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Evaluating the diffusive gradients in thin films technique for the detection of multi-element anomalies in soils

INTRODUCTION

Soil sampling and chemical analysis is widely evaluated and applied by researchers and by mining companies for the purpose of geochemical exploration (Kelley *et al.* 2006). This sampling is usually undertaken as a first-pass evaluation of potential for mineralisation, and has become increasingly important due to the need for simple, low-cost methods that detect the presence or absence of mineralisation concealed by transported overburden (Kelley *et al.* 2006; Anand *et al.* 2007; Cohen *et al.* 2010). However, questions remain regarding the mobility and speciation of key elements in soils (Ma & Rate 2009), as these elements can exist in a variety of forms, including discrete phases (e.g. as minerals or salts) or as complexes adsorbed on to mineral surfaces. A variety of analytical methods can be used to determine the concentrations and fixation of elements in soils, including: Mobile Metal Ions™ (MMI), (Mann *et al.* 1998), Enzyme Leach © (Clarke 1993) and sequential extractions (Tessier *et al.* 1979; Chao 1984). While these methods are broad in scope and diverse in results (Mazzucchelli 1996; Hall 1998; Kelley *et al.* 2006; Cohen *et al.* 2010), the main objective remains the same: to correctly define any anomaly related to mineralization and enhance its expression (Cameron *et al.* 2004). Partial extraction techniques have been demonstrated to better highlight anomalies as compared to total digestion techniques (Cohen *et al.* 2010). The use of more rigorous statistical analyses of geochemical results to enhance signal detection has also gained prominence in recent years (Garrett *et al.* 2008). However, separating geochemical signals related to underlying mineralisation from the background continues to pose a challenge, despite the growing array of tools available to exploration geochemists.

One of the inherent difficulties with using methods such as partial extractions for determining the mobility and speciation of trace elements in soils, and thereby the presence or absence of geochemical anomalies, is the effect of the analytical techniques on the soils and on the aqueous environment immediately surrounding the wetted particles of soil, i.e. the soil solution (Zhang *et al.* 1998). Ideally, mobility and speciation measurements in soil solution should be *in situ,* facilitated by procedures that minimise disturbance of the soil solution. Chemical separation techniques not only alter the spatial variability of soil-solution properties (Sposito 2008), but can also affect the distribution of elemental species in solution (Zhang *et al.* 1998); therefore such an analysis does not represent a natural, undisturbed soil system. For example, the widely-used sequential extraction procedure as outlined by Tessier et al. (1979) examines the soil sample as a combination of five separate fractions which require a specific chemical attack in order to evaluate the geochemistry of the sample. Selective partial extractions can provide better anomaly contrast as compared to total element determination methods (Filipek & Theobald Jr. 1981), provide information on the mode-of-occurrence of elements (Chao 1984), and may allow discrimination between metal enrichment mechanisms and determination of whether the elements are natural or anthropogenic in origin (Hall 1993). There have been a number of modifications to sequential extraction methods over the years, including variations in the steps required e.g. concentrations of reagents, pH used, time required per step, the fractions targeted and the extractants used (Hall et al. 1996; Gray et al. 1999; Reith & McPhail 2007); however, these steps rely on chemically perturbing the soil in order to elicit a response. Research on the actual mechanisms of extraction and response of the soils to the leaching agents has, to date, been limited (Cohen et al. 2010). To address this issue, a technique that measures element concentrations without the associated perturbations of physicochemical techniques is needed.

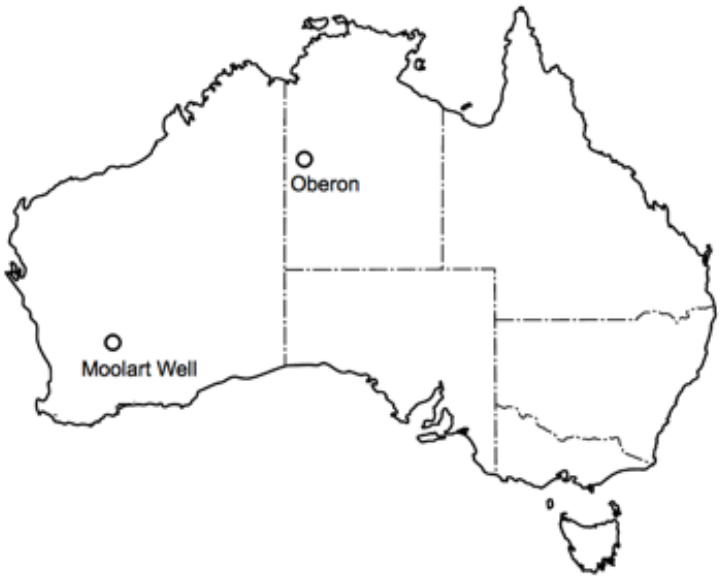

Figure 1. Location of the Moolart Well and Oberon prospects, adapted from Anand et al. (2007).

continued on page 3

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Evaluating the diffusive gradients in thin films technique...

continued from page 1

The diffusive gradients in thin films (DGT) technique

The diffusive gradients in thin films (DGT) technique potentially offers a new tool in the assessment of element speciation in soils for the purpose of geochemical exploration. The technique uses a device containing a binding resin gel (e.g. Chelex®-100 in a cross-linked polyacrylamide gel), diffusive gel (polyacrylamide or agarose, 0.8 mm thick) and filter membrane (cellulose-nitrate, 0.45 μm porosity, 0.13 mm thick) in a specially-designed plastic housing (Davison & Zhang 1994). The device, depicted in Figure 2, can be placed in either waters or wetted soils. The diffusive hydrogel limits the rate at which the flux of dissolved inorganic and organic species are captured by the resin layer (Zhang & Davison 1995). In soils, the technique removes labile

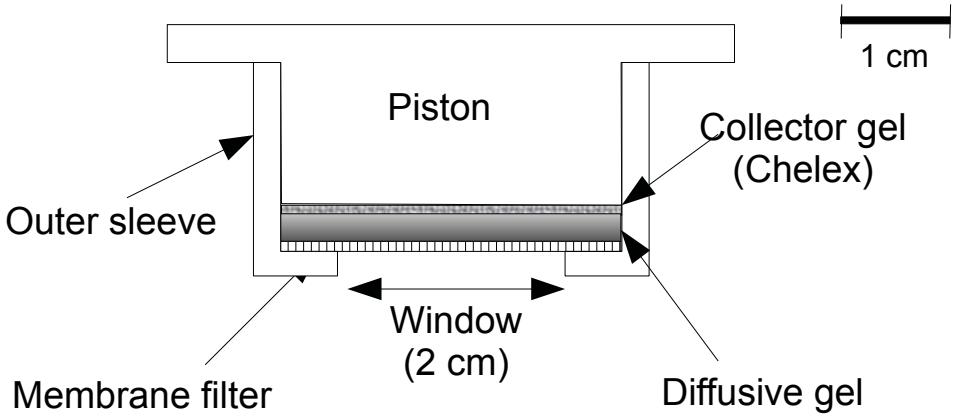

Figure 2. Schematic of the DGT device (Zhang & Davison 1995).

continued on page 4

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Evaluating the diffusive gradients in thin films technique... continued from page 3

elements from soil solutions and thus induces desorption or dissolution of the elements from solid phases, as depicted in Figure 3 (Zhang *et al.* 1998).

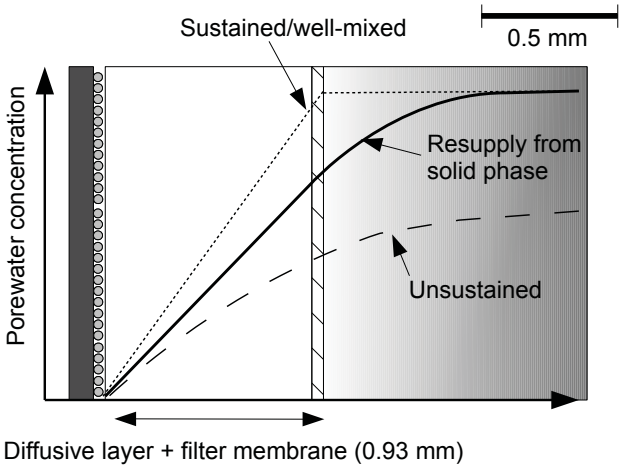

Figure 3. Schematic cross section through the DGT device and the adjacent soil solution (Zhang et al. 1998). The dotted line illustrates uptake by the DGT device in well-mixed solutions (e.g. flowing waters). The large-dashed line shows uptake when supply to the DGT device is by diffusion only. Commonly, there is some resupply from the solid phase, as depicted by the solid line.

The DGT technique presents several advantages for measuring element concentrations in soils, namely that the technique: pre-concentrates metals via diffusive transport through the soil solution (Zhang *et al*. 1998); induces resupply from elements bound to the solid phase (Harper *et al.* 1998); has very good sensitivity, especially when deployment times are extended (Davison & Zhang 1994); does not significantly alter the soil either chemically or physically; and has been demonstrated to behave analogously to plant roots for a variety of trace elements, including Cu (Zhang *et al.* 2001) and Zn (Koster *et al.* 2005). These last two features are of particular interest to geochemical exploration due to the uncertainty regarding the role of vegetation in generating surficial anomalies of mineralisation and associated uptake mechanisms (Ma & Rate 2009). While these features of DGT have been extensively evaluated for the purpose of environmental monitoring of soils (Harper *et al.* 1998; Zhang *et al.* 2001; Bade *et al.* 2012), no research has been carried out to date on assessing the suitability of the technique for mineral exploration using soil geochemistry.

The concentration of elements measured by DGT is determined using equation 1:

$$C_{DGT} = \frac{M\Delta g}{(D\ t\ A)} \quad (1)$$

where C_{DGT} is the concentration of target element in the soil solution, M is the mass of that element accumulated onto the resin gel, Δg is the thickness of the diffusion layer, D is the diffusion coefficient of the element, t is the deployment time and A is the area of the DGT device window. The following elements are known to be detectable using the Chelex DGT: Co, Ni, Cu, Zn, Cd, Pb, Al, Mn, Ga, as well as the rare earth elements over a wide range of pH values and ionic strengths (Garmo *et al.* 2003). However, Chelex DGT performance is known to be pH-dependent for the following elements: V, Cr, Fe, U, Mo, Ti, Ba, and Sr (Garmo *et al.* 2003), and poor for the following elements: Li, Na, K, Rb, Mg, Ca, B, Tl, P, S, As, Bi, Se, Si, Sn, Sb, Te, Zr, Nb, Hf, Ta, W, Th, and Ag (Garmo *et al.* 2003).

This study tested soils with anomalous Au contents but focused on elements other than Au as part of a typical multi-element exploration or research program. The current study aimed to evaluate DGT as a 'first-pass' technique for soils obtained from two Au prospects in Australia (Fig. 1), with a focus on the following metals of interest: Al, Cd, Co, Cu, Mn, Ni, U and Zn. Note that Al, while not necessarily an element of interest for Au exploration, is both detectable by DGT and the subject of scrutiny regarding its bioavailability in soils (Violante *et al.* 2010). As DGT uptake is known to be analogous to plant uptake for a number of metals (Zhang *et al.* 2001), we have therefore included Al in this study. The first set of soils was obtained from an archived collection derived from a prospect that exhibited a vegetation anomaly (Anand *et al.* 2007) while the second set of soils were obtained as a part of two studies examining hydrogeochemical and biogeochemical anomalies for Au (Reid & Hill 2013; Lucas *et al.* 2013, in preparation). It is hypothesized that standard DGT soil deployments (Chelex-based units deployed for 24 hours) can be used to identify multi-element anomalies in residual or transported soils over mineralisation, thereby supplementing current methods for geochemical exploration using soils.

METHODS

General procedures

For laboratory work, all plastic containers (70 ml transparent polypropylene, Sarstedt®) and pipette tips (1 ml, Sarstedt®) used were acid-washed (10% HCl) for at least 24 hours prior to rinsing with milli-Q water (Millipore, 18.2 MΩ cm). All reagents used were analytical grade. All experiments were undertaken in duplicate where possible, with some experiments not replicated due to an insufficient quantity of soil. Quality control during analysis included regular calibration of equipment, as well as analysis of solution blanks and standards of known concentration (Intertek Genalysis, Perth). Chelex DGT devices were purchased from DGT Research Ltd (www.dgtresearch.com). Four Chelex DGT devices were separately analysed as manufacturing blanks. A series of experimental blanks were also run in conjunction with the main experiment, using acid-washed sand instead of soil.

Soils

Soils used in this study are from two prospects located in Australia (Fig. 1). The prospects were: 1) the Moolart Well prospect, located in the northern Yilgarn Craton of Western Australia (27° 37' S, 122° 20' E), for which both

continued on page 6

Evaluating the diffusive gradients in thin films technique... continued from page 4

TABLE 1. Physical characteristics of soils used in this study

Soil location	Code	Soil description	Mean pH	Mean E.C. (µs/cm)	Total Organic C %	Total N %
Oberon	OB	Sandy ferruginous, fine	5.99	60.1	0.15 – 0.27	0.017 – 0.025
Moolart Well topsoil	MW	Ferruginous clayey sand	5.64	25.0	0.86 – 1.36	0.069 – 0.132
Moolart Well subsoil	MA	Gravelly sandy clay	6.23	56.7	0.08 – 0.15	0.015 – 0.028

surface samples (7 samples, 0-20 cm depth, MW-series) and subsoil (13 samples, 0.5 – 1.5 m depth, MA-series) samples were obtained; 2) the Oberon prospect, located in the Tanami desert in the Northern Territory (20° 16' S, 129° 59' E), for which only surface soils (9 samples, 0-20 cm depth, OB-series) were obtained. Physical characteristics of these soils were determined using standard techniques (SSSA 1996), and total organic carbon and nitrogen contents of the soils were determined using an Elementar vario MACRO instrument (www.elementar.de). The soils were obtained from at least one transect across each prospect. The OB samples are from a NW-SE diagonal transect over mineralization, and were sourced from the same sites as previous samples used to study the use of DGT deployed in boreholes (Lucas *et al.* 2013, in preparation). The MW surface soils were obtained from two separate E-W transects, with one transect overlying mineralisation and the second transect over background distal to known mineralisation. The MA subsurface soils were collected from three E-W closely spaced transects; again, some of the soils overlie mineralisation, and the remainder overlie background areas. In the results section below, the data are plotted according to E-W alignment, as this provides the best indication of element responses over mineralisation.

The soils were separated into 'anomalous' and 'background' populations in terms of Au concentrations (CSIRO, unpublished data). Four of the seven surface soil samples obtained from MW contain low-level Au concentrations (Au >1 ppb), although they do not indicate Au mineralisation. The remaining three samples represent the background signal (Au <1 ppb). The thirteen deep samples from MA were all obtained from Au-rich colluvium-alluvium; three samples exhibit strongly anomalous signatures for Au (>30 ppb) and the remaining ten exhibit what are considered to be local background signatures (Au <15 ppb), although some of these background soils are situated over mineralisation. Of the nine soil samples obtained from Oberon (OB), two are known to have a low-level Au anomaly (Au >1 ppb), while the remaining seven samples are indicative of the background signature (Au <1 ppb). At all three sites, MW, MA and OB, Au anomalies measured previously in soils, vegetation and groundwater have been expressed almost directly over mineralisation (Anand *et al.* 2007; Reid & Hill 2010).

Multi-element DGT response in soils over mineralisation

Procedures for deploying DGT devices involve gradually equilibrating the soils with milli-Q water to 100% water holding capacity (WHC) over 72 hours (Zhang *et al.* 1998). Equilibrating the soils with water ensured that the DGT devices were sampling the labile component. Note that, aside from this equilibration step, the soils do not necessarily need to be pre-sieved or pre-treated for DGT; indeed, it is preferable that the soils remain as 'natural' as possible. DGT can also be deployed *in situ* if desired, so long as soil moisture content is >27% (Hooda *et al.* 1999). Large hand-retrievable organic material (e.g. twigs and leaves) was removed from the soils prior to use, although inorganic material (e.g. pebbles and large stones) was not removed.

The Chelex DGT devices were deployed on all soils following standard DGT soil deployment practices (Zhang *et al.* 1998; Zhang *et al.* 2006). Prior to deployment of the DGT devices, the soils were equilibrated as follows: around 20 g of soil was placed in a sealable 70 ml plastic container; the soil was wetted to 60% WHC for 48 hours and then wetted to 100% WHC and left for a further 24 hours. After the soils had been equilibrated, the DGT devices were deployed on the soils as follows: a small quantity of the soil slurry was smeared onto the DGT device face; the DGT was placed on the soil, ensuring no gaps formed between the DGT window and the soil; and the container was capped in order to minimize evaporation, but not so tightly that anoxic conditions would occur within the container. The container was then placed in a temperature-controlled laboratory at 25°C for 24 hours (the standard deployment time for DGT), after which the DGT devices were removed and thoroughly washed with milli-Q water to remove soil. The Chelex gels were removed from the DGT devices and eluted with 1 ml of 1 M HNO_3. The resulting sample was diluted to 20 ml with milli-Q water for analysis via ICP-MS (Intertek Genalysis). The method detection limit, MDL, for DGT was determined by calculating 3 × the standard deviation of the deployment blanks (Long & Winefordner 1983) and applying equation 1 for the timeframe of the deployment (Luo *et al.* 2010). The MDL for each element is shown in Table 2.

The concentrations of elements in the porewaters were also determined after the DGT devices had been removed by the following procedure: the remaining saturated soil sample was placed in a 50 ml centrifuge tube and centrifuged at 3,500 rpm for 1 hour; the porewater was extracted using a 0.2 μm graduated filter syringe; 1 ml of cold concentrated HNO_3 was added to the porewater in order to stabilise any elements present, and the solution was diluted to 20 ml with milli-Q water for analysis of elements via ICP-MS at Intertek Genalysis, Australia. All reported DGT and porewater concentrations account for volumes extracted and dilution. The instrument detection limit (IDL) of the ICP-MS is shown in Table 3, and represents the lowest concentration detectable following dilution of the sample.

continued on page 7

Evaluating the diffusive gradients in thin films technique...

continued from page 6

Table 2. DGT-measured concentrations of nine elements in soils, in μg/L. Soils that are known to have anomalous Au concentrations are highlighted in bold. MDL indicates the method detection limit, with values less than MDL shown by a dash. Errors are reported as +/- one standard deviation of duplicate results where applicable.

Site	Al	Cd	Co	Cu	Fe	Mn	Ni	U	Zn
MDL	2.7	0.04	0.11	1.1	14.4	1.18	2.18	0.01	4.7
OB62	14.1 ± 6.7	0.07 ± 0.01	–	1.2	–	7.7 ± 2.5	–	0.03 ± 0.003	36.0 ± 6.4
OB67	9.4 ± 0.04	0.06 ± 0.01	–	–	–	8.8 ± 2.4	–	0.03 ± 0.02	3.1 ± 2.2
OB69	24.9 ± 0.1	0.06 ± .0.02	0.2	–	33.1 ± 6.1	17.1 ± 0.8	–	0.06 ± 0.02	4.7
OB70	8.1 ± 0.05	0.06 ± 0.01	–	–	–	2.4	–	–	1.6
OB72	20.8 ± 4.9	0.05 ± 0.01	–	–	–	3.5 ± 1.7	–	0.07 ± 0.05	6.3 ± 2.4
OB73	7.4 ± 2.9	0.05	–	–	–	2.9 ± 0.8	–	–	5.5 ± 3.0
OB83	7.4 ± 4.8	0.05	–	–	–	5.9 ± 1.6	–	0.01 ± 0.005	3.1
OB86	25.5 ± 7.3	0.06	–	–	–	6.5 ± 2.5	–	0.05 ± 0.004	2.3 ± 1.1
OB89	24.2 ± 2.9	0.06 ± 0.01	–	–	–	3.5	–	0.03 ± 0.004	3.1 ± 0.8
MW9	65.9	0.09	5.2	–	4281	1735	5.4	0.15	12.5
MW10	44.4 ± 1.9	0.1	3.9 ± 0.1	1.2	1859 ± 695	734 ± 47	3.8 ± 0.8	0.10 ± 0.005	13.3 ± 0.5
MW11	45.7	0.08	3	1.7	2212	441	5.4	0.11	9.4
MW12	139 ± 16	0.12 ± 0.02	4.5 ± 0.2	2.2 ± 0.5	6291 ± 1495	652 ± 37	8.7 ± 1.5	0.3 ± 0.003	20.3 ± 0.2
MW20	264 ± 27	0.1 ± 0.01	1.1	7.5 ± 4.6	67.7 ± 38.7	726 ± 2	4.9 ± 0.8	0.16 ± 0.01	18.8 ± 4.4
MW21	106	0.12	2.3	2.5	372	887	4.4	0.22	11
MW23	78.6 ± 21.9	.22 ± 0.08	1.4 ± 0.2	2	115 ± 33	839 ± 272	2.7 ± 0.8	0.12 ± 0.03	9.4 ± 1.0
MA28	35	0.09	0.6	2.2	28.8	40.1	–	0.05	1.6
MA29	8.1	0.08	0.2	1.1	–	27.1	–	0.03	4.7
MA30	39.7 ± 20.0	0.05 ± 0.02	0.2 ± 0.08	–	40.3 ± 20.4	10.6 ± 1.4	–	0.02 ± 0.01	3.1 ± 0.01
MA31	23.5 ± 9.9	0.08 ± 0.04	0.2 ± 0.09	1.6 ± 0.7	–	10.0 ± 0.8	–	0.04 ± 0.01	3.9 ± 1.1
MA32	6.7	0.05	0.1	2.2	–	16.5	2.2	0.04	1.6
MA33	5.4	0.17	0.8	–	–	112	4.4	0.02	3.1
MA34	8.1	0.08	0.7	2.6	–	38.9	2.2	0.05	4.7
MA36	7.4 ± 0.9	0.06	0.2	–	–	14.7 ± 7.4	–	0.01 ± 0.009	3.1 ± 2.2
MA37	73.3 ± 28.8	0.06 ± 0.02	0.1	2.3	–	5.7 ± 1.7	–	0.02 ± 0.003	18.8 ± 5.6
MA38	12.8 ± 4.8	0.08 ± 0.02	0.2	–	–	15.3 ± 1.7	–	0.01 ± 0.01	7.8 ± 0.6
MA39	22.9 ± 5.9	0.06 ± 0.04	0.2	1.6 ± 0.8	–	9.4 ± 3.3	–	0.02 ± 0.01	3.9 ± 1.1
MA40	–	0.05	0.2	1.7 ± 0.8	–	8.8 ± 0.8	–	0.02 ± 0.01	1.6
MA41	4.7 ± 1.0	0.06 ± 0.02	0.5 ± 0.2	–	–	17.1 ± 4.2	–	0.02 ± 0.02	–

continued on page 8

Evaluating the diffusive gradients in thin films technique...

continued from page 7

Table 3. Porewater concentrations of nine elements for all soils, in μg/L. These concentrations account for both the volume of porewater extracted and dilution required for analysis. Soils that are known to have anomalous Au concentrations are highlighted in bold. IDL indicates the instrument detection limit for diluted samples, with values less than IDL shown by a dash. Errors are reported as +/- one standard deviation of duplicate results where applicable.

Site	Al	Cd	Co	Cu	Fe	Mn	Ni	U	Zn
IDL	2	0.02	0.1	1	10	1	2	0.1	1
OB62	57.5	0.77 ± 0.06	–	–	–	–	–	–	–
OB67	30.6	0.72 ± 0.06	–	–	–	–	–	–	–
OB69	43	0.62 ± 0.08	–	–	–	–	–	–	–
OB70	28.7	065 ± 0.11	–	–	–	–	–	–	–
OB72	86.3 ± 13.6	0.77	–	–	–	–	–	–	–
OB73	70.4 ± 30.1	0.63 ± 0.04	–	–	–	–	–	–	–
OB83	92	0.81	–	–	–	–	–	–	–
OB86	53	0.71	–	–	–	–	–	–	–
OB89	–	0.7	–	–	–	–	–	–	–
MW9	907	0.46	15.6	9.2	5095	5434	27.5	0.53	18.3
MW10	1581	0.43	18.5	28.6	4265	3269	38.2	0.77	38.2
MW11	513	0.45	16.2	18	5130	2565	36	0.59	27
MW12	849 ± 118	0.50 ± 0.02	9.9 ± 1.4	24.9 ± 0.9	4998 ± 948	1276 ± 251	37.3 ± 1.4	0.76 ± 0.11	30.9 ± 7.6
MW20	1710 ± 528	0.65 ± 0.06	7.1 ± 0.25	35.5 ± 1.2	694 ± 193	2394 ± 50	35.5 ± 1.2	0.89 ± 0.06	53.0 ± 6.5
MW21	1251	0.64	7.7	12.8	1315	1532	–	0.68	12.8
MW23	660 ± 17	0.73 ± 0.11	2.8 ± 1.7	14.9 ± 2.1	511 ± 112	956 ± 309	–	0.28 ± 0.67	–
MA29	–	0.53	–	10.5	–	21	–	0.09	–
MA31	57.5	0.77	–	–	–	–	–	–	–
MA32	–	0.4	–	–	–	30.3	–	0.5	–
MA33	45.9	0.76	–	–	–	198.7	–	–	–
MA34	–	0.85	–	17	–	17	–	–	–
MA36	–	0.64 ± .017	–	–	–	14.2	–	–	–
MA37	–	0.67 ± 0.14	–	–	–	–	–	–	–
MA40	–	0.69 ± 0.11	–	–	–	–	–	–	–

Statistical analysis

The determination of significant differences between known anomalous soils and background soils can be undertaken using a two-sample Welch's t-test for data obtained from each site. Welch's t-test, an adaptation of Student's t-test, can be used when the sample sizes and the variances between datasets are not equal (Welch 1947). The t-statistic can be evaluated using equation 2:

$$t = \frac{(X_1 - X_2)}{\sqrt{\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}}} \quad (2)$$

where t is Student's t-distribution for the data, X_1 and X_2 are the means of each sample set, s_1 and s_2 are the standard deviations for each sample set and N_1 and N_2 are the sample sizes for each data set. The degrees of freedom for testing can be determined from the Welch–Satterthwaite equation (equation 3):

$$d.f. = \frac{\left(\frac{s_1^2}{N_1} + \frac{s_2^2}{N_2}\right)^2}{\frac{s_1^4}{N_1^2 d_1} + \frac{s_2^4}{N_2^2 d_2}} \quad (3)$$

where *d.f.* is the degrees of freedom, s_1 and s_2 are the standard deviations for each sample set, N_1 and N_2 are the sample size and d_1 and d_2 are the degrees of freedom for each sample set, (determined as $N_1 - 1$ for each N). Data obtained in this study were analysed using the software package *R* (R Core Team 2012), which was used to apply Welch's t-test for each set of elements compared and provided both *d.f.* and the relevant p-value for the *t*-statistic determined in equation 2. For this work, the testing was undertaken per site for each element.

continued on page 9

Evaluating the diffusive gradients in thin films technique...

continued from page 8

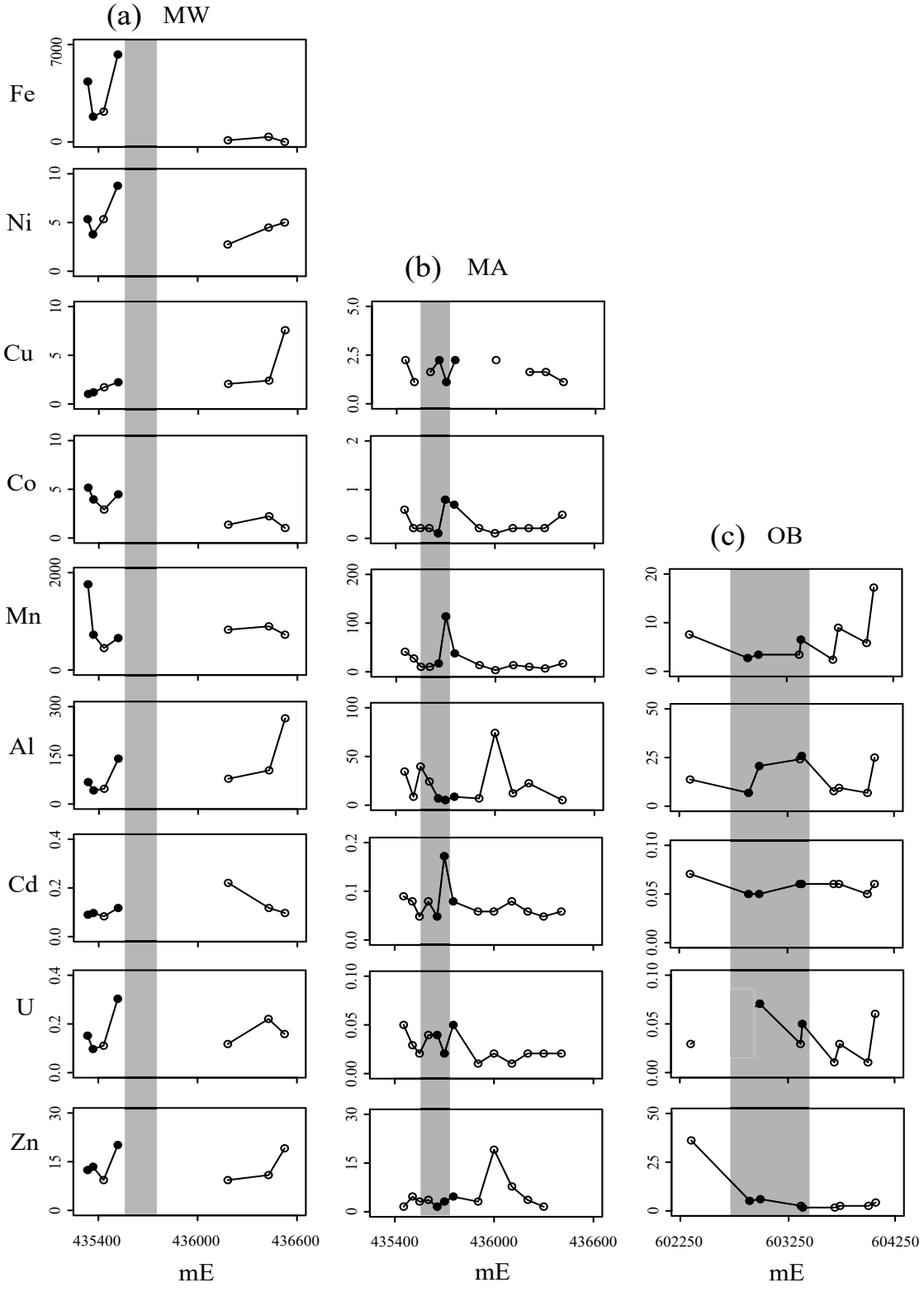

Figure 4. Transects showing concentration of elements as measured by DGT at (a) MW, (b) MA, and (c) OB. All concentrations are shown in μg/L. The OB transect is roughly 20° 16' S, 129° 59' E. Both MW and MA transects are roughly 27° 37' S, 122° 20' E. The y-axis scale for each prospect is adjusted to highlight detail, and the grey shading indicates the approximate vertical projection of gold mineralisation. Soils with known anomalous Au concentrations are shown as black circles, and background soils are shown as clear circles.

continued on page 10

Evaluating the diffusive gradients in thin films technique...

continued from page 9

RESULTS

Broad geochemical characteristics of the soils

The pH, electrical conductivity (EC), and percentage of total organic carbon and nitrogen of the soils are shown as ranges in Table 1. The soils are acidic, with the lowest mean pH being 5.64 for soils sourced from MW, and the highest mean pH being 6.23 for soils sourced from the MA hardpan layer. The mean EC values of the soils ranged from 25.0 μS/cm to 60.1 μS/cm. Both the OB and MA soils had very low total organic carbon contents with that of the MW surface soils being slightly higher, at up to 1.36%. This higher quantity of organic matter in the MW surface soils is also reflected in the nitrogen content of these soils when compared with the OB and MA samples.

DGT-measured concentrations

The data for the concentrations of elements detected by DGT are shown in Table 2, and are also plotted on the soil sampling transects, along with the zones of known Au mineralisation, in Figure 4. Table 2 shows that a range of elements (Al, Cd, Co, Mn, Zn and U) were detected by DGT in almost all soils. The values for Cu are close to the detection limit of the technique; these less than detection limit values might be increased in future deployments by extending the deployment time (Zhang *et al.* 1995; Zhang *et al.* 1998). As stated previously, the measurement of Fe and U with Chelex DGT is pH dependent. This was taken into account following the methods of Garmo *et al.* (2003). Table 2 shows that there is a clear difference in the concentrations of elements measured at each of the sites in that higher concentrations of all elements were detected in the MW samples than in either the OB and MA samples, by both the DGT and porewater methods. For example, the DGT-determined concentrations of Fe and Mn in the MW surface samples are greater than an order of magnitude higher than the concentrations in the OB and MA soils. Nickel was not detected at all in the OB soils, and was detected in only three MA samples. Interestingly, these same three MA samples are also known to be anomalous for Au, likely as a consequence of the mineralisation at Moolart Well being hosted in ultramafic greenstones.

Figure 4 shows the concentrations of DGT-measured elements along the sampled transects. More element concentrations were reported to be greater than detection limit by DGT at MW (a total of 9) than at either MA (7) or OB (5). At MW (Fig. 4a), Al, Fe, Ni, U, and Zn follow a similar trend over the length of the transect, with the highest concentrations of these elements (excluding Al) being found over mineralisation. Element concentrations over background, indicated on the eastern side of the figure, appear to be flatter than those over mineralisation, with the exception of Cu and Al. At MA (Fig. 4b) Co, Mn, and Cd follow a similar trends over the length of the transect, with the highest concentrations of these elements over mineralisation. Both Al and Zn show elevated concentrations to the east of mineralisation, with concentrations decreasing still further towards the east. For the OB soils (Fig. 4c), Al and U show a marginal elevation over mineralisation; the remaining elements do not show significant variation over mineralisation.

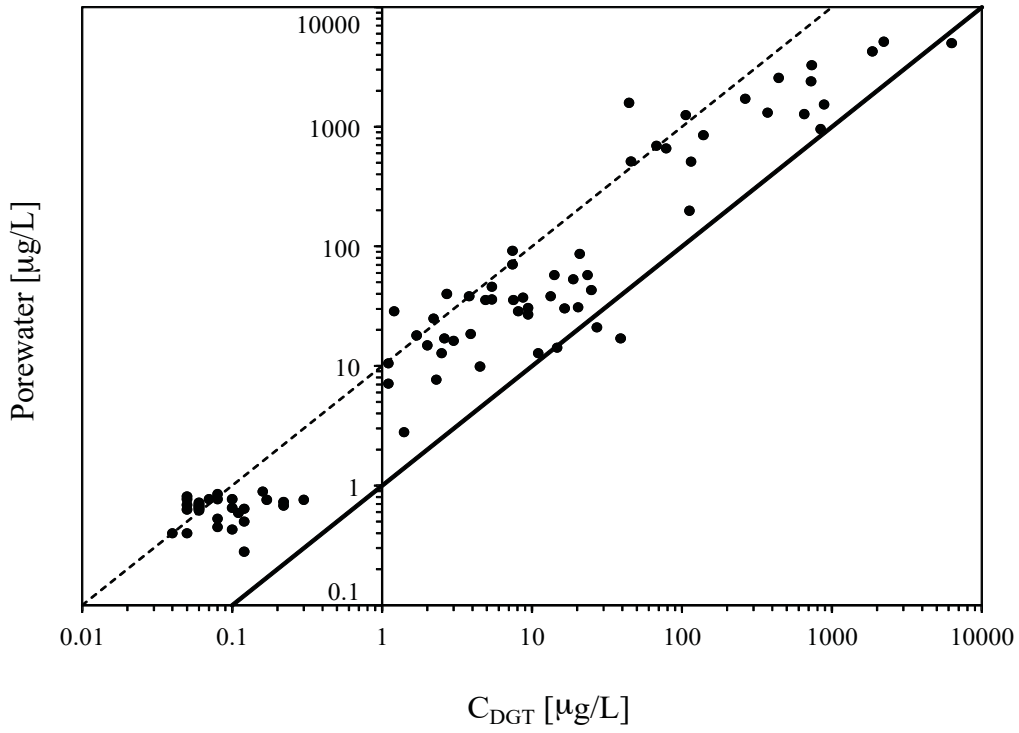

Figure 5. Log-log plot of all porewater concentrations vs. C_{DGT} for all elements detected by both techniques. The solid line represents a 1:1 relationship, and the dashed line represents a factor of 10 greater than the 1:1 line.

continued on page 11

Evaluating the diffusive gradients in thin films technique... continued from page 10

Porewater concentrations

The concentrations of elements in the soil "porewaters" (post-DGT deployment) are shown in Table 3. Difficulties were encountered in extracting a sufficient quantity of porewater for analysis. This was particularly true for both the sandy OB soils and the highly lateritic MA soils with five MA soils – MA28, MA30, MA38, MA39 and MA41 – generating insufficient volumes for analyses. Porewater volumes extracted from the soils were often <0.2 ml, due to low initial WHC. In addition, the porewater concentrations of elements from these sites were more often below the detection limit. The overall distribution of metal concentrations in porewater mirrors that of the DGT-measured concentrations (Fig. 5), although concentrations in the porewaters are often greater than an order of magnitude higher than DGT values. The reasonable correlation suggests that DGT is a suitable method for assessing porewater element concentration trends along these transects, and furthermore, as the concentrations were more often measurable (due to the lower detection limit of DGT than porewater analysis), DGT would appear to constitute a methodological improvement over porewater centrifugation.

Statistical interpretation of results

Table 4 shows the results of the Welch's t-testing of concentrations of elements between soils that are anomalous for Au (highlighted in bold in Tables 2, 3, and 4) and the background soils (plain text in Tables 2, 3, and 4). Note values that were below detection limit were excluded from testing, as opposed to assigning an arbitrary or statistically derived value. In the DGT dataset Welch's t-testing shows that: Mn concentration is significantly different between anomalous and background samples in the OB soils; Co and Fe concentrations are significantly different in the MW soils; and Al concentration is significantly different in the MA soils where it is likely due to a pH anomaly existing in these soils (Table 1). For porewater data, only Al and Cd concentration were above detection limit for the OB soils, neither of which were significantly different between anomalous and background samples. In the MW soils, both Co and Fe concentrations were significantly different between anomalous and background soils as with the DGT dataset. However, for the MA soils, both Cd and Co concentrations were significantly different between anomalous and background soils, which contrasts with the DGT dataset.

DISCUSSION

The main objective of this study was to assess whether DGT was capable of being used as a tool for geochemical exploration as a 'first-pass' technique, with the hypothesis that DGT was able to determine multi-element anomalies in soils that relate to underlying mineralisation. On the limited selection of soils tested, the DGT technique appears to have both successfully met the objective and confirmed the hypothesis. In particular, DGT is more sensitive at detecting labile elements in porewaters than conventional porewater extractions due to the preconcentration of elements onto the Chelex resin. In this discussion, we assess the DGT technique on the basis of its use as a tool for geochemical exploration in soils, and as a tool for simultaneous detection of multi-element anomalies.

Using DGT as a tool for exploration

As a general tool for geochemical exploration in soils, the DGT technique is simple to prepare and deploy, either in laboratory-based studies such as this one or *in situ*. The analysis of the resin gels is also straightforward; an elution step with concentrated acid, which can be undertaken at any stage after the deployment, minimizes the risk of contamination. This feature would be particularly advantageous in *in situ* field deployments. The pre-concentration of elements onto a resin gel ensures low detection limits, which become even lower when deployment times are extended (Davison & Zhang 1994; Zhang *et al.* 1998).

We can broadly compare the DGT technique to the better-known exploration tool of partial extractions. The first part of most soil partial extraction techniques usually

continued on page 12

Evaluating the diffusive gradients in thin films technique...

continued from page 11

Table 4. Significance testing between background soils and Au-anomalous soils, using unpaired 2-sample Welch's t-test. A p-value ≤0.05 indicates a significant difference between the background soils and anomalous soils. Testing is inclusive of all replicates.

		DGT			Porewater		
	Element	p-value	degrees of freedom	Significantly different?	p-value	degrees of freedom	Significantly different?
OB	Al	0.86	6.3	No	0.17	7.7	No
	Cd	0.32	13	No	0.98	13.8	No
	Fe	0.23	1.2	No	-	-	No
	Mn	0.03	17	Yes	-	-	No
	U	0.36	3.9	No	-	-	No
	Zn	0.37	14.1	No	-	-	No
MW	Al	0.42	6.4	No	0.83	8.8	No
	Cd	0.49	5.2	No	0.1	6.4	No
	Co	>0.01	8.8	Yes	0.03	8.9	Yes
	Cu	0.19	5.3	No	0.82	9	No
	Fe	0.02	4.9	Yes	0.01	6.6	Yes
	Mn	0.51	5.2	No	0.24	5.3	No
	Ni	0.19	5.6	No	0.98	4.5	No
	U	0.41	5.2	No	0.39	7.1	No
	Zn	0.33	9	No	0.96	5.5	No
MA	Al	0.01	16.3	Yes	0.35	4.2	No
	Cd	0.45	2.1	No	0.01	8.8	Yes
	Co	0.33	2.1	No	>0.01	8.7	Yes
	Cu	0.62	2.7	No	0.95	3	No
	Mn	0.28	2	No	0.07	2.5	No
	U	0.19	2.6	No	0.69	6.5	No
	Zn	0.29	17.1	No	0.99	5.7	No

focuses on the water-soluble or ion-exchangeable fraction, and uses a small portion of soil (e.g. 5 g) with a known volume of leaching agent (e.g. 90 ml) such as water (Reith & McPhail 2007), $MgCl_2$ or CH_3COONH_4 (Tessier *et al.* 1979; Gray *et al.* 1999). This fraction is likely to contain the lowest concentration of elements, and is the fraction that has been previously assumed to correlate best with bioavailability (Peijnenburg *et al.* 2007). There are at least two issues with this assumption however. First, the proportion of soil to extractant used (e.g. 1:8 or greater) effectively ensures that concentrations of elements measured will be low. This limitation could potentially be alleviated by use of a pre-concentrating agent e.g. an ion-exchange resin. Second, the partial extraction procedure does not ensure the soil is unperturbed; speciation measurements cannot be easily made as the separation of solution and solid phases disrupts the physicochemical equilibrium, which affects the distribution of species in solution (Zhang *et al.* 1998). The DGT technique avoids both issues by: 1) preconcentrating elements at a well-defined rate of uptake *via* diffusion, and; 2) minimally disturbing the soil porewater and thus allowing for an assessment of speciation.

While the DGT technique does not rely on chemical leaching, the uptake of elements through the diffusive layer, coupled with the associated dynamics of the soil solution, not only provides specific information regarding the exchange dynamics within the soil but also provides a tool for evaluating bioavailability. By analogy with partial extractions, there is scope to expand the DGT technique to include chemical modification of the soil, but this was beyond the scope of this initial study.

The use of DGT to detect multi-element anomalies

As stated in the introduction, one of the objectives of a soil sampling program is to assess whether an anomalous signal related to mineralization can be separated from background values. In this study, we obtained soils that have previously been determined to contain either an anomalous or background signature for Au and examined other elements to see whether anomalies could be detected by Chelex DGT. As a tool for the simultaneous detection of multiple elements in soils, the DGT technique was limited for Cu and Ni in the soils (Table 2), likely due to the negligible amount of a labile fraction of these elements in the soils generally. Cadmium was detected in almost all soils, but the concentrations were barely above the detection limit. Measured concentrations of a number of

continued on page 13

Evaluating the diffusive gradients in thin films technique... continued from page 12

elements were, however, more likely to exceed detection limits for DGT than for porewater extraction and analysis.

Elements such as As and Cu are known to exhibit pathfinder behavior for Au (Ashton & Riese 1989); however, As was not examined in this study due to poor uptake by the Chelex resin, and concentrations of Cu in both DGT and porewater were very low. Both of these issues are also relatively easy to address with DGT for future experiments. First, DGT devices equipped with either ferrihydrite gels or mixed binding layer gels are able to detect As (Mason *et al.* 2005; Panther *et al.* 2008), and second, increasing the sensitivity of the DGT technique for elements like Cu may simply be a matter of increasing the deployment time (Zhang & Davison 1995). There are some considerations with regards to increasing deployment times: firstly, the ion holding capacity of the Chelex resin needs to be accounted for, as exceeding the resin's sorption capacity by an excessively long deployment will invalidate equation 1 (Zhang & Davison 1995); secondly, other processes, such as changes to redox conditions and increased biological activity within the soil, may affect the lability of elements in the soil solution (Ernstberger *et al.* 2002). A deployment time of 24 hours is recommended for DGT when these other processes need to be avoided (Hooda *et al.* 1999); however, for exploration purposes, reducing the limit of detection is advantageous, and longer DGT deployments are recommended as long as the possibility of a change in soil conditions is accounted for.

In this study, we demonstrate the variation in element concentrations over mineralisation, and have ascertained that there is an observable multi-element difference between soils over mineralisation and soils from background areas. This difference, namely that anomalous values are higher than background values, can be seen both visually in Figure 4 as well as statistically in Table 4 for elements such as Co and Mn (and Cd for MA). The Chelex DGT devices used in this study do not sample for Au (Lucas *et al.* 2012); however, the DGT has recently been modified for uptake of Au through the use of activated carbon as an adsorbent (Lucas *et al.* 2012), and evaluation of Au-DGT in soils is currently underway.

This study did not include an analysis of the total concentrations of elements and metals in the soils; instead, only the DGT-detectable and porewater-extractable fractions were evaluated. A comparison of total elements with the DGT-detectable fraction, which can be considered as approximation to bioavailability, c.f. Mann *et al.* (2012), may help shed light on the interaction and exchange of elements between the biosphere and the lithosphere, and a better understanding of the surficial expression of mineralisation.

As mentioned in the introduction, the DGT technique for soils was originally developed to assess toxicity and plant uptake for environmental monitoring and regulation. The detection of highly elevated concentrations of elements such as Cu and Cd in soils was not to be viewed as a positive result; if anything, excessive quantities of these elements have implications ranging from the health of vegetation and ecosystems to human health and food security (McLaughlin *et al.* 2000; Zhang *et al.* 2006). Although an evaluation of the technique in a wider range of prospective soils and environments is required, this study demonstrates a new field of application of the DGT technique to low-level measurement of elements for the detection of mineralisation.

CONCLUSIONS

The DGT technique shows potential as a tool to augment current geochemical exploration efforts. The technique is relatively simple to apply, and is very sensitive for a range of elements even when deployments are restricted to 24 hours. The initial potential shown by DGT soil deployments at two Australian Au prospects suggests that further evaluation of DGT as a geochemical exploration tool would be a productive direction for research in other environments.

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continued on page 14

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continued on page 15

Evaluating the diffusive gradients in thin films technique... continued from page 14

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