N. ed. *Australia: a Geography, Volume 1, The Natural Environment*, pp. 97-116. University of Sydney, Sydney.

O'Connell, A.M. and Grove, T.S. (1996). Biomass production, nutrient uptake and nutrient cycling in the jarrah (*Eucalyptus marginata*) and karri (*Eucalyptus diversicolor*) forests of South-western Australia. In: P.M. Attiwill and M.A. Adams, Editors, *Nutrition of Eucalypts*, CSIRO, Australia, pp. 155–189.

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

Pain, C.F., Chan, R.A., Craig, M.A., Hazell, M., Kamprad, J. and Wilford, J. (1991). RTMAP BMR regolith database field handbook. BMR Record 1991/29.

Pain, C.F., Chan, R.A., Craig, M.A., Gibson, D., Kilgour, P. and Wilford, J. (2007). RTMAP Regolith Database Field Book and Users Guide (Second Edition). *CRC LEME Open File Report 231*.

Parr, J.M. (1994). The Geology of the Broken Hill-Type Pinnacles Pb-Zn-Ag Deposit, Western New South Wales, Australia. *Economic Geology*. Vol 89. 778-790 pp.

Pate, J.S., Jeschke, D.W. & Aylward, M.J. 1995. Hydraulic architecture and xylem structure of the dimorphic root systems of South-West Australian species of Proteacea. *Journal of Experimental Biology* **46**: 907-915.

Pate, J.S., Jeschke, D.W., Dawson, T.E., Raphael, C., Hartung, W & Bowen, B.J. 1999. Growth and seasonal utilisation of water and nutrients by *Banksia prionotes*. *Australian Journal of Botany* **46**: 511-532.

Pilbeam, D.J. and Morley, P.S (2007). Calcium. In: *Handbook of Plant Nutrition*. (eds) Barker, A.V. and Pilbeam, D.J. CRC Press, Florida.

Pittman, E.F. (1894). Appendix K. Department of Mines and Agriculture New South Wales, Annual Mining Report for 1894, 110-112.

Plimer, I.R. (1984). The mineralogical history of the Broken Hill Lode, NSW. *Australian Journal of Earth Sciences*, **31**: 379-402pp.

Potts, P. J. (1987). *A handbook of silicate rock analysis*. Blackie, Glasgow and London.

Preiss, W.V. (1983). Adelaide Geosyncline - A general overview. In: *South Australia - Exploration Potential*. AMF Symposium in association with SADME, 7-8 December 1983. Abstracts volume. South Australia. Department of Primary Industries and Resources. Report Book, 84/00015

Preiss, W.V. compiler, (1987). The Adelaide Geosyncline – Late Proterozoic stratigraphy, sedimentation, palaeontology and tectonics. South Australia Geological Survey, Bulletin 53.

Preiss, W. V. (1990). A stratigraphic and tectonic overview of the Adelaide Geosyncline, South Australia. In: Jago, J. B. and Moore, P. S., (eds.), The evolution of a late Precambrian-early Palaeozoic rift complex; the Adelaide Geosyncline. Geological Society of Australia, Sydney, N.S.W., Australia, 16: 1-33.

Preiss, W.V. (1995). Delamerian Orogeny. In: Drexel, J.F. and Preiss, W.V. (editors), The geology of South Australia, vol. 2, The Phanerozoic. South Australia Geological Survey, Bulletin 54, 45-59.

Preiss, W.V., Belperio, A.P., Cowley, W.M., Rankin, L.R. (1993). Neoproterozoic. In: Drexel, J.F., Preiss, W.V. and Parker, A.J. (Eds), The Geology of South Australia. Vol. 1, The Precambrian. South Australia. Geological Survey. Bulletin, 54: (1) 170-203.

Rai, S.N. and Proctor, J. (1986). “Ecological studies on four rainforests in Karnataka, India. I. Environment, structure, floristics and biomass. II. Litterfall.” *Journal of Ecology*, **74**: 439-463.

Raich, J.W. (1998). “Above ground productivity and soil respiration in three Hawaiian rain forests.” *Forest Ecology and Management*, **107**: 309-318.

Rattigan, J.H., Gersteling, R.W. and Tonkin, D.G. (1977). Exploration geochemistry of the Stuart Shelf, South Australia. *Journal of Geochemical Exploration*. **8**: 203-217.

Reid, N., Hill, S.M. and Lewis, M.D. (2009). Biogeochemical expression of buried gold mineralization in semi-arid northern Australia: penetration of transported cover at the Titania Gold Prospect, Tanami Desert, Australia. *Applied Geochemistry: Exploration, Environment, Analysis*; 2009; v. 9; issue.3; p. 267-273.

Reimann, C. and de Caritat, P. (1998). Chemical elements in the environment: Factsheets for the geochemist and environmental scientist. Springer. Verlag Berlin ; Heidelberg and New York.

Reuter, D.J. and Robinson, J.B. (1997). Plant analysis: an interpretation manual. CSIRO Publishing, Collingwood, Victoria. pp 572.

Robertson, R.S., Preiss, W.V., Crooks, A.F., Hill, P.W. and Sheard, M.J. (1998). Review of the Proterozoic geology and mineral potential of the Curnamona Province in South Australia. *AGSO Journal of Australian Geology and Geophysics*, 17 (3): 169-182.

Robertson, R.S.; Connor, C.H.H.; Preiss, W.V.; Crooks, A.F. and Sheard, M.J. Curnamona Province. South Australia. Department of Primary Industries and Resources. Open file Envelope, 09898.

Rodgers, W.C. (1890). Mining Warden’s report, Albert District-Wilcannia Division. Department of Mines New South Wales, Annual Report for 1890, 21 and 126-127.

- Rodgers, W.C. (1891). Mining Warden's report, Albert District-Wilcannia Division. Department of Mines and Agriculture New South Wales, Annual Report for 1891, 138.
- Rogers, P.J., Dunn, C.E. (1993). Trace element chemistry of vegetation applied to mineral exploration in eastern Nova Scotia, Canada. *Journal of Geochemical Exploration*. **48**: 71-95.
- Rollinson, H. (1993). Using geochemical data: evaluation, presentation, interpretation. Harlow, Essex, England.
- Rose, G. and Brunner, R.L. (1968). The Upper Proterozoic & Phanerozoic Geology of North-Western New South Wales- Report GS68/002.
- Rose, G., O'Connell, P. and Menzies, I.A. (1967). Milparinka 1:250 000 Geological Sheet SH54-07. New South Wales Geological Survey, Sydney.
- Rowntree, D. (1981). Statistics without tears: A primer for non-mathematicians. Penguin Books, London.
- Rugless, C.S. and Govett, G.J.S. (1984). Exploration rock geochemistry for Pinnacle-type mineralisation at Broken Hill, N.S.W., Australia. *Journal of Geochemical Exploration*: **22** 133 – 160.
- Ruperto L. (2004). Teilta regolith project: basement modelling. *CRC LEME Open File Report* 157.
- Sahukar, R., Gallery, C., Smart, J. and Mitchell, P. (2003). NSW National Parks and Wildlife Service. The Bioregions of New South Wales: their biodiversity, conservation and history, NSW National Parks and Wildlife Service. Hurstville NSW.
- Sala, O. E., Parton, W.J., Joyce, L.A. and Lauenroth, W.K. (1988). "Primary production of the central grassland region of the United States." *Ecology*, 60: 40-45.
- Salisbury, F.B. and Ross, C.W. (1992). *Plant Physiology* (4<sup>th</sup> edition), Wadsworth Publishing Company, California. 682 pp.
- Schlesinger, W.H. (1991). Biogeochemistry: An analysis of global change. San Diego, California, Academic Press.
- Senior, A.B. (2000). The Regolith Geochemistry of Pinnacles West, Broken Hill, New South Wales. University of Canberra B. All.Sc (Hons) Thesis (unpublished).
- Senior, A.B. and Hill, S.M. (2002). Regolith-landforms of the Pinnacles 1:25 000 sheet, western NSW: mapping and geochemical characterisation. In: ROACH I.C. ed. *Regolith and Landscapes in Eastern Australia*. CRC LEME, 113-118.
- Senior, A.B., Debenham, S.C. and Hill, S.M. (2002). Pinnacles Regolith-Landform Map (1:25 000 scale). Cooperative Research Centre for Landscape, Environments and Mineral Exploration, Canberra.

- Skertchly S.B.J. (1897). The copper plant (*Polycarpha spirostylis* F. von Mueller), *Queensland Geological Survey Publication* 119. p51-53.
- Smith, P.F. (1962). Mineral analysis of plant tissues. *Annual Review of Plant Physiology* **13**: 81-108.
- Sprigg, R.C. (1954). Geology of the Radium Hill mining field. In: Uranium deposits in South Australia, South Australia. Geological Survey. Bulletin, 30.
- Spry, P.G. (1987). A sulphur isotope study of the Broken Hill deposit, New South Wales, Australia. *Mineral. Deposita* **22**: 109-115.
- Staaf, H. (1987). Foliage litter turnover and earthworm populations in three beech forests of contrasting soil and vegetation types. *Oecologia*. **72**: 58-64.
- Stednick J.D., Klem R.B. and Riese W.C. (1987). Temporal Variations of Metal Concentrations in Biogeochemical Samples over the Royal Tiger Mine, Colorado, Part 1: Within Year Variation. *Journal of Geochemical Exploration* **28**: 75-88.
- Steel, P.M. (1881). Mining Warden's report, Albert District-Wilcannia Division. Department of Mines New South Wales, Annual Report for 1881, 106.
- Stevens, B.P.J., 1971. Brief notes on the Pinnacles mine, Broken Hill, N.S.W.: New South Wales Geological Survey Report GS1971/188, 6p
- Stevens, B.P.J. (1986). Post-depositional history of the Willyama Supergroup in the Broken Hill Block, N.S.W. *Australian Journal of Earth Sciences*, **33**: 73-98.
- Stevens, B.P.J. and Etheridge, L.T. (1989). Traverse geology of the Tibooburra inliers. Geological Survey of New South Wales, Department of Mineral Resources. Sydney. Report GS 1989/390.
- Stevens, B.P.J. and Burton, G.R. (1998). The Early to Late Proterozoic Broken Hill Province, New South Wales. *AGSO Journal of Australian Geology and Geophysics*, 17 (3): 75-86.
- Stott, J.E. (1996), A Biogeochemical Survey of the Ballarat East Gold Mine, Ballarat, Victoria, B.Sc. Honours Thesis, University of Ballarat, Ballarat, Vic. Unpublished.
- Stout, P.R.; Meagher, W.R.; Pearson, G.A. and Johnson, C.M. (1951). Molybdenum nutrition of plant crops: I. The influence of phosphate and sulfate on the absorption of molybdenum from soils and solution cultures. *Plant Soil* **3**: 51-87.
- Swanson, C.A. (1957). Translocation in trees. Forest Tree Physiology Symposium. The Ohio *Journal of Science*. 57 (6): 331-336.
- Teale, G.S. and Flint, R.B. (1993). Curnamona Craton and Mount Painter Province. In: Drexel, J.F., Preiss, W.V. and Parker, A.J. (Eds), 1993. The geology of South Australia. Volume 1. The Precambrian. *South Australia. Geological Survey. Bulletin* 54: 147-156.

- Thalhammer, O.A.R. (1991). Indications for the source of gold in the Milparinka-Tibooburra vein-type gold deposits, NSW, Australia-Geochemical and isotopic evidences. In: Pagel and Leroy (eds), Sources, Transport and Deposition of Metals, Balkema. Rotterdam, pp. 363-366.
- Thalhammer, O.A.R; Stevens, B.P.J; Gibson, J.H. and Grum, W. (1998). Tibooburra Granodiorite, western New South Wales: emplacement history and geochemistry. *Australian Journal of Earth Sciences*, **45**: 775-787.
- Thornburn, P.J. and Walker, G.R. (1994). Variations in stream water uptake by *Eucalyptus camaldulensis* with differing access to stream water. *Oecologia* **100**: 293-301.
- Timperley, M.H., Brooks, R.R. and Peterson, P.J. (1970). The significant of essential and non-essential trace elements in plants in relation to biogeochemical prospecting. *Journal of Applied Ecology*, **7**: 429-439
- Tucker, M. (1988). *Techniques in Sedimentology*. Blackwell, Edinburgh.
- Tyne, E.D. and Webster, S.S. (1988). Surface and Borehole Electrical Surveys at the Flying Doctor Prospect, Broken Hill - A Case Study. Departmental Geological survey report. GS1988/101
- Wakelin-King, G. (1999). Banded mosaic ('tiger bush') and sheetflow plains: a regional mapping approach. *Australian Journal of Earth Sciences*. **46**: 53-60.
- Walker, N.C. (1979). Trace elements in vegetation and soils over the Key Lake uranium-nickel orebody Northern Saskatchewan, Canada. Proceedings-International Geochemical Exploration Symposium. pp 361-369.
- Warren, H.V. and Delavault, R.E. (1952). Trace elements in geochemistry and biogeochemistry: Scientist: Monthly: New York, Vol, 75, pp. 26-30.
- Warren, H.V. and Delavault, R.E. (1970). Biogeochemistry in Canada. In: Smith, D.H. (eds), Background Papers in the Earth Sciences in Canada. Geological Society Canada, Paper. 69-58, 276-289.
- Wedepohl, K.H. (1969-1978). *Handbook of geochemistry*. Springer. Berlin ; Heidelberg and New York.
- West, N.E. (1979). Formation, distribution, and function of plant litter in desert ecosystems. Pages 647-659 in J.A. Perry & D.W. Goodall (eds.) Arid land ecosystems. Structure, function, and management. IBP vol 16. Cambridge University Press, Cambridge.
- Wilkinson, C.S. (1889). Notes on the Geology of the Barrier Ranges District, and Mount Browne and Tibooburra Gold-fields. Records of the Geological Survey of New South Wales, Department of Mines, Sydney Vol: (1), 1-9.
- Willis, I.L., Brown, R.E., Stroud, W.J. and Stevens, B.P.J. (1983). The Early Proterozoic Willyama Supergroup: stratigraphic subdivision and interpretation of high to low-grade metamorphic rocks in the Broken Hill Block, New South Wales. *Geological Society of Australia. Journal*, **30**: 195-224.

Wood, P. (1988). Exploration report for the six month period ending 12<sup>th</sup> August, 1988 and relinquishment report for EL 2649 (Bunker) and EL 2650 (Silverfield), Broken Hill District, New South Wales, CRA Exploration Pty. Limited, Broken Hill New South Wales, Report No: GS1988/237.

Yates, K.R. and Randell, M.H. (1994). Review of company mineral exploration, Curnamona 1:250 00 sheet, South Australia. South Australia Departments of Mines and Energy, Report Book 93/48