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Biogeochemical expression of buried iron-oxide-copper-gold (IOCG) mineral systems in mallee eucalypts on the Yorke Peninsula, southern Olympic Domain; South Australia

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ABSTRACT

We report on the results of a regional scale biogeochemical sampling program conducted on the Yorke Peninsula, South Australia, utilising four locally occurring *Eucalyptus* species with mallee-form. Our purpose is to determine if there is an empirical relationship between Cu accumulation in the mallee leaves and elevated Cu in the underlying basement rocks – such that the mallee species might be a useful biogeochemical exploration tool in this area. The basement rocks of the Yorke Peninsula are prospective for iron oxide-copper-gold (IOCG) mineralisation but are mantled by Cambrian to Quaternary sedimentary rocks of variable thickness that inhibit traditional surface geochemical exploration techniques. There is no evidence to link Cu concentrations to dust contamination or fertiliser usage. Leaves of the four mallee species have comparable log normal population distributions of Cu, with a range between 1.6 ppm and 10 ppm. Higher concentrations of Cu (> 6 ppm) occur more commonly within 3 km of known Cu occurrences. These results suggest that all four mallee species have the ability to concentrate higher amounts of Cu in their leaves when the underlying/local geology also contains elevated Cu. The results suggest that biogeochemical sampling of multiple mallee species over large regions could be a useful exploration technique in covered areas of southern Australia where mallee species are widespread and densely populated.

1. Introduction

Australia has vast areas of cover sediments ranging in depth from a few metres to a few hundred metres (Anand, 2005), which are an impediment to mineral exploration (e.g. Fabris, 2010; Hillis et al., 2014; Noble, 2012; Reid et al., 2008). Exploring these areas can be costly and time consuming when using traditional methods such as drilling (e.g. Hillis et al., 2014; Hulme and Hill, 2003; Reid and Hill, 2010). The use of biogeochemistry for identifying mineralisation through variable depths of cover is becoming well established and is a non-invasive, efficient and cost effective exploration method (e.g. Hulme and Hill, 2003; Lintern et al., 2013b; Reid and Hill, 2010).

Globally, biogeochemistry has been used for detection of a wide range of mineral commodities including Au, Pt, Pd, base metals and rare earth elements (e.g. Cohen et al., 1987; Dunn, 1986, 2007; Kovalevsky, 1987; Lintern et al., 2013b; Närhi et al., 2014; Rencz and Watson, 1989). In Australia, studies have also shown that various plant species have the ability to concentrate elements of interest (e.g. Au, Cu, Zn, As, Cr and Pb). These species include pine and native cypress (*Pinus radiata* and *Callitris* sp.: Arne et al., 1999; Ashley and Wolfenden, 2005; Cohen et al., 2005), gum trees (*Eucalyptus* including *camaldulensis*, *brevifolia*, *pruinosa* and *concinna*: Hulme and Hill, 2003; Lintern et al., 2013b; Reid and Hill, 2010; van der Hoek et al., 2012), 'mulga' wattle (*Acacia aneura*: Lintern et al., 2013a), saltbush (*Atriplex*: Brown and Hill, 2005), spinifex (*Triodia pungens*: Reid and Hill, 2010; Reid and Hill, 2013) and bluebush (*Maireana*: Lintern et al., 1997). Thus far, biogeochemistry in the Australian context has most commonly been restricted to local-scale 'orientation' sampling across areas of known mineralisation or less often, laboratory experimentation (e.g. Lintern et al., 2013a). Sampling programs of regional-scale are less common (although see Brown and Hill, 2005; Mitchell et al., 2015) but are an important component of the research agenda as they provide an unbiased, empirical measure of the entire sample population, which in turn provides the opportunity to differentiate 'anomalous' results from

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Fig. 1. Photo image of *Eucalyptus* that grow throughout the Yorke Peninsula. This photo shows the deep rooted nature of these genera. This species is an *E. gracilis* which also clearly displays the mallee-form with a visible lignotuber at the base of the trunk. Person pictured for scale is approximately 1.5 m tall.

'background'.

The success of biogeochemistry as an indicator of mineralisation relies on the ability of the plant to transfer ore or pathfinder elements from depth through the roots upwards to the bark, twigs, fruit and leaves, which can then be sampled and analysed using similar methods as for rock or soils (e.g. Närhi et al., 2014; Reid and Hill, 2010). In order to penetrate thick cover and interact with a large volume of regolith and basement materials it is desirable that the target species for biogeochemical sampling have deep and/or laterally extensive root systems. Eucalypts are particularly suitable as they typically form extensive root systems that penetrate deeply into the cover sediments (e.g. Fensham and Fairfax, 2007; Handreck, 1997; Hulme and Hill, 2003; Lintern et al., 2013b; Lintern et al., 1997; Wrigley and Fagg, 2010), (Fig. 1). Hulme and Hill (2003) reported that *Eucalyptus camaldulensis* has root systems that can occupy soil volumes > 4000 m^3. Other eucalypts such as *Eucalyptus marginata* have roots that may penetrate as deeply as 40 m (Wrigley and Fagg, 2010).

Eucalyptus is the most widespread native genus throughout Australia (Brooker et al., 2002; Hulme and Hill, 2003). There are at least 783 *Eucalyptus* species of which 60% may have a 'mallee' growth habit under appropriate conditions (e.g. Slee et al., 2006). Mallee describes a growth habit where multiple trunks emerge from a lignotuber at, or just below ground level and serve the purpose to re-sprout from dormant buds following fire or other disturbance (e.g. Brooker et al., 2002; Butt, 2005; Slee et al., 2006). Eucalypts tend to adopt the mallee form in drier climates and are common across arid southern Australia (e.g. Australian Native Vegetation Assessment, 2001, Fig. 2). Approximately 96 species of *Eucalyptus* are found in South Australia and 75 of those are considered mallee (Slee et al., 2006). Hybridisation can be characteristic of mallee species and this complicates identification (Brooker et al., 2002).

The ability of eucalypts to concentrate trace metals within their organs (e.g. leaves, twigs, bark and fruit) has been established in several studies (e.g. Dunn, 2007; Butt et al., 2005a and references therein). Consequently *Eucalyptus* biogeochemistry has the potential to identify areas of anomalous trace metal concentrations within the regolith or underlying basement (e.g. Butt et al., 2005a; Dunn, 2007; Hulme and Hill, 2003; Reid and Hill, 2010; van der Hoek et al., 2012). There are no published studies investigating the ability of mallee-eucalypts to incorporate Cu for the purpose of mineral exploration.

The basement rocks of the Yorke Peninsula region of South Australia are considered highly prospective for iron oxide-copper-gold mineralisation (IOCG) (e.g. Conor et al., 2010). The region has < 5% exposed basement rocks, the remainder being covered by a diverse range of sediments (e.g. Cowley et al., 2003; Wolff et al., 2017; Zang et al., 2006). These cover sediments form a barrier to geochemical exploration (e.g. Fabris, 2010; Mokhtari et al., 2009; Salama et al., 2016). Thirteen mallee *Eucalyptus* species are distributed throughout this region (Brooker et al., 2002), and some trees are proximal to known Cu mineralisation (Fig. 3).

In this paper we present the results of a regional-scale sampling program (218 samples over an area of 4000 km^2), focussing on Cu concentration in the leaves of mallee-eucalypt species across the Yorke Peninsula. Our purpose is to characterise the sample population and determine if there is an empirical relationship between elevated Cu concentration in the mallee leaves and elevated Cu in the underlying basement rocks – such that the mallee leaves might be a useful biogeochemical exploration tool in this area. In order to achieve this purpose we first seek to rule out potential sources of contamination in the leaf chemistry (wind-blown dust and fertiliser), assess variations in the population statistics that might indicate inter-species differences in Cu accumulation and then apply some simple tests to determine if higher concentrations of Cu in the mallee leaves correlate with known Cu accumulations in the basement rock.

2. Study area

2.1. Geological setting and mineralisation

The Yorke Peninsula is within the Olympic Domain on the south-eastern margin of the Gawler Craton (Fig. 2). Iron-oxide-copper-gold (IOCG) mineralisation hosted within the broader Olympic Domain includes the supergiant Olympic Dam as well as the Prominent Hill and Carrapateena deposits (Fig. 2) (Conor et al., 2010). IOCG mineralisation in the Olympic Domain is hosted within variable rock types including the Proterozoic Wallaroo Group and Hiltaba Suite granites (Conor et al., 2010; Cowley et al., 2003). The Wallaroo Group in the central and northern Yorke Peninsula hosts IOCG mineralisation of varying concentration and depth, including the historic Moonta-Wallaroo district and the Hillside deposit (Conor et al., 2010; Zang et al., 2006), (Fig. 2).

The Moonta-Wallaroo Cu mining district on the western Yorke Peninsula (Fig. 3) hosts vein style Cu mineralisation in shear zones that cross cut Paleo- to Mesoproterozoic rocks (Conor et al., 2010). The depth of Cu mineralisation, in the Moonta-Wallaroo district, ranges from 100 m to 300 m in mined locations and around 15 m or less at some prospects (Department of the Premier and Cabinet, 2017). Historically, the average grade of Cu mined throughout the district was around 5% (Conor et al., 2010). At Hillside on the eastern Yorke Peninsula (Fig. 3), Cu mineralisation is hosted by Proterozoic basement rocks within a shear zone beneath 5 to 10 m of cover and sub-cropping in the vicinity of the historic Hillside mine shaft (Fabris, 2010). As at Moonta-Wallaroo, historic mining activity included a significant component of shallow, oxidised material (native Cu and Cu-carbonates) with grades up to 44% Cu, whereas current identified resources are dominated by sulphide material with typical concentrations of 0.5 to

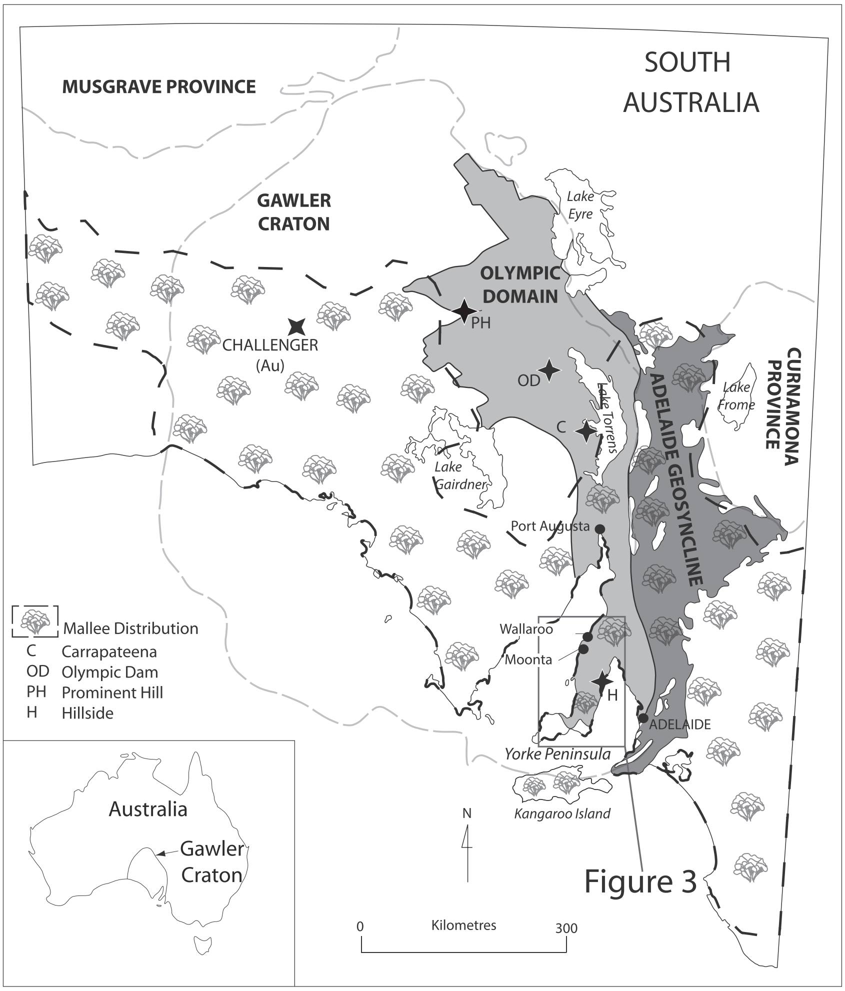

Fig. 2. Simplified geological map of South Australia showing study location within the Olympic Domain of the Gawler Craton (modified after Conor et al., 2010). Also shown is mallee distribution across South Australia (modified after Australian Native Vegetation Assessment, 2001). Inset: Australia showing location of the Gawler Craton.

2% Cu (Department of the Premier and Cabinet, 2017).

Copper has also historically been mined around Maitland and at scattered locations along the east-coast (Fig. 3). Maitland Copper Mine (Fig. 3) hosts high-grade Cu in surface carbonates (up to 25% Cu) whilst the primary Cu lodes (typically 0.3–11% Cu) are in quartz vein fractures within schist from the Wallaroo Group between 10 m and 70 m deep (Department of the Premier and Cabinet, 2017). Harts Mine (Fig. 3), contained up to 40% Cu sulphides in quartz vein fractures, with lesser concentrations as Cu carbonate found in weathered Wallaroo Group rocks exposed at the surface (e.g. Conor, 1995; Department of the Premier and Cabinet, 2017). Parara Mine (Fig. 3) was mined for Cu sulphides to a depth of 60 m (Zang et al., 2006) and produced 23.4 t at 25% Cu (Department of the Premier and Cabinet, 2017). Copper, as azurite and malachite also occurs in Cambrian carbonate rocks at Curramulka (Zang et al., 2006) and Kurra Murka, albeit in only minor concentrations (e.g. deposit no. 5122, Department of the Premier and Cabinet, 2017). Other Cu occurrences, prospects and abandoned mines are shown in Fig. 3.

The Wallaroo Group forms the basement in the central and northern Yorke Peninsula and is unconformably overlain by younger Cambrian to Quaternary sediments of < 1 m and up to at least 1500 m thickness (Crawford, 1965; Drexel and Preiss, 1995; Zang et al., 2006; Zang and Hore, 2001) (Fig. 3). Cambrian sediments include alternating limestone, sandstone and mudstone of up to 1400 m (Drexel and Preiss, 1995; Zang et al., 2006). Carboniferous to Permian sedimentation is dominated by glaciogenic sedimentary rocks including glacial diamictite, till, and shallow marine sedimentary rocks containing glacial erratics (Drexel and Preiss, 1995; Zang et al., 2006). Cenozoic sediments include fossiliferous and sandy limestone of the St Vincent Basin and Pirie Basin, clays and sands as well as aeolian dunes, beach and tidal sediments and soil (Zang et al., 2006). There has been extensive development of indurated pedogenic materials, particularly pedogenic carbonates which are typically located at, or within meters of, the current erosion surface within the sedimentary cover rocks (e.g. Cowley et al., 2003; Wolff et al., 2017; Zang et al., 2006).

2.2. Landscape

The Yorke Peninsula is mostly of low relief and comprises gentle undulating slopes and plains with an average height of 150 m above sea level (ASL) (DEWNR, 2013; Roberts, 2007). The highest elevations across the Yorke Peninsula occur in the central region surrounding Arthurton (250 m ASL) (Crawford, 1965; DEWNR, 2013; Zang et al., 2006). The coastline varies from sandy or rocky beaches to cliffs and steeply eroded hills (Roberts, 2007). Large areas of sand dunes and swales dominate portions of the north-west and central to south-east areas of the Yorke Peninsula, whilst playa salt lakes and clay pans dominate the landscape to the south. The water table generally occurs at 2 m or greater below the surface (DEWNR, 2017). There is a NNE-SSW trending escarpment extending along the eastern coastline northwards from Ardrossan (Crawford, 1965) forming rugged, eroded cliffs and steep-sloped hills.

2.3. Climate

The climate across the Yorke Peninsula is typically 'Mediterranean'

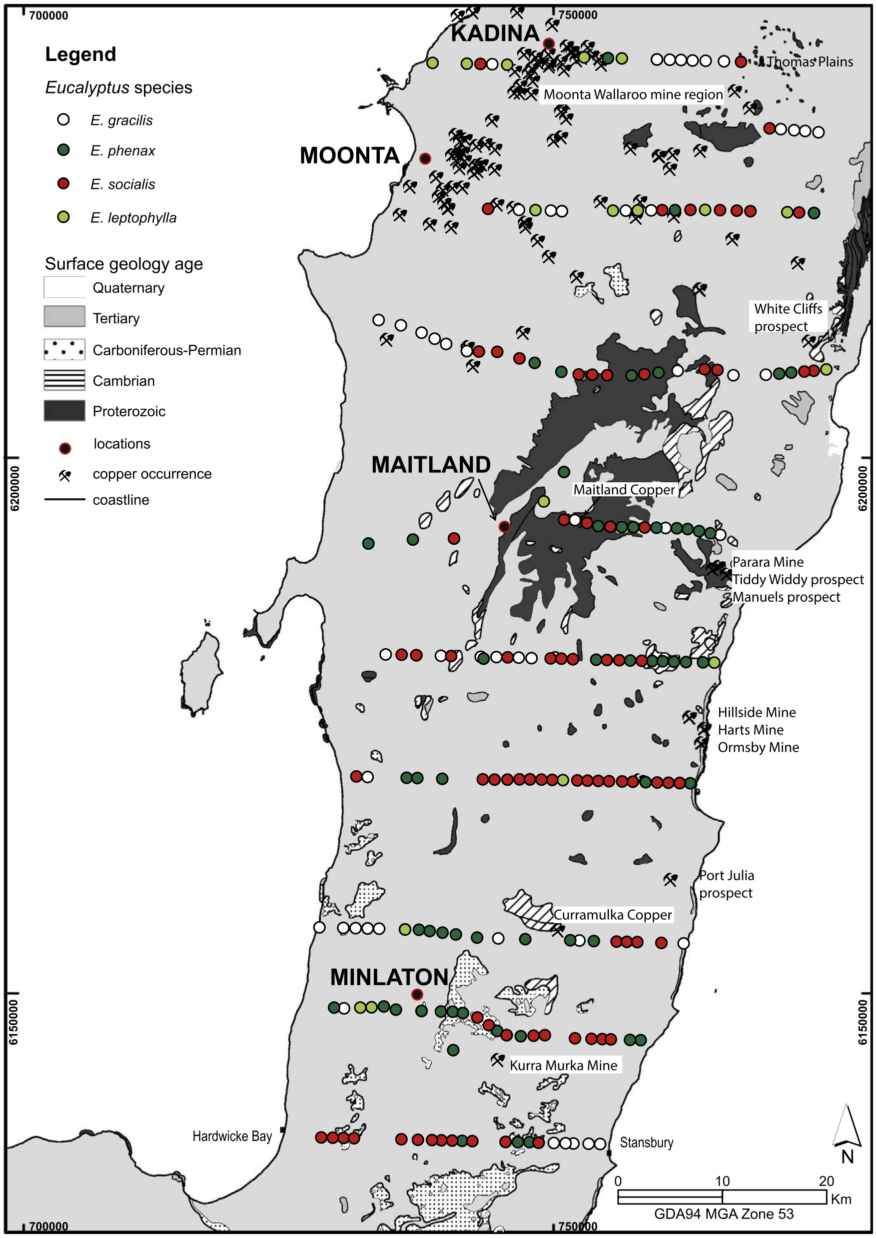

Fig. 3. Simplified surface geology map of Yorke Peninsula (downloadable GIS data extracted from SARIG: https://map.sarig.sa.gov.au Last accessed 04/04/2017). The location of the various *Eucalyptus* species sampled is shown. The location of this map, within South Australia, is shown in Fig. 2.

with hot dry summers and mild and wetter winters (Neagle, 2008). The maximum average temperature ranges from 27 °C to 30 °C during summer and 15 °C to 16 °C during winter. Rainfall across the Yorke Peninsula typically averages around 500 mm per year with June recording the greatest rainfalls (~70 mm) (Bureau of Meteorology, 2017). Annual evaporation rate of rainfall is high. The general direction of the prevailing wind is from the west, being more from the north-west during the warmer months and the south-west during the cooler months.

2.4. Vegetation

Most of the natural vegetation, i.e. that which occurred prior to European settlement across the Yorke Peninsula, has been cleared for grazing and cropping (DEWNR, 2013; McDowell et al., 2012; Neagle, 2008; Zang et al., 2006). Widespread cropping includes cereal grains, oil grains and legumes as the majority of the region contains moderately fertile soils (DEWNR, 2017). Much of the remaining native vegetation is restricted to corridors along roadside verges and fence lines, which act as windbreaks. Patches of woodland typically remains on ground that is the least suitable for agriculture (Neagle, 2008).

The majority of the native vegetation can be broadly characterized as open mallee woodland and shrubland (Neagle, 2008). The woodlands contain *Eucalyptus*, *Melaleuca* (Tea tree), *Acacia* (wattle), *Allocasaurina* (sheoak) and *Callitris* (cypress) with an understory of grasses or sedges such as *Triodia* (spinifex), *Gahnia* (sedge), *Lomandra* (a perennial herb), *Atriplex* (saltbush) and *Lepidosperma* (sedge). Coastal shrublands and lowlands contain *Eucalyptus*, *Avicennia marina* (mangrove), *Atriplex* (saltbush), *Maireana* (bluebush) and *Halosarcia* (samphire), while watercourse communities contain *Eucalyptus*, *Acacias* and various understory grasses (Neagle, 2008; Zang et al., 2006).

There are fourteen species of *Eucalyptus* (*E.*) that occur across the Yorke Peninsula of which thirteen are considered mallee (Brooker et al., 2002). With the exception of *E. diversifolia* (*Eucalyptus sub genera Eucalyptus*) all other eucalypts fall into various sections of the sub genera *Symphyomyrtus* as follows: *E. angulosa*, *E. rugosa*, *E. incrassata*, *E. dumosa*, *E. percostata*, *E. brachycalyx* and *E. phenax* subsp. *phenax*, *E. calycogona* subsp. *calycogona*, *E. gracilis*, *E. leptophylla*, *E. socialis* subsp.

socialis, *E. socialis* subsp. *glossy leaves* and *E. oleosa* subsp. *oleosa*. *Eucalyptus* sub genera *Exsertaria*; *E. camaldulensis* subsp. *camaldulensis* (River Red Gum) is the only native occurring eucalypt-tree (single trunk, tree form) found on the Yorke Peninsula. Hybridisation of species from sub genera can occur which makes identification difficult (Brooker et al., 2002). Natural integration between more closely related species found throughout the region such as *E.incrassata* and *E. angulosa* can also occur (Brooker et al., 2002).

3. Materials and methods

3.1. Sampling strategy

This study differs from typical ‘orientation’ style biogeochemical surveys in that there are not specific positive or negative control points. Although there are areas of known mineralisation within the survey area we have not sought to establish key locations where it is possible to compare known Cu concentrations in the subsurface with Cu concentrations in the sampled leaves. Nor do we have access to data from which we can independently determine the bioavailability of key elements in the subsurface. Rather, our strategy has been to collect regional samples in a program that is subject to the same practical considerations as experienced by exploration companies operating in covered terrains – where there may be little or no prior knowledge of the subsurface metal distribution or speciation *but* where biogeochemistry offers the potential for cheap, rapid and environmentally sensitive first pass reconnaissance sampling. The most relevant question in this survey is; can the biogeochemistry be used as an empirical tool to highlight sub regions within the survey area where there is a greater likelihood of discovering economic Cu mineralisation and where further exploration should be focussed?

In order to answer this question we first need to characterise the entire sample population (by systematic sampling avoiding the temptation to focus on known mineralisation) and then determine if there is a spatial relationship between elevated concentrations of ore and pathfinder elements and areas of known mineralisation.

The framework of our sampling program was provided by the grid-like distribution of remnant mallee forest along road corridors throughout the Yorke Peninsula. Samples of leaves from mallee-eucalypts were collected approximately every 1 km along ten, east-west road corridors with a north-south spacing of roughly 10 km (Fig. 3). Samples from four different mallee-form sub-species of *Eucalyptus* were collected and include *E. gracilis*, *E. phenax*, *E. socialis* and *E. leptophylla* (Fig. 3). Individual eucalypts were identified using EUCLID (Brooker et al., 2002). A variety of species were sampled as individual sub-species of *Eucalyptus* have preferred habitats e.g. inland, dunes and swales, or coastal cliff-tops (Neagle, 2008). Where no eucalypts were present at designated sample locations, the spacing was extended slightly until a suitable tree could be located. Overall, a grid pattern was formed that extended from Stansbury and Hardwicke Bay in the south to Kadina and Thomas Plains in the north (Fig. 3).

Samples were collected at the end of summer (March through to April 2012) prior to winter rainfall. In other studies from arid Australia (e.g. Hulme and Hill, 2003; Reid and Hill, 2010) this timing has been associated with maximum biogeochemical expression, with the inference that water and metal are sourced from the deeper parts of root systems during times of scarce surface water. This timing is also prior to application of fertilisers used during and following crop sowing (Department of State Development, 2014), which may be a potential source of contamination.

3.2. Sampling methods

A total of 218 leaf samples were collected from trees that appeared healthy and mature (i.e. not a sapling). Hands were cleaned and dried between samples in order to minimise potential contamination transferred by hand. Approximately 200 g of leaves were collected at each site and where possible, were sampled from trees on the southern side of the road and at the farthest side of the tree from the road. This method was chosen to reduce contamination from road dust. All samples were placed in calico bags to allow air circulation and delay the onset of rotting as per Dunn (2007). Samples were later dried in their original calico bags in an oven at 60 °C for 36–48 h. Dried samples were sorted by separating the leaves from any twigs which may have remained attached and discarding any leaves that did not appear to be healthy. Approximately 60–80 g of the best leaves were reserved for analysis.

Dust contamination may result in analytical data that reflect the composition of the dust rather than the concentration of metals accumulated in the tissues of the plant (Lintern et al., 2013b; Mitchell et al., 2015). Such contamination may be minimized by sampling methodology, for example by ensuring hands are cleaned and dried between samples and choice of sample location (as above) and by post sampling treatment, for example washing with water prior to drying (e.g. Arne et al., 1999; Hulme, 2008; Mitchell et al., 2015). Some studies (e.g. Dunn, 2007; Hulme and Hill, 2003) have shown that dust contamination on Eucalyptus leaves is negligible and not greatly improved by washing. This led Hulme and Hill (2003) and Dunn (2007) to infer that dust particles shed easily from the waxy surfaces of eucalyptus leaves and that washing is not a critical component of the sampling protocol for eucalypt species. Following this advice we did not wash the samples collected in this study. However we have analysed for a range of elements typically enriched in wind-born dust (Al, Fe, Zr) as a means of quantifying potential dust contamination.

As the application of fertiliser is widespread across the entire sampling area, and also represents a potential wind-born contaminant, the chemistry of a locally used fertiliser (urea and diammonium phosphate (DAP), Fabris, 2010) was used to determine any contamination and/or influence on the leaf chemistry.

Samples were sent to ACME Analytical Laboratories in Vancouver, Canada for analysis. Samples were first macerated to 100-mesh prior to aqua regia digestion of 5 g aliquots. Inductively-coupled plasma-mass spectrometry (ICP-MS) was used to determine element concentrations. Included with these analyses were ACME Laboratories standards as well as additional duplicates. One in every 10 samples were replicated in the laboratory. Laboratory standards were included in the analytical batches at a rate of 1 standard for every ten unknowns. The standards included; STD CDV-1 ($n = 8$), STD V14 ($n = 2$) and STD V16 ($n = 10$). Laboratory blanks were also included at a rate of one in every ten unknowns. All analyses of standards and blanks fell within acceptable range of the expected values, with expected and mean ± standard deviation of the measured Cu concentrations (ppm) as follows: CDV-1 (8.61, 8.49 ± 0.84), V14 (4.8, 4.85 ± 0.23), V16 (6.69, 6.65 ± 0.67), and blank (< 0.01, 0.003 ± 0.01).

3.3. Data treatment and statistics

The biogeochemical data were imported into ioGAS™ software in order to characterise population statistics, determine the extent of dust and fertiliser contamination, compare between mallee species and assess spatial relationships with areas of known mineralisation.

Standard data treatment included constructing histograms and probability plots of both the raw concentration data and $\log_{10}$ concentration data of the mallee leaf analyses. As a general rule the trace metal concentrations, including Cu, tend to have log normal population distributions and as such it is appropriate to report key population statistics (mean, standard deviations, range) of the $\log_{10}$ data. We used such statistics as a means of comparing the concentrations of numerous elements in the leaves of the four main mallee species analysed in this study, in order to test if there were systematic, species-dependent differences in element uptake. X-Y plots were used to assess the potential for dust and fertiliser contamination, in particular seeking to identify linear trends in suspected contaminants (Al, Fe and Zr in dust; K, P and Zn in fertiliser) and determine any correlation between these elements and Cu.

Lastly, we have applied a simple test to determine if elevated concentrations of Cu in mallee leaves are likely to be spatially correlated with Cu mineralisation in the subsurface. Our options for geostatistical correlation are limited in this survey area because the distribution of Cu concentration in the subsurface is largely unknown. We do not have access to a regional Cu-in-basement dataset of comparable spatial resolution to the mallee data and instead have used the distribution of historic Cu prospects as an imperfect first pass approximation. Our approach is to apply a 3 km search radius around known Cu prospects and compare the populations of Cu in mallee leaves from inside and outside the search radius.

4. Results

4.1. Distribution of mallee

The distribution of mallee-eucalypt species sampled is shown in Fig. 3. 218 samples were taken from four species as follows; *E. gracilis* (53), *E. phenax* (60), *E. socialis* (87), and *E. leptophylla* (18). *E. gracilis* was found to be concentrated in the north and south of the study area. *E. phenax* was found to be broadly distributed across the central and southern regions of the study area, with only a few sampled in the northern area. *E. socialis* was the most commonly sampled and most widespread species. The northern-most transect had the least amount of *E. socialis* sampled. *E. leptophylla* was found to be concentrated in the northern portion of the study area, with only sparse distribution in the central and southern areas.

4.2. Chemistry

Of the 53 elements analysed, 28 were above analytical detection limits in the leaf samples. Results for these are included in Supplementary data Appendix 1. Representative data for selected elements are given in Table 1. The focus of this paper is on Cu as there is not enough Au above detection limits to be useful (Appendix 1). There are no particularly useful patterns in the other 21 elements.

Leaves from all mallee species contain Cu ranging from 1.59 ppm to 10.04 ppm (Table 1). The distribution of Cu in all species is shown in Fig. 4. The average Cu for all species sampled is 3.80 ppm (Table 1). Both the lowest and highest concentrations occur in *E. phenax*. *E. phenax, E. socialis* and *E. gracilis* contain similar average Cu concentrations while *E. leptophylla* contains the highest average Cu ppm concentration (Table 1; Fig. 4). The widest range in Cu concentration is found in *E. phenax* (Table 1; Fig. 4).

Aluminium, Fe and Zr results are included as measures of dust contamination. Aluminium was measured at or slightly above analytical detection limit in 92 samples (Table 1, Appendix 1). Concentration of Al ranged from 0.01% to 0.03% which is barely above detection limit (Al, 0.01%). Up to half of each species sampled contained Al concentrations above detection limits. Of these only half again were above detection limits by only 0.01% or 0.02%. Iron was measured in all leaf samples

Table 1
Biogeochemistry summary statistics of *Eucalyptus* leaves representative of the Yorke Peninsula.

Eucalyptus species	*n*	Element	Method	Detection	Min	Max	Mean	Median	Std deviation
E. gracilis	53	Cu			1.95	8.35	4.09	3.89	1.41
E. phenax	60				1.59	10.04	3.86	3.46	1.53
E. socialis	87		ppm	0.01	1.67	7.77	3.29	3.01	1.16
E. leptophylla	18				2.15	8.83	5.21	5.02	1.75
All species	218				1.59	10.04	3.8	3.44	1.48
E. gracilis	53	Cu	$\log_{10}$		0.29	0.92	0.59	0.59	0.15
E. phenax	60				0.20	1.00	0.56	0.54	0.16
E. socialis	87			n/a	0.22	0.89	0.49	0.48	0.14
E. leptophylla	18				0.33	0.95	0.69	0.70	0.16
All species	218				0.20	1.00	0.55	0.54	0.16
E. gracilis	53	P	%		0.05	0.13	0.08	0.07	0.02
E. phenax	60				0.04	0.16	0.07	0.06	0.03
E. socialis	87			0.001	0.04	0.13	0.07	0.06	0.02
E. leptophylla	18				0.06	0.11	0.08	0.08	0.02
All species	218				0.04	0.16	0.07	0.07	0.02
E. gracilis	53	K	%		0.31	0.87	0.46	0.45	0.10
E. phenax	60				0.29	0.87	0.55	0.54	0.13
E. socialis	87			0.01	0.30	0.83	0.52	0.51	0.10
E. leptophylla	18				0.36	0.90	0.56	0.52	0.14
All species	218				0.29	0.90	0.52	0.50	0.12
E. gracilis	22	Al	%		0.01	0.03	0.01	0.01	0.01
E. phenax	19				0.01	0.02	0.01	0.01	0.00
E. socialis	44			0.01	0.01	0.03	0.02	0.02	0.01
E. leptophylla	7				0.01	0.02	0.02	0.02	0.00
All species	92				0.01	0.03	0.01	0.01	0.01
E. gracilis	53	Fe	%		0.01	0.03	0.01	0.01	0.00
E. phenax	60				0.01	0.02	0.01	0.01	0.00
E. socialis	87			0.001	0.01	0.03	0.01	0.01	0.00
E. leptophylla	18				0.01	0.02	0.01	0.01	0.00
All species	218				0.01	0.03	0.01	0.01	0.00
E. gracilis	53	Zn	ppm		4.7	22	12.35	12.10	3.28
E. phenax	60				5.4	24	12.22	11.45	4.46
E. socialis	87			0.1	7	26.7	13.65	13.40	3.37
E. leptophylla	18				7.5	23.4	14.57	14.95	4.24
All species	218				4.7	26.7	13.01	12.75	3.81
E. gracilis	53	Zr	ppm		0.02	0.18	0.06	0.06	0.03
E. phenax	60				0.03	0.14	0.06	0.06	0.02
E. socialis	87			0.01	0.02	0.21	0.08	0.07	0.04
E. leptophylla	18				0.03	0.13	0.07	0.06	0.03
All species	218				0.02	0.21	0.07	0.06	0.03

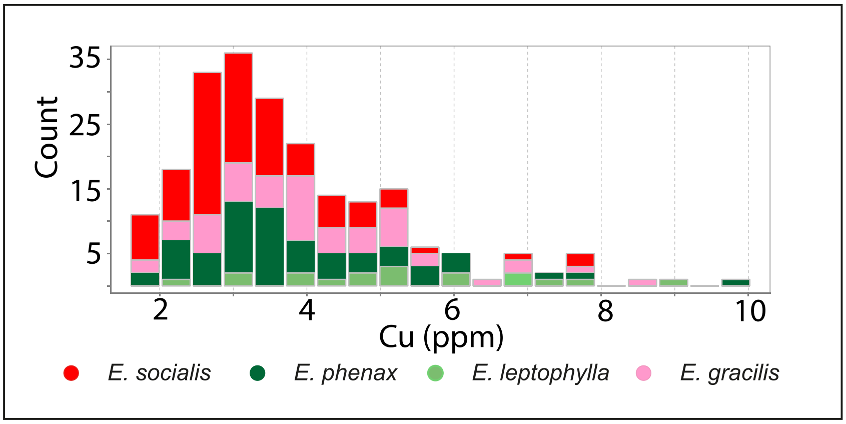

Fig. 4. Stacked histogram plot showing distribution of Cu in each species of mallee-eucalypt.

and concentrations ranged from 0.006% to 0.028% (Table 1). The range in Fe concentration was similar for all four species. Zirconium was measured in all samples and concentration ranged from 0.02 ppm to 0.21 ppm. There were minimal differences in Zr concentration among eucalypt species with *E. socialis* containing the highest average concentration (Table 1). Aluminium and Zr display a mutual linear relationship although the low detection values and fewer results affect how these appear (Fig. 5a). Iron and Zr share a very close positive linear relationship (Fig. 5a). Copper has a poorly correlated relationship with Zr (Fig. 5a).

Potassium, P, and Zn results are included as potential measures of fertiliser contamination and to measure any potential preference for

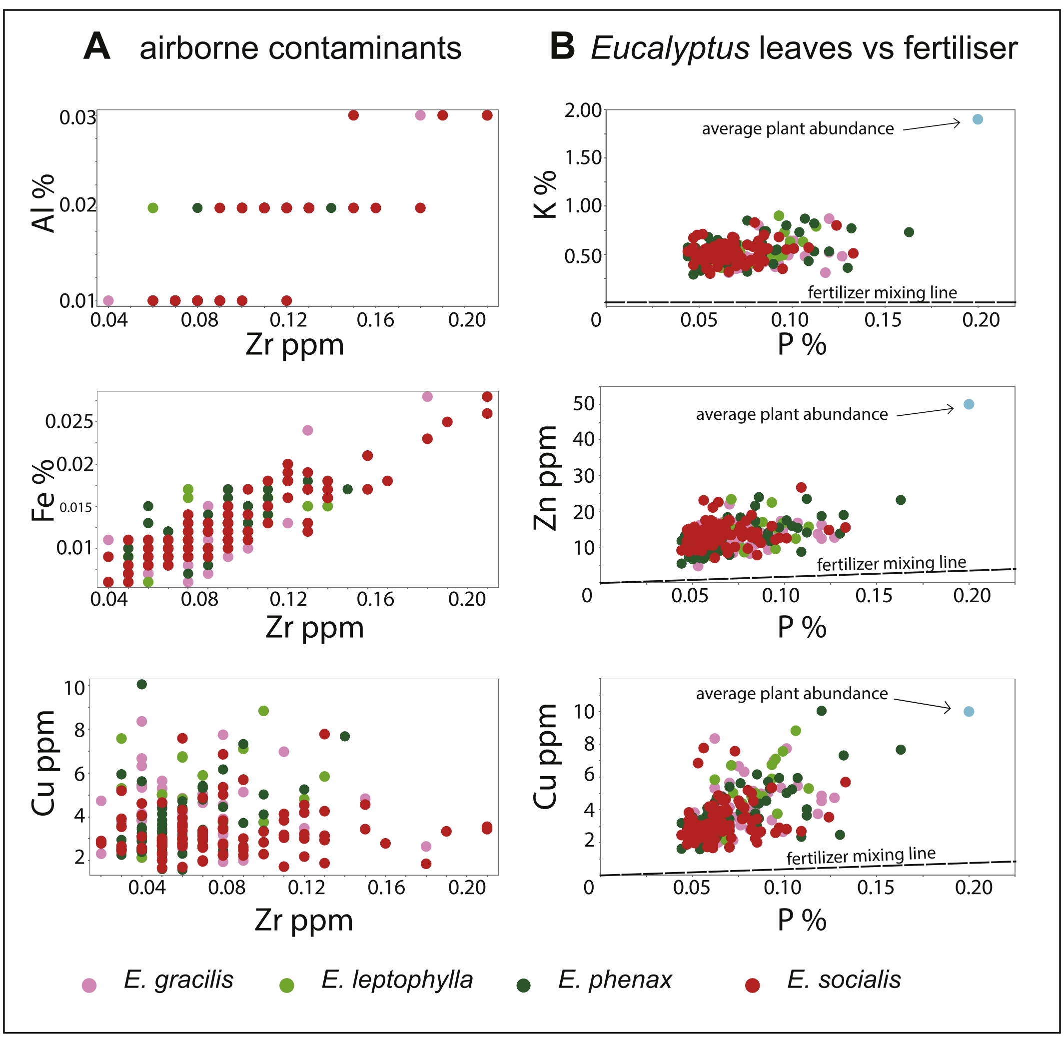

Fig. 5. XY plots of various element concentrations found in mallee-eucalypt leaves from the Yorke Peninsula; A: concentrations of dust contaminants (Al, Fe and Zr) plotted against Cu; B: elements found in fertiliser (P, K and Zn) plotted against Cu concentration. A fertiliser mixing line based on di-ammonium phosphate (DAP) data from Fabris (2010) shows the expected trend in concentration based on fertiliser uptake. The blue dots indicate the average abundance of respective elements in all plants based on Dunn (2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

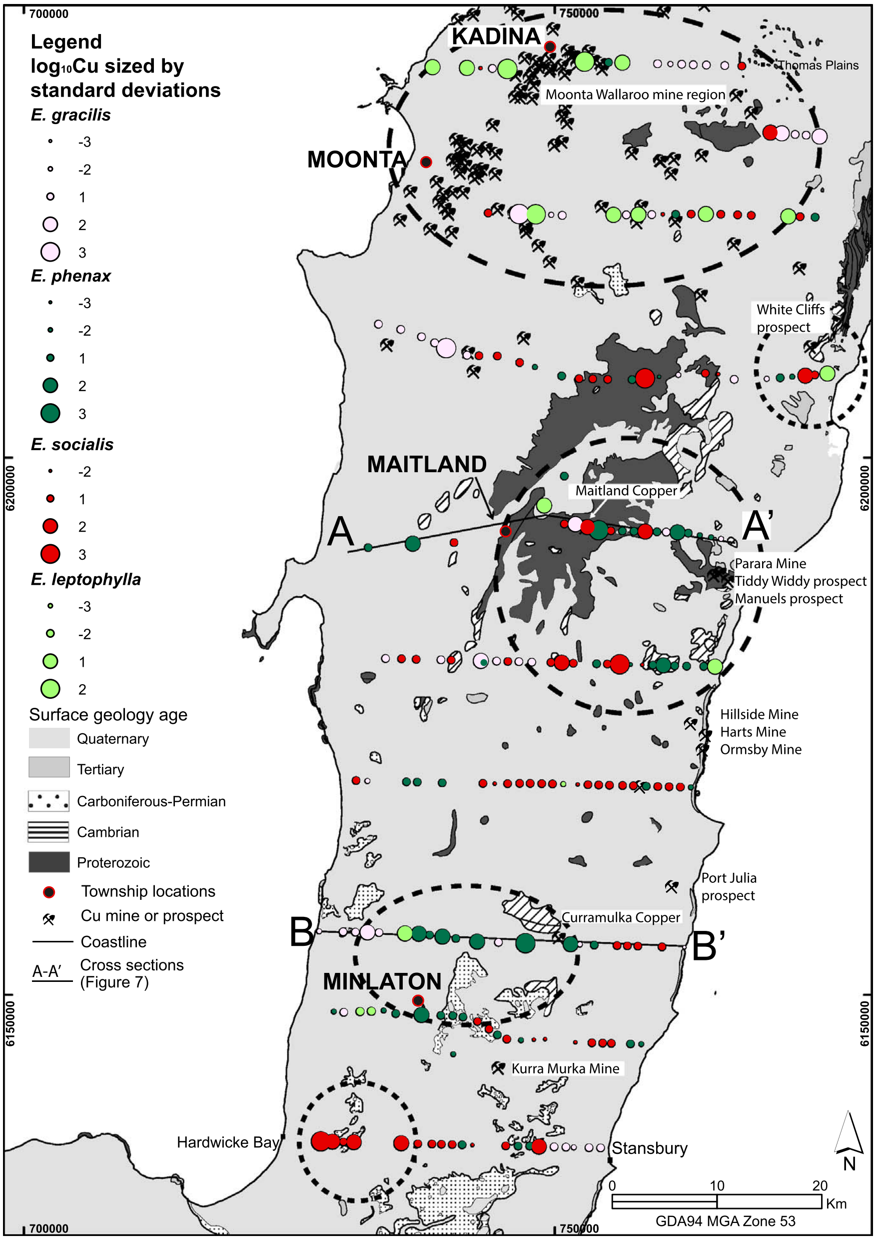

Fig. 6. Distribution of $\log_{10}$Cu in mallee across Yorke Peninsula. The overall pattern of the various species of Eucalyptus display a trend for concentrating higher levels of Cu into their leaves nearby to regions where Cu is known to occur as indicated. Regions of elevated Cu concentration are indicated by dashed lines. Cross sections A-A′ and B- B′ are presented in Fig. 9.

trace element uptake related to plant physiology and growth (Table 1, Fig. 5b). Phosphorus was measured in all samples and concentrations ranged from 0.04% to 1.63% (Table 1). There were minimal differences in average P concentrations across all four species with *E. phenax* containing the highest average concentration (Table 1, Fig. 5b). Potassium was measured in all samples and concentrations ranged from 0.29% to 0.90% (Fig. 5b). The range of K concentration was similar in all four species (Table 1). Zinc was detected in all samples and concentrations ranged from 4.7 ppm to 26.7 ppm (Table 1). Similar Zn average concentrations were found within all four species. There is no clear relationship between K and P. Potassium and P concentrations are clustered, with little scatter, above the fertiliser mixing line and below the average plant composition (Fig. 5b). Zinc and P appear to have a very weak positive relationship with a slight clustering of data points and some scatter but also well above the fertiliser mixing line (Fig. 5b). Copper and P do not show strong correlation of results (Fig. 5b).

5. Discussion

5.1. Potential sources of contamination

Dust and fertilisers are considered the two largest sources of potential contamination of the mallee leaves throughout the study area. Dust contamination needs to be considered as airborne particles may be enriched in Cu from nearby mining. Fertilisers used in cropping can contain Cu and therefore may influence the apparent Cu content of the mallee leaves. The influences of these contaminants on the geochemical data have been assessed by comparing the concentrations and associations of typical aeolian contaminants and various elements found in fertiliser samples.

5.1.1. Dust contamination

Airborne and/or roadside dust contamination can be assessed by comparing relationships between Al, Fe, Zr and Cu (e.g. Kabata-Pendias and Pendias, 2001). Within dust, Al and Fe are mostly found in fine grained clay (i.e. aluminosilicates) and iron-oxide particles. Both Al and

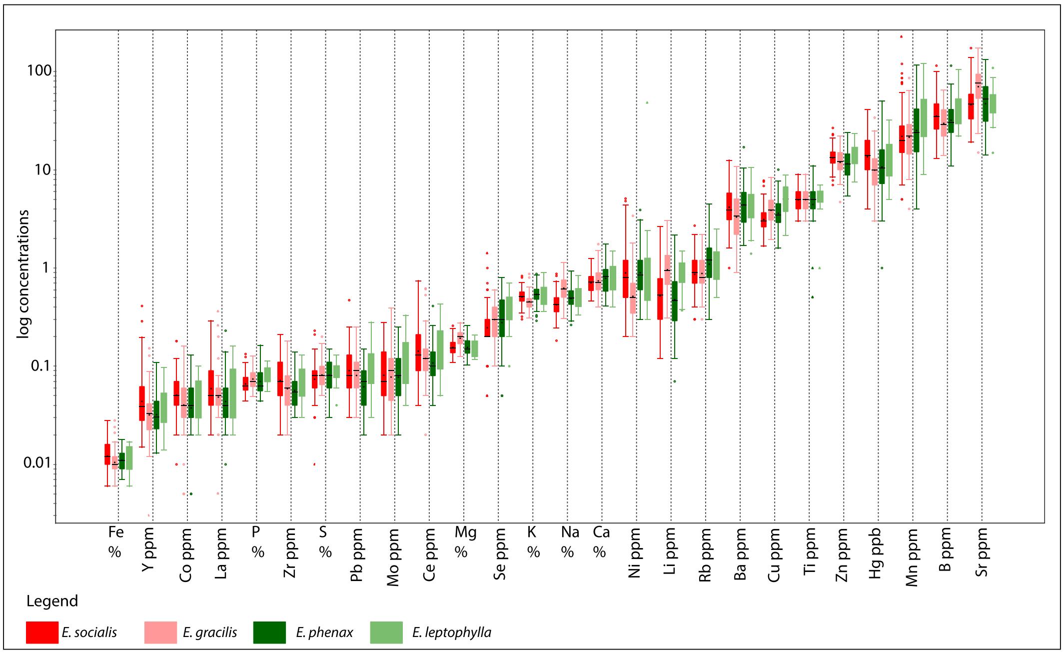

Fig. 7. Tukey box plots for all elements on a common Y axis and logged. Elements with > 90% of their results above detection were used. Solid rectangles represent data that is within 1 standard deviation of the mean. Lines represent 2 standard deviations from the mean and outliers are represented by dots. Within the solid rectangles the black dash is the mean and the black dot is the median.

Fe are major constituents in soils (Kabata-Pendias and Pendias, 2001). Zirconium is mostly found in sand (Fitzpatrick and Chittleborough, 2002), which occurs extensively throughout the region. Within plants, Al and Zr are not essential elements for growth and Fe is only required in trace amounts (e.g. Dunn, 2007) therefore small amounts of dust contamination would be expected to have a strong influence on the Al, Fe and Zr concentrations in the leaves.

Relationships between Al, Fe, Zr and Cu are shown in Fig. 5a. A strong positive linear relationship is shown between Fe and Zr. A similar relationship is observed between Al and Zr, albeit not as distinctly linear due to Al concentrations being so close to detection levels (Fig. 5a). Although these elements are at very low concentrations, the linear relationships are consistent with dust contamination (e.g. from soil components, Kabata-Pendias and Pendias, 2001; Fitzpatrick and Chittleborough, 2002). There is no relationship between Cu and Zr (Fig. 5a) as would be expected if dust contamination contributed substantially to the total Cu detected in leaf samples. This suggests that Cu is being incorporated into the eucalypts independently from the elements that comprise windblown dust and is sourced from elsewhere. The very low concentration levels of these elements (Al, Fe and Zr) also indicate that dust contamination has not impacted the overall chemical content of the leaves and that the improvement to data quality, by having pre-washed the samples, would be negligible.

5.1.2. Fertiliser contamination

Fertiliser application during the cropping season is widespread throughout the Yorke Peninsula (Department of State Development, 2014). Use of phosphate fertilisers have been shown to significantly increase the foliar content of P (e.g. Bennett et al., 1996; Crous et al., 2015) and could conceivably result in increased uptake of other essential nutrients or trace elements, either directly from the fertiliser or from the substrate as a result of more vigorous plant growth. Therefore, it is important to determine the impact, if any, of fertilisers on the Cu concentration in the eucalypt leaves. Whilst it is unknown exactly how much fertiliser the eucalypts have access to and are taking up, the concentrations of P, K, Zn and Cu in the leaves can be directly compared to actual fertiliser that is used throughout the region (Fig. 5b).

Di-ammonium phosphate (DAP) fertiliser is commonly used throughout Yorke Peninsula (Fabris, 2010). This fertiliser contains relatively high concentrations of Cu (75 ppm) which may be taken up by eucalypts dependant on root access, quantity applied and proximity to fertiliser application. This would therefore suggest that Cu concentrations in the eucalypts may merely be reflecting the fertiliser usage.

A fertiliser mixing line based on P, K, Zn and Cu concentrations in the DAP is shown in Fig. 5b. Both K and Zn versus P concentrations sit well above the fertiliser mixing line (Fig. 5b). Copper and P concentrations are also observed well above the fertiliser mixing line (Fig. 5b).

The broad scatter of data points for Cu concentration versus P is different to the narrower range in concentrations for K and Zn versus P (Fig. 5b) suggesting that there is no relationship of Cu to K, Zn or P and that these concentration patterns do not reflect contamination from fertiliser.

5.2. Natural uptake of elements

Essential elements for healthy plant growth such as P, K, Zn and Cu were not only included for fertiliser analysis but also used to assess whether the four species of mallee-eucalypts in this study are taking up elements in a similar manner. Phosphorus and K are considered major essential elements for plant growth while Zn and Cu are only required in trace amounts (Dunn, 2007). These elements were compared with ranges of plant concentrations reported by other authors (e.g. Attiwill and Adams, 1996; Barrow, 1977; Dunn, 2007; Gazola et al., 2015).

Phosphorus and K are both major essential elements that are taken up by eucalypts for growth but tend to have narrow concentration ranges in all species (e.g. Gazola et al., 2015; Grove and Thomson, 1986; Judd et al., 1996). Similar narrow ranges in concentration of P and K are also observed in the eucalypts of this study (Fig. 5b).

Zinc is required in trace amounts and tends to have an uptake synergistic with P (Kabata-Pendias and Pendias, 2001), implying that Zn, where available, will also be incorporated into the eucalypt along with P. A weak positive relationship between P and Zn was observed in the Yorke Peninsula data, (Fig. 5b) suggesting the uptake of Zn reflects the natural uptake by the eucalypts in this region.

Copper is also required in trace amounts by eucalypts and similarly

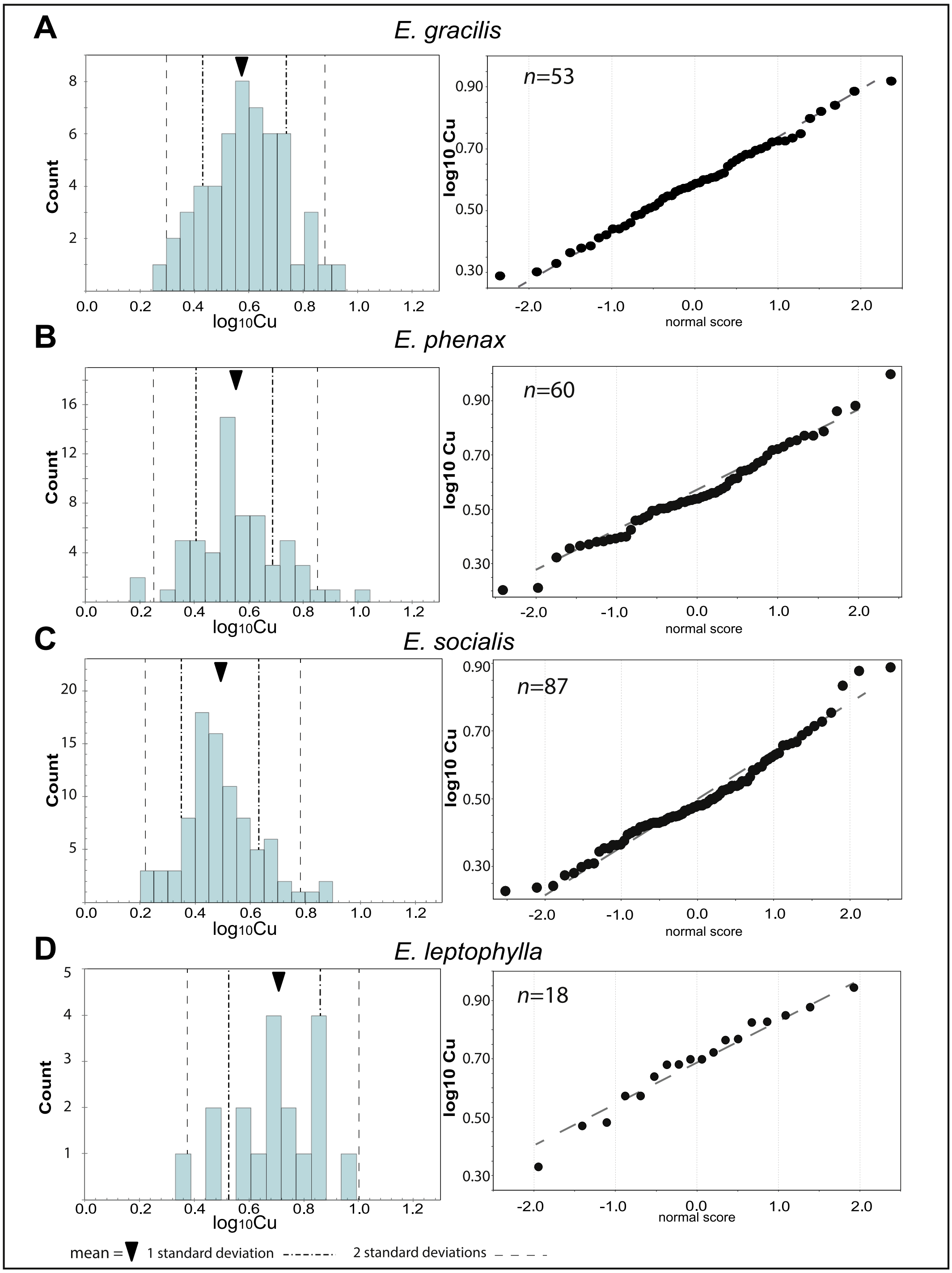

Fig. 8. Histograms (left) and normal probability plots (right) for A. *E. gracilis*; B. *E. phenax*; C. *E. socialis*; and D. *E. leptophylla*. Although *E. leptophylla* (D) has a higher overall concentration of Cu, the values remain within the ranges observed for the other species (A, B and C). Black arrow: (arithmetic) mean; dark dashed lines: 1 standard deviation; light dashed lines: 2 standard deviations.

shares a synergistic partnership with P (Kabata-Pendias and Pendias, 2001). This also implies a natural uptake of Cu where P is available. The Yorke Peninsula data does not show any obvious relationship between Cu and P (Fig. 5b); however, the broader range of Cu concentrations may mask any subtle relationships that may be present. The natural background levels of Cu taken up by the mallee in this region is suggested to be reflected by the dominant (average) population of Cu values (Fig. 4; i.e. an average of Cu 3.8 ppm). The Cu data also shows a population of samples with above average Cu concentrations (Fig. 4), suggesting an active enrichment process other than natural uptake of elements.

Plants growing in a Cu-rich substrate will naturally take up higher concentrations of Cu (Dunn, 2007; Kabata-Pendias and Pendias, 2001). Kabata-Pendias and Pendias (2001) also suggest that when there are higher concentrations of trace elements in soils, plants will take up more of that element even though it may not necessarily be a hyper-accumulator by definition (e.g. Kabata-Pendias and Pendias, 2001). The broad range of Cu concentrations within the Yorke Peninsula data and the observation of a population of samples with above average Cu concentrations (Fig. 5b) suggests there are mallee-eucalypts that are

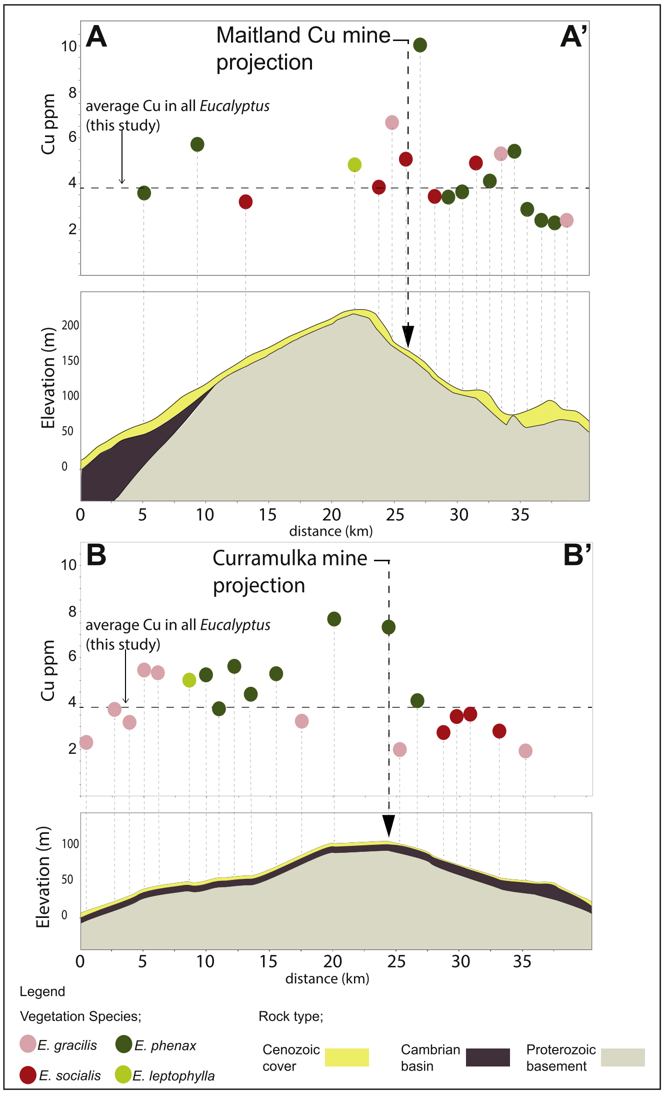

Fig. 9. Biogeochemical cross sections through transects containing Maitland Copper Mine (A to A′ Fig. 6) and Curramulka Copper Mine (B to B′ Fig. 6). The position of each mine is indicated within the respective transect. Both sections demonstrate a trend of decreasing Cu concentration in leaves of various *Eucalyptus* species with increasing distance from the mine.

taking up Cu in excess of biological requirements. Samples with higher Cu concentration are located in the north, east and southwest of the study area, and in most cases are coincident with regions of known Cu mineralisation (Fig. 6). The spatial relationship between the higher Cu concentrations in the leaves to Cu occurrences suggests that there is elevated Cu in the substrate that the trees have access to.

5.3. Statistical considerations for Cu in eucalypts

Previous authors (e.g. Butt et al., 2005b; Dunn, 2007) suggest that complications may arise if sampling a variety of different vegetation or by mixing species from the same genus, therefore there is a need to address any differences in the uptake of trace elements between *E. gracilis*, *E. phenax*, *E. socialis* and *E. leptophylla*. In this study, we are particularly interested in whether or not each species is taking up Cu in the same way. As there is limited existing data regarding trace element uptake in mallee eucalypts, we are limited in this study to comparing population statistics from each species (Table 1) in order to identify any systematic variations between them.

Comparison of data for all elements in the four species (Fig. 7) shows they have very similar means and standard deviations, with each species overlapping in range within the first and third quartiles. We infer from these data that the four species have a very similar uptake of a wide range of nutrients and other trace elements which suggests that their biogeochemical response is comparable. Thus, we consider it reasonable to pool the data from the four species without performing any further normalisation.

E. leptophylla has slightly more Cu than the other three species, although still with overlapping populations at the first and third quartiles (Fig. 7). Cu concentrations for *E. gracilis* (n = 53), *E. phenax* (n = 60) and *E. socialis* (n = 87) have similar mean $\log_{10}$ Cu concentrations of between 0.49 and 0.59 ppm. *E. leptophylla* (n = 18) has a higher average $\log_{10}$ Cu concentration of 0.69 ppm (Fig. 8). The probability plots for *E. gracilis*, *E. phenax* and *E. socialis* are comparable, with relatively straight lines between − 2 and + 2 standard deviations (Fig. 8). *E. leptophylla* also forms a straight line on the probability plot, although displaced to higher values than the other species and with a higher mean (Fig. 8). Although the Cu concentrations are slightly higher for *E. leptophylla*, the uptake of Cu displays a similar pattern for all four species (Fig. 8) with the higher concentrations coinciding with nearby Cu occurrence (Fig. 6).

E. leptophylla samples are more common in the Cu mining regions of Kadina and Moonta (Figs. 3 and 6). As the biogeochemical uptake of trace elements (including Cu) is comparable for all four species, the possibility that higher concentrations of Cu in the plants are related to

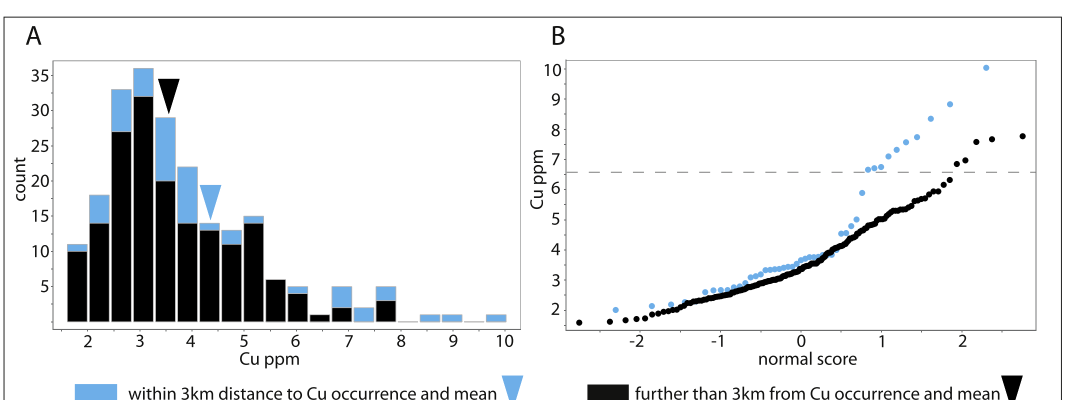

Fig. 10. A; histogram and B; probability plot showing relationship of Cu concentration in trees that are within 3 km (blue) to known Cu occurrence compared to trees > 3 km away from Cu occurrence (black). Trees within 3 km to known Cu occurrence have a higher mean Cu concentration (4.3 ppm indicated by blue marker) and standard deviation (2 ppm) with a longer tail skewed to the right with a broader spread towards higher Cu concentrations (2–10 ppm) compared with those that are further than 3 km away (mean 3.6 ppm indicated by black marker) and standard deviation (1.2 ppm). The dashed line in B identifies a breakpoint in both populations which we interpret as a threshold value of interest for this region. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

higher Cu concentration in the substrate and potentially proximity to buried Cu mineralisation needs to be considered.

5.4. Eucalypt expression of Cu nearby to Cu occurrence

Dietman (2009) demonstrated that the soils surrounding the Hillside Cu mine (Figs. 3 and 6), are elevated in Cu. Likewise, clays, transported sediments and carbonate rocks that make up the soils surrounding the Moonta mining region contain elevated Cu compared to regional background levels (e.g. Keeling et al., 2005; Wolff et al., 2017). These studies suggest that Cu is mobile within the transported sediments and regolith materials overlying basement rocks enriched in Cu, and thus has the potential to be biologically available.

The tendency for the mallee eucalypt leaves to be slightly elevated in Cu in the vicinity of known mineral occurrences is supported by the results of this study (Figs. 6 and 9). Mallee-eucalypts occurring nearby the Maitland and Curramulka Cu mines show elevated Cu in the leaves compared to the more distal eucalypts (Fig. 9). Additionally, in the northern Yorke Peninsula, there is a complex pattern of elevated Cu concentration in *Eucalyptus* leaves throughout the Moonta-Wallaroo mine region and in the vicinity of White Cliffs prospect (Fig. 9). This trend of Cu in *Eucalyptus* adjacent known Cu occurrence is observed independent of the species. This further supports the proposition that all four mallee-eucalypt species are taking up Cu similarly, and that they can collectively be used to identify regions of elevated Cu in soil and in the underlying basement.

The relationship between elevated Cu in mallee leaves and proximity to known mineralisation on a regional scale is illustrated by comparing the population statistics of trees within 3 km of known Cu occurrences to those that are > 3 km from known occurrences (Fig. 10). The trees closest to known Cu occurrences have a higher mean, greater standard deviation and are more skewed to higher values (Fig. 10a). The elevated concentrations in trees within 3 km of a known Cu occurrence are also highlighted as being a separate data population with Cu concentrations > 4 ppm and again at 6 ppm (Fig. 10b). This implies that trees within a relatively short distance of a Cu occurrence have a greater probability of taking up Cu in higher concentrations compared with those that are further away.

It is acknowledged that there are some trees that grow nearby to Cu occurrence that do not contain elevated Cu concentrations. There are various factors that may impact the trees ability to transfer Cu from the substrate to the leaves. For example, the depth of Cu-rich substrate may be beyond the depth of root penetration, the particular soil horizon that the roots reside in may not be elevated in Cu, or individual trees may have differing abilities to collect and store trace elements in their leaves (e.g. Dunn, 2007). As the trees were sampled 1 km apart, subtle variations in depth of cover or the lithology of underlying basement rocks may hamper root access, which could also affect the ability for a tree to take in more Cu. Higher density sampling may resolve these issues.

5.5. Elevated Cu concentrations in trees that are not nearby to Cu occurrences

In comparing these two populations (i.e. trees within 3 km from a Cu occurrence and trees > 3 km, Fig. 10), the population within 3 km of known Cu occurrences, has a higher proportion of samples above 4 ppm Cu and a distinct sub population above 6 ppm Cu. This Cu concentration (> 6 ppm) also corresponds to an apparent break on the Cu probability plot (Fig. 10b) for the remaining samples that are not within 3 km. This serves as a useful threshold for identifying interesting results worthy of follow up.

The Hardwicke Bay area has mallee-eucalypts that contain elevated concentrations of Cu yet are not directly adjacent to known Cu occurrences (Fig. 6). The group of mallee-eucalypts at Hardwicke Bay (Fig. 6) occur as a cluster of 3 samples that are spaced 1 km apart. It is possible that this cluster of trees with elevated Cu represents the surface expression of buried mineralisation. This area is underlain by thick Carboniferous-Permian sedimentary rocks (up to 500 m e.g. Drexel and Preiss, 1995; Zang and Hore, 2001) that have not been reported to host mineralisation on Yorke Peninsula or elsewhere across South Australia (Drexel and Preiss, 1995). A possibility that cannot be ruled out is that the elevated Cu in mallee leaves at Hardwicke Bay is a transported signal, either via physical transport of Cu in Quaternary sediments or via groundwater.

5.6. Implications for biogeochemical exploration for Cu

The widespread occurrence of mallee-eucalypts and their ability to transfer elemental signals from deep in the substrate they grow in makes them a potential tool for exploration. There are limitations that should be considered in designing a mallee biogeochemical survey:

- Identify the species of vegetation and the extent of its occurrence within the region of interest.
- Identify potential sources of contamination that occur throughout the region. This may include land use such as farming or mining.
- Sample at a density that produces robust statistics to identify background levels versus concentrations that are above background.
- Understand the regolith landscape processes in the region to determine whether biogeochemical signatures may reflect buried mineralisation or are the effect of physical and/or chemical element transport.

6. Conclusions

A variety of mallee-eucalypt species are shown to accumulate Cu in their leaves in areas of known Cu mineralisation across the Yorke Peninsula. The mallee-eucalypts contain background Cu concentrations of ~3.8 ppm with higher Cu concentrations above 6 ppm and up to 10.04 ppm. The higher concentrations of Cu are located nearby to Cu mines or prospects. The widespread distribution of mallee-eucalypt across southern Australia and their ability to access and transfer geochemical signals from deep within the substrate implies they are a readily available biogeochemical sample medium. This implies that sampling mallee-eucalypts in an environment such as Yorke Peninsula may be an effective, rapid, cheap and non-invasive exploration method that can be applied at large scales.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.gexplo.2017.11.017.

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