



Establishing geochemical background variation and threshold values for 59 elements in Australian surface soil



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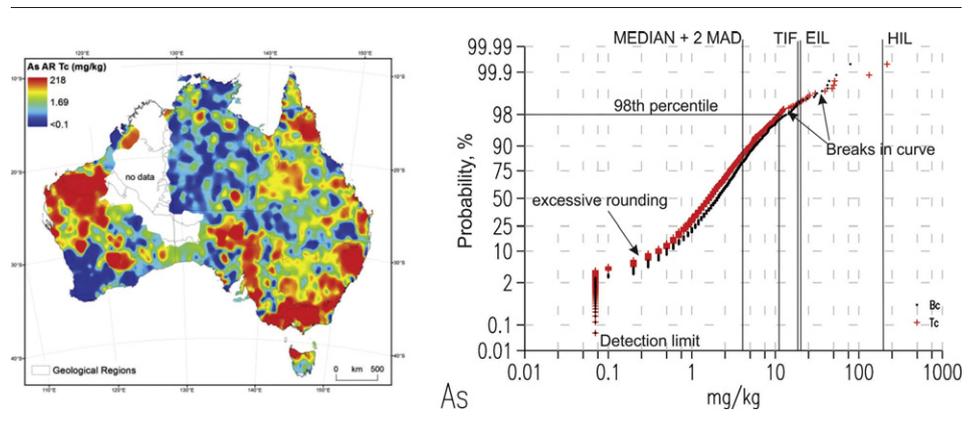
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HIGHLIGHTS

- Aqua regia concentrations for 59 elements in Australian surface soil presented.
- Terminology and methods to determine background and threshold discussed.
- Very few samples exceed Western Australian 'ecological investigation levels'.
- No major diffuse contamination of Australian soil by PTEs at continental scale
- Few outliers mostly reflect geology, minor contamination or mineral potential.

GRAPHICAL ABSTRACT



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ABSTRACT

During the National Geochemical Survey of Australia over 1300 top (0–10 cm depth) and bottom (~60–80 cm depth) sediment samples (including ~10% field duplicates) were collected from the outlet of 1186 catchments covering 81% of the continent at an average sample density of 1 site/5200 km². The <2 mm fraction of these samples was analysed for 59 elements by ICP-MS following an aqua regia digestion. Results are used here to establish the geochemical background variation of these elements, including potentially toxic elements (PTEs), in Australian surface soil. Different methods of obtaining geochemical threshold values, which differentiate between background and those samples with unusually high element concentrations and requiring attention, are presented and compared to Western Australia's 'ecological investigation levels' (EILs) established for 14 PTEs. For Mn and V these EILs are so low that an unrealistically large proportion (~24%) of the sampled sites would need investigation in Australia. For the 12 remaining elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sn and Zn) few sample sites require investigation and as most of these are located far from human activity centres, they potentially suggest either minor local contamination or mineral exploration potential rather than pollution. No major diffuse source of contamination by PTEs affects Australian soil at the continental scale. Of the statistical methods used to establish geochemical threshold values, the most pertinent results come from identifying breaks in cumulative probability distributions, the Tukey inner fence and the 98th percentile. Geochemical threshold values for 59 elements, including emerging 'high-tech' critical elements such as lanthanides, Be, Ga or Ge, for which no EILs currently exist, are presented.

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1. Introduction

'Geochemical background' and 'threshold' are two essential concepts in exploration and environmental geochemistry. It is surprising, however, how poorly they are defined and how differently they have been used in the literature (e.g., Matschullat et al., 2000; Reimann and Garrett, 2005; Reimann et al., 2005). In environmental geochemistry these ill-defined terms are often used to distinguish between natural and anthropogenic element concentrations, or to define action levels in environmental legislation, which are element concentrations above which further investigation or site clean-up needs to take place (Reimann, 2007). Reimann and Garrett (2005) cite some of the many different definitions of the term 'background' used in the literature. Because action or investigation levels can have severe economic consequences, poor definition and loose usage of terminology should be avoided.

Some authors use the mean concentration of the investigated element in the average upper continental crust as the background for the expected concentration of this element in environmental samples. This usage is probably based on the definition of the global clay standard of Turekian and Wedepohl (1961). This definition ignores the fact that background varies from place to place and should thus logically be a range of values rather than a single value. Other authors suggest that deeper soil layers, presumed unaffected by contamination, can be used to represent the background for topsoil (e.g., Facchinelli et al., 2001; Massas et al., 2009; Yang et al., 2009). Others still try to do this using 'enrichment factors' based on the work of Zoller et al. (1974) and Duce et al. (1975) in atmospheric chemistry. These methods neglect, among other things, the facts that weathering and pedogenesis will lead to quite different compositions in different soil horizons and that surficial organic and deeper minerogenic soils are not comparable (e.g., Reimann and Caritat, 2000, 2005; Sucharova et al., 2012).

In environmental geochemistry the main purpose of the term background is probably to distinguish between natural concentrations of potentially toxic elements (PTEs; e.g., As, Cd, Cr, Hg, Pb, Zn) and anthropogenic contamination. The main assumption is that contamination will lead to unusually high element concentrations in the samples, which can then be separated from the main body of data using statistical techniques (Matschullat et al., 2000). Exceedingly high geogenic (natural) concentrations of toxic elements are well documented (e.g., the case of natural Pb toxicity to plants in certain areas of Norway (Bølviken and Låg, 1977); or the naturally elevated U levels which result in Australian aboriginal people recognising parts of the Northern Territory as 'sickness country' (Shepherd, 1997)). Of importance is whether an element concentration is toxic or not (which relates to availability and speciation), and if so to what organisms, regardless of the source of the high concentration. This approach would then lead to the definition of toxicological threshold values, soil guideline values or maximum acceptable concentration levels. Exploration geochemistry is most often based on the detection of (naturally) high element concentrations derived from the existence of mineral deposits in an area (note that element depletion can also be indicative of mineral systems). Even unmineralised rock types can give rise to elevated natural element concentrations. Soils developed on ultramafic rocks, for instance, are well known for the Ni-adapted plant communities that thrive in them (Brooks et al., 1995). Using statistically (and quite likely also toxicologically) derived action levels to clean up such sites would actually destroy a unique ecosystem that in fact requires special management.

There are instances where the difference between 'geogenic' and 'anthropogenic' element derivation is important. Examples include industrial or brownfield sites and mining areas that are commissioned for shutdown. In such cases element concentration values to which the area has to be returned before a company is allowed to leave may be required. Here a readily defined source of the high element concentrations exists and the spatial scale of contamination can easily be established by geochemical mapping. However, even if toxicologically

derived action levels are used to define clean-up levels, the geogenic distribution of the elements in question must be known first as naturally occurring high element concentrations due to the occurrence of a particular lithology or mineral deposit cannot be 'cleaned up'.

Such examples demonstrate that the geochemical background needs to be established at a variety of scales, preferably before any major human activity takes place. Large, continental-scale geochemical mapping results have been published recently, for instance from the United States (Smith et al., 2014) and Europe (Reimann et al., 2014a, 2014b). These datasets have been used to establish the geochemical background variation at the continental scale and, in Europe, for risk assessment of metals in the environment (e.g., Oorts and Schoeters, 2014; Birke et al., 2016).

Geoscience Australia recently published a Geochemical Atlas of Australia (Caritat and Cooper, 2011a). The atlas covers about 81% of Australia or approximately 6,174,000 km² (Fig. 1) with top (0–10 cm depth) and bottom (on average ~60–80 cm depth) catchment outlet sediment samples collected at an average sample density of 1 site per 5200 km². The project provides the first internally consistent and completely harmonised dataset for (among others) 59 aqua regia soluble chemical elements in surficial materials at the Australian continental scale (www.ga.gov.au/ngsa). The resulting geochemical maps show the concentrations and spatial distributions of all these elements across Australia, with applications to resource exploration and environmental studies (Caritat and Cooper, 2016). The purpose of this paper is to use the National Geochemical Survey of Australia (NGSA) public domain dataset to establish the geochemical background variation of the aqua regia soluble elements at the continental scale for Australia.

The Western Australian Department of Environment and Conservation (DEC) has compiled assessment levels for soil, sediment and water from Australian and international data sources (DEC, 2010). These are to be used in the context of a 'Tier 1' screening assessment (DEC, 2006) to determine whether substances present at a site are at concentrations that may potentially present a risk to human health, the environment or an environmental value. These investigation levels, named 'ecological investigation levels' (EILs) and 'health investigation levels' (HILs), are based on toxicity/phytotoxicity criteria (see DEC, 2010).

Here we use the data from the NGSA to:

- Compare the concentrations of aqua regia soluble elements in the coarse fraction (<2 mm) of soil collected at two different depths.
- Apply different techniques to calculate threshold values at the Australian continental scale and establish the background variation of 59 elements for the two soil depths.
- Compare the statistically derived threshold values with the ecological and health investigation levels of the DEC.
- Report how many samples fall above DEC's ecological investigation levels (for the 14 elements where these exist), where they are located, and discuss the possible reasons for these exceedances.
- Provide national geochemical threshold levels for many additional parameters, e.g., critical elements for a 'high-tech' world, which presently are not covered by DEC regulations.

2. Methods

2.1. The NGSA project

The National Geochemical Survey of Australia (NGSA) project, a cooperative venture between the Federal and State/Northern Territory geoscience agencies in Australia, was part of the 5-year Onshore Energy Security Program led by Geoscience Australia between 2006 and 2011 (Johnson, 2006). The NGSA was initiated to fill a significant knowledge gap regarding the composition of surface regolith at the continental scale in Australia by providing internally consistent pre-competitive

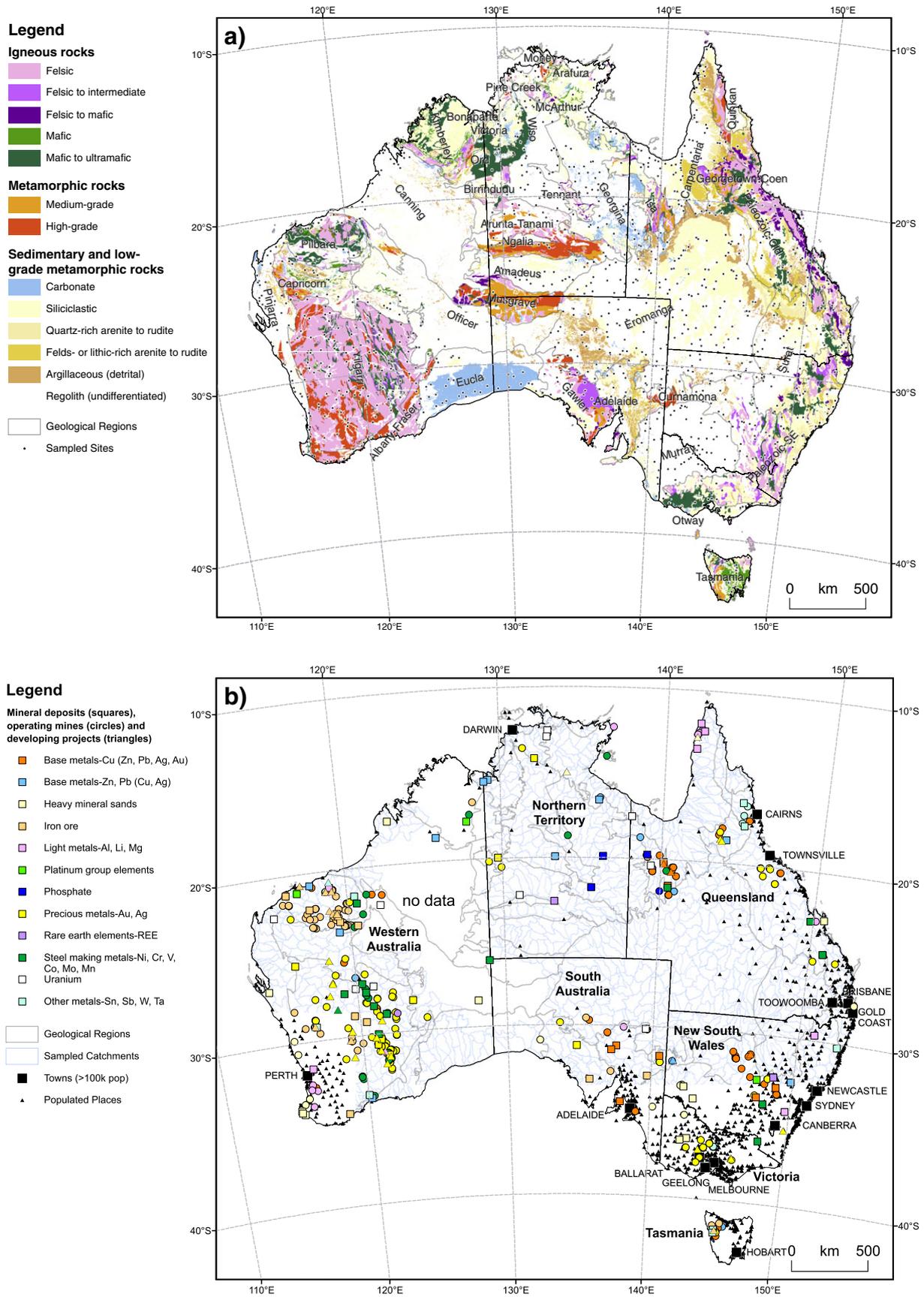


Fig. 1. Maps of Australia showing (a) surface geology (coloured polygons), NGSa sampling sites (black dots), and (named) geological regions (grey polygons); and (b) known mineral deposits, operating mines and developing mines (coloured squares, circles, and triangles, respectively), NGSa catchments (blue polygons), (named) towns with population exceeding 100,000 (black square), populated places (black triangles), (named) States/Northern Territory (black polygons), and geological regions (grey polygons). The 'no data' label refers to the absence of NGSa samples in this region. Sources: Blake and Kilgour (1998), Caritat and Cooper (2011a), McPherson et al. (2011), Raymond (2012), Gazetteer of Australia (2013), Senior (2014).

data and knowledge to aid exploration for energy and mineral resources (www.ga.gov.au/ngsa).

Previously existing geochemical data in Australia was perceived to have limited spatial coverage, poor internal comparability and inadequate extent of reported elemental compositions (Caritat et al., 2008a). During a series of pilot projects that preceded the NGSa a variety of sampling media, depths and grain-size fractions were tested at different sampling densities (Caritat et al., 2005, 2007, 2008b; Caritat and Lech, 2007; Lech and Caritat, 2007a, 2007b). It was found that regolith samples collected on floodplains or similar low-lying landforms near the outlet of large catchments (referred to as 'catchment outlet sediments') provided a suitable sampling medium for low-density geochemical mapping. These materials are usually a fine-grained mixture of detrital material originating from the main rock and soil types found within a catchment (Ottesen et al., 1989; Bølviken et al., 2004). To the extent that the sampled catchment outlet sediments are supporting biological activity, they also can be defined as soils (SSSA, 2008); thus the terms 'sediment' and 'soil' have been used interchangeably to refer to the sampling medium in various publications on NGSa data (e.g., Caritat et al., 2011, 2012; Reimann et al., 2012).

Many geochemical surveys have been carried out in Australia by Federal and State geoscience agencies, industry, and/or academic institutions. Examples of these are (1) the multi-media geochemical survey of a 14,000 km² area in the Clarence River catchment in northeastern New South Wales (Cohen et al., 1999), (2) the ~80,000 km² stream sediment geochemical survey in North Queensland (Bain and Draper, 1997), (3) the regolith geochemical mapping program of about twenty 1:250,000-scale map sheets in Western Australia (each 1.5 degree of longitude × 1 degree of latitude in extent, or ~16,000 km²) during the late 1990's (e.g., Morris et al., 2003), or (4) the industry sponsored laterite geochemical survey of 400,000 km² in the western Yilgarn Craton (Cornelius et al., 2008). Before NGSa, none was continental in scope mainly because a 'universal' sampling medium had not been recognised and also because of the perception that a relatively high sampling density was required, which would have been prohibitively expensive; nonetheless the desirability of a national-scale geochemical survey was well established (Walker, 1978; L. Wyborn, pers. comm., 2003). As such, the NGSa was the first local attempt at a uniform, internally consistent geochemical atlas and database using a common sampling medium and harmonised sampling protocols, along with state-of-the-art, multi-element analyses for an area in excess of 6,000,000 km². By necessity, the sampling density of NGSa was very low, on average 1 site/5200 km², similar to the Forum of European Geological Surveys (FOREGS) project in Europe (Salminen et al., 2005).

2.2. Sampling

Sampling for the NGSa took place during 2007–2009 and followed the detailed instructions of the project's field manual (Lech et al., 2007). Project staff travelled to each State/Northern Territory for a week-long training fieldtrip with the sampling teams from the local geoscience agency. All field equipment, including hardware (e.g., augers) and consumables (e.g., sampling bags) were purchased centrally and distributed to the field teams. The selected sampling medium was 'catchment outlet sediment' from floodplains or similar landforms located near the spill point or lowest point of large catchments. Here a surface (0–10 cm deep) 'Top Outlet Sediment' or TOS sample, and a deeper (on average 60–80 cm deep) 'Bottom Outlet Sediment' or BOS sample were collected. Both samples were taken as composite samples either from a shallow ~1 m² soil pit (TOS) or from generally at least 3 auger holes within an area of ~100 m² (BOS). Where augering was not possible, soil pits were dug. Site descriptions, GPS coordinates and digital photographs were recorded in the field as were texture, dry (where possible) and moist soil Munsell colours, and field pH (Cooper et al., 2010; Caritat et al., 2011). In total 1315 TOS and 1315 BOS samples (including ~10% field duplicates) were collected from 1186 catchments.

Randomised sample numbers were pre-allocated to each site. The average weight of a sample was 9 kg.

2.3. Sample preparation

All samples were prepared in a central laboratory (Geoscience Australia, Canberra). The samples were oven-dried at 40 °C, homogenised and riffle split into an archive sample for future investigations and an analytical sample for immediate analysis. The latter was further riffle split into a bulk subsample, a dry sieved <2 mm (US 10 mesh) grain size fraction subsample and a dry sieved <75 µm (~US 200 mesh) grain size fraction subsample (Caritat et al., 2009). Each of these subsamples was further split into aliquots of specific mass/volume as per analytical requirements.

2.4. Analyses and quality control

The analytical program for the NGSa project was extensive (see Caritat and Cooper, 2016), with the relevant analyses for the present study being the determination of aqua regia (1:3 M HNO₃:HCl mixture) soluble concentrations of 59 elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Re, Sb, Sc, Se, Sm, Sn, Sr, Tb, Te, Th, Tl, Tm, U, V, W, Y, Yb, Zn, Zr) using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) on the four subsamples at each site (TOS <2 mm, TOS <75 µm, BOS <2 mm and BOS <75 µm). A 60th element, Ta, was also analysed for, but all results were below the lower limit of detection (LLD; 0.05 mg/kg) and accordingly it is not discussed further. While most geoscientists are more familiar with 'total' analyses, the aqua regia digestion, which tends not to dissolve silicates, is the standard method in environmental applications and for environmental legislation (ISO 11466:1995, see ISO, 2016). Full method descriptions can be found in Caritat et al. (2010), whilst quality assessment is detailed in Caritat and Cooper (2011b). In summary, elements with >50% censored values (<LLD) were B, Ge, Hf, Lu, Re, and W; those with >50% relative standard deviation (RSD) on laboratory duplicates (assessing sample preparation and analysis uncertainty) were B (note: numerous censored values), Na, Re (note: numerous censored values), and Se; those with >20% positive or negative bias were Mn; and those with >70% RSD on field duplicates (assessing sample collection – including natural heterogeneity such as the nugget effect –, preparation and analysis uncertainty) were Ag, Au, Cd, Re (note: numerous censored values), and Te. Here we focus on the aqua regia results for 59 elements in the coarse fractions of TOS and BOS samples from here on referred to as Tc and Bc respectively.

2.5. Data analysis

The analysis of geochemical data has to take into account the 'closure' effect (Aitchison, 1986). Significant problems with closure occur in bivariate plots based on element concentrations within one sample material, because each data point – representing one sample – could be shifted along a straight line $y = ax$ through this point by changing the abundance of other elements within this sample. The effect can be substantial (Filzmoser et al., 2010; Reimann et al., 2012). Calculated bivariate relations on raw data (e.g., expressed in mg/kg units) therefore have to be interpreted as being exploratory and qualitative at best, or an appropriate transformation must be performed first (e.g., Filzmoser et al., 2010; Scaely et al., 2015). They cannot be quantitatively compared if they relate element concentrations within the same sample. For comparing two sample materials (e.g., Tc vs Bc) bivariate plots can be used normally because the values plotted do not come from a single, closed composition, and are therefore independent. In this paper we either perform univariate statistics or compare two sample media, and have not log-ratio transformed the raw geochemical data but rather used standard log-transformation where appropriate. Data analysis was

performed using a combination of R scripts (e.g., StatDA 1.6.9; Filzmoser, 2015), ioGAS 6.1 (Reflex, 2016) and ArcGIS 10 (Esri, 2016) software.

2.6. Determination of threshold values – comparison of different approaches

Methods to derive threshold values, concentrations of an element above which further investigation is required, vary substantially. The original approach, Mean + 2 Standard Deviations (SD) of a given dataset, was developed in exploration geochemistry to detect data outliers (Hawkes and Webb, 1962; Matschullat et al., 2000; Reimann and Garrett, 2005). This approach is now outdated (Reimann et al., 2005). Reimann et al. (2005) suggested that it may be useful to replace the Mean + 2 SD statistic with Median + 2 Median Absolute Deviation (MAD), which is much more robust against the effect of data outliers that are common in geochemical datasets. The disadvantage of this method is that it delivers very conservative (low) threshold values, i.e., it produces a lot of sites needing to be investigated further. Environmental agencies may, however, favour it because of this ‘conservatism’ (e.g., Rothwell and Cooke, 2015). The reason for the ‘conservative’ threshold values is actually the strong right-skew that most geochemical data distributions show. When using the formula correctly one assumes a symmetrical data distribution. In geochemistry the statistically correct approach would thus be to calculate Median + 2 MAD on the log-transformed data and to then back-transform the resulting threshold value. Ultimately any risk analysis should be accompanied by a cost-benefit analysis to ensure any decision is economically, socially and environmentally viable and fit-for-purpose.

Kürzl (1988) originally suggested using Tukey boxplot boundaries (Tukey, 1977) for class selection in geochemical mapping. The International Organization for Standardization (ISO, 2005, Annex B) has proposed to detect outliers in soil geochemical data based on the (upper) Tukey inner fence (TIF) or upper whisker in a boxplot. The method has many advantages, including the fact that it is based on the boxplot and depends solely on the data distribution, and that it allows the definition of a threshold for outliers even if none is present in the dataset (i.e., $\text{Max} < \text{TIF}$), as it extrapolates from the robust inner core (25th to 75th percentiles) of the data’s structure. The TIF is calculated as follows:

$$\text{TIF} = \text{Q3} + 1.5 \text{ IQR}$$

where Q3 stands for the 3rd quartile (equivalent to the 75th percentile), and IQR is the inter quartile range (75th – 25th percentile). The multiplying factor of 1.5 is based on the assumption of a symmetrical data distribution. The TIF must be calculated on log (or otherwise, e.g., box-cox) transformed data (Reimann et al., 2008). Jarva et al. (2010) applied this approach for identifying areas in Finland needing closer attention.

In Great Britain, cumulative probability (CP) distribution diagrams and percentiles (most frequently the 95th percentile) have been used to detect samples deviating from the ‘normal background variation’ and to identify a case-specific threshold (e.g., Cave et al., 2012; Johnson et al., 2012; Ander et al., 2013). Using breaks of slope on CP distribution diagrams is the most rigorous procedure, but it requires an expert to carefully assess the concentration distributions within any given area and involves a certain amount of subjectivity, unless as done here calculation of the first derivative of the CP distribution is performed. Other researchers have suggested simply using a percentile-based approach and proposed either the 90th percentile, 95th percentile or 98th percentile of a given dataset to define the threshold (see Ander et al., 2013). The 98th percentile, which identifies 2% of all samples as upper ‘outliers’, comes closest to the original method of calculating Mean + 2 SD in the case of a normal distribution, which would result in ~2.5% of upper outliers.

3. Results

In the following we will focus principally on the 14 elements for which Australian ecological investigation levels (EILs) have been published (DEC, 2010). Table 1 summarises the results of the aqua regia digestion analysis of both Tc and Bc sample types for 14 elements. The LLD, number and proportion of samples <LLD, minimum, 25th percentile, 50th percentile (median), 75th percentile and maximum concentrations of the dataset are presented. Table 1 also documents the correlation coefficient r between the two layers (based on log-transformed data), as well as the ratio Tc/Bc calculated for the median and the 98th percentile values. More detail is available for all elements in the Supplementary material (Table 1SM). Two elements (Al and Sr, both in Supplementary material) show a few values above the upper limit of detection (ULD; 100,000 and 1000 mg/kg, respectively) in both sample types. For statistical analysis, values <LLD were replaced by 2/3 LLD, and those >ULD were replaced by 3/2 ULD.

Fig. 2 shows examples of surface distribution maps obtained by inverse distance weighting (IDW) interpolation for six elements from the DEC (2010) list (As, Cd, Cu, Ni, Pb and V). The same maps for all 59 elements are available in the Supplementary material (Fig. 2SM). These maps document the spatial variation of these elements at the continental scale and can be used to locate at a glance areas where concentrations may exceed various thresholds (see next Section and Table 2).

Fig. 3a shows two CP distribution diagrams (Cd and Pb) demonstrating what information can be interpreted from them. Note that by changing one or both of the scales on these diagrams quite a different and detailed impression of different parts of the data structure can be gained (see Fig. 3.12 in Reimann et al., 2008). The CP diagrams for the other 12 of the 14 elements for which EIL values (DEC, 2010) exist are shown in Fig. 3b. The location of the Median + 2 MAD threshold value is marked in these diagrams in addition to the 98th percentile, the TIF and the EIL. Cumulative probability distribution diagrams for all elements can be found in the Supplementary material (Fig. 3SM).

The EILs of the 14 elements for which DEC (2010) had defined EILs or HILs are displayed in Table 2 in relation to basic statistics and results from different techniques to derive a threshold (Mean + 2 SD, Median + 2 MAD, TIF, CP, 90th, 95th and 98th percentile).

Fig. 4 presents six maps showing the location of all samples with values exceeding various thresholds as discussed herein. In all these maps, the symbol is outlined by a black line if the concentration in Tc is greater than in Bc ($\text{Tc/Bc} > 1$). Figs. 4a,b,c relate to samples above the EIL thresholds (DEC, 2010). Due to the high proportion of samples above the EIL for Mn and V separate maps are shown for these two elements (Figs. 4a,b). The distribution of felsic-to-mafic, mafic and ultramafic igneous rocks is also shown in these two maps (see also Fig. 1a).

Fig. 5a shows a comparison of element levels and variation between the different Australian States in the form of boxplots (Tukey, 1977). Fig. 5b does not use the artificial State boundaries for this comparison but rather the boxplots are constructed by geological regions (Blake and Kilgour, 1998).

Table 3 shows the median values of the Tc samples of the whole Australian dataset in comparison to those for Tasmania only, results from a southernmost New Zealand soil survey (Martin et al., 2015) and the European GEMAS survey (Reimann et al., 2014a, 2014b). For ease of comparison the median ratios between these different surveys are also provided.

4. Discussion

4.1. Regional distribution

The maps in Fig. 2 clearly illustrate how background values (i.e., those below a specified threshold such as EIL) vary substantially across the continent and are far from constant even at the State scale. In many cases, geochemical patterns conform well to geological regions (e.g.,

Table 1

Statistical summary of aqua regia soluble concentration of 14 elements in coarse fraction (<2 mm) sample types of the NGSAs Top Outlet Sediment (Tc; 0–10 cm) and Bottom Outlet Sediment (Bc; ~60–80 cm). The number of samples analysed (N), the lower limit of detection (LLD) and the number and proportion of samples <LLD are given for each element. The observed minimum (Min), 25th percentile, 50th percentile (Median), 75th percentile and maximum (Max) concentrations of the dataset are presented. The correlation coefficient *r* between the Tc and Bc sample types (based on log-transformed data) and the ratio Tc/Bc calculated for the median and the 98th percentile are also shown. For statistical analysis, values <LLD were replaced by 2/3 LLD, and those >ULD were replaced by 3/2 ULD. (Table 1SM in Supplementary material has additional information for all 59 elements).

Element	LLD	TYPE	N	N < LLD	% < LLD	Min	Percentile			Max	<i>r</i> (LogTc vs LogBc)	MedTc/MedBc	98%Tc/98%Bc
							25%	50%	75%				
	(mg/kg)				(%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)				
As	0.1	Tc	1313	52	4	<0.1	0.9	1.6	2.9	218			
As	0.1	Bc	1314	35	3	<0.1	1.1	2	3.4	79	0.74	0.80	0.83
Ba	0.5	Tc	1313	1	0	<0.5	30.6	66.8	118	466			
Ba	0.5	Bc	1314	3	0	<0.5	34.5	70.1	124	612	0.76	0.95	1.04
Cd	0.01	Tc	1313	245	19	<0.01	0.02	0.04	0.07	5.09			
Cd	0.01	Bc	1314	323	25	<0.01	0.01	0.03	0.05	7.52	0.58	1.33	1.44
Co	0.1	Tc	1313	6	0	<0.1	2.6	6.3	10.8	70.1			
Co	0.1	Bc	1314	9	1	<0.1	3.2	6.8	10.8	141	0.78	0.93	0.95
Cr	0.5	Tc	1313	2	0	<0.5	14.9	23.6	37.4	1660			
Cr	0.5	Bc	1314	3	0	<0.5	16.7	26	39.7	1310	0.83	0.91	0.91
Cu	0.01	Tc	1313	4	0	<0.01	5.42	11.2	18	150			
Cu	0.01	Bc	1314	6	0	<0.01	6.26	11.85	18.38	670	0.78	0.95	1.07
Hg	0.01	Tc	1313	473	36	<0.01	<0.01	0.01	0.03	3.07			
Hg	0.01	Bc	1314	505	38	<0.01	<0.01	0.01	0.02	0.26	0.35	1.00	1.50
Mn	1	Tc	1313	1	0	<1	109	281	486	3740			
Mn	1	Bc	1314	5	0	<1	96	246	452	4090	0.80	1.14	1.13
Mo	0.01	Tc	1313	72	5	<0.01	0.11	0.2	0.35	18.2			
Mo	0.01	Bc	1314	69	5	<0.01	0.13	0.23	0.41	63.7	0.65	0.87	0.82
Ni	0.1	Tc	1313	10	1	<0.1	4.6	9.8	17	387			
Ni	0.1	Bc	1314	8	1	<0.1	6	11.6	18.5	458	0.79	0.84	0.91
Pb	0.01	Tc	1313	2	0	<0.01	3.95	7.22	11.2	1090			
Pb	0.01	Bc	1314	1	0	<0.01	4.16	7.36	10.9	789	0.82	0.98	1.21
Sn	0.05	Tc	1313	31	2	<0.05	0.4	0.65	0.99	73.2			
Sn	0.05	Bc	1314	21	2	<0.05	0.47	0.72	1.04	67	0.64	0.90	1.03
V	1	Tc	1313	6	0	<1	20	32	50	469			
V	1	Bc	1314	6	0	<1	24	39	56	389	0.76	0.82	0.94
Zn	0.1	Tc	1313	50	4	<0.1	13.4	26.3	43.5	262			
Zn	0.1	Bc	1314	45	3	<0.1	13.7	26.1	41.8	330	0.66	1.01	1.14

Pilbara geological region is elevated in Ag, Cd, Cu, Ni and V; Eucla geological region is depleted in Ag and V, and elevated in Cd, Cu, Ni and Pb; and Paleozoic-SE geological region is elevated in Ag, Cd, Ni and Pb; see Fig. 1a for geological regions names and boundaries). This attests to a fundamental control on surface soil geochemistry from the underlying or catchment lithology. Other processes are also visible, including surface lateral transport by water (fluvial) and/or wind (aeolian) (e.g., smearing of elevated Cu concentrations from the base metal-rich Isa geological region (Queensland) east and southeast into the neighbouring Carpentaria and Eromanga geological regions. No pattern that could be linked to a broad scale contamination problem of the Australian Top Outlet Sediments by PTEs is evident. However, some of the high values observed may be linked to local contamination sources. These maps (Fig. 2 and Fig. 2SM) could be used to select areas for mineral exploration surveys based on geological models without any further statistical treatment. The potential of these data in terms of use for mineral exploration purposes will be discussed in a separate article. In the remainder of this paper, different methods used to derive threshold values in order to identify sites that need further attention from an environmental point of view and their suitability to detect contamination will be discussed and compared to the DEC (2010) EILs.

4.2. Exceedances of different threshold values

The diagrams in Fig. 3a,b show that the Median + 2 MAD approach to defining a threshold based on the original (non-transformed) data indeed results in low values, commonly around the 90th percentile. The EILs defined by DEC (2010) often sit close to the 98th percentile; it seems possible that not only toxicological but also statistical considerations influenced their definition. There are two elements, namely Mn and V (see Fig. 3b), for which the EIL is, however, very low and coincides approximately with the 75th percentile of the data distribution. A break in the data distribution quite often occurs near the 98th percentile (the

values for the CP breaks are given in Table 2). It is also possible to assess whether a given soil layer, Tc or Bc, is generally enriched in an element, and in which layer the most extreme outliers occur. Cadmium and Hg are the two elements generally slightly enriched in the Tc compared to the Bc samples (see also Tc/Bc ratios in Table 1). Arsenic and Hg are the two elements where the Tc samples show the strongest deviation from the Bc samples in terms of 'extreme outliers'. Fig. 3 demonstrates the power of using the CP distribution diagram for identifying 'unusual samples' and interesting geochemical processes in a given dataset.

Table 2 demonstrates that quite a range of values can be obtained depending on the method used to define a geochemical threshold. Together with the 90th percentile, the Median + 2 MAD consistently delivers the most conservative estimates, i.e., it results in a high number of sites that would require further investigation. By contrast the TIF method does not assume the presence of outliers and, depending on the data distribution, no outliers may be defined (e.g., see Ba and Mn in Table 2). Table 2 and Fig. 3 demonstrate that the 98th percentile often coincides with a break in the CP distribution, which an expert may pick as the threshold. Moreover the EIL is often close to the 98th percentile of the data distribution for the Tc samples. Manganese and V (Fig. 3b) are two examples where the EIL identifies a very high number of samples as being above threshold (discussed below in relation to their spatial distributions). It is apparent that the chosen EILs for these two elements do not reflect the Australian background variation. In general it can be concluded that either the CP breaks, the TIF or the 98th percentile appear to deliver the most appropriate threshold values for differentiating between 'background' and 'follow-up being required'. Relevant authorities could of course define a more conservative level at the 95th percentile or even 90th percentile. This would result in more sites needing to be assessed before any decision about further action can be taken. Defining higher values, where possible based on toxicological considerations, could be used to reduce the number of sites requiring a further check. Table 2SM in the Supplementary material

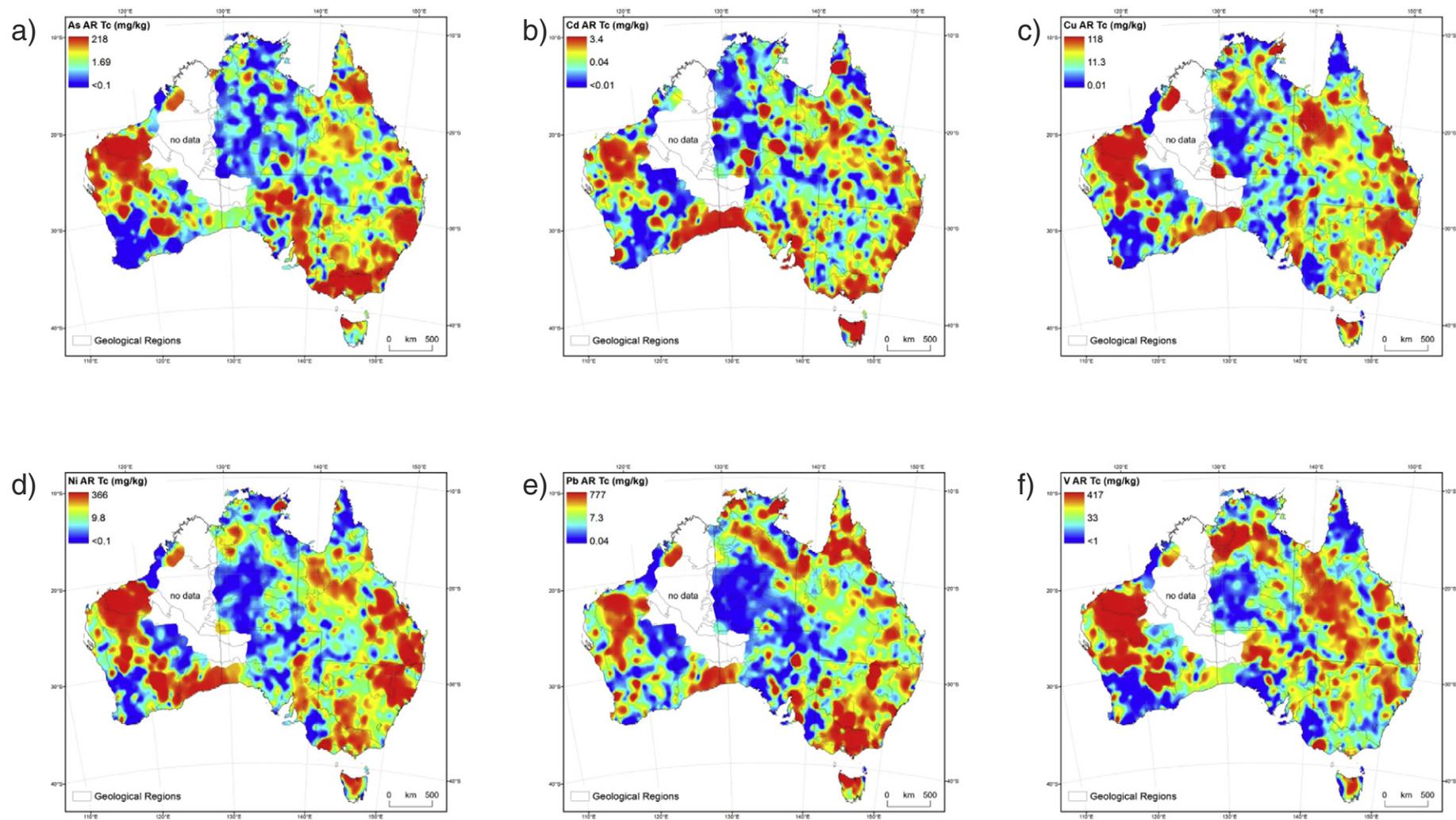


Fig. 2. Inverse distance weighting raster maps of Australia showing the distribution of (a) As, (b) Cd, (c) Cu, (d) Ni, (e) Pb and (f) V in the coarse (<2 mm) fraction of NGS's Top Outlet Sediments (Tc) after aqua regia (AR) digestion (in mg/kg). Geological regions are shown as grey polygons (see Fig. 1a). (Fig. 2SM in Supplementary material contains the same information for all 59 elements). Sources: Blake and Kilgour (1998), Caritat and Cooper (2011a).

Table 2
Comparison of Finland's (MEF, 2007) threshold values (Thresh) and lower guideline values (LGV), Australia's (DEC, 2010) ecological investigation levels (EIL) and health investigation level class 'E' (HIL 'E'), and various statistical methods of deriving thresholds discussed herein (Mean + 2 SD, Median + 2 MAD, 95th percentile, 98th percentile, Tukey's inner fences (TIF) and analysis of cumulative probability (CP) distribution diagrams) for 14 elements with available EILs DEC (2010) in NGSAs Top Outlet Sediment (TOS; 0–10 cm) coarse fraction (<2 mm) samples. Also given are the numbers of samples above the various possible threshold values. (Table 2SM in Supplementary material has additional information for all 59 elements).

Element	Finland		Australia		Possible threshold values based on NGSAs data						Number of exceedances above						
	Thresh	LGV	EIL	HIL 'E'	Mean + 2 SD	Med + 2 MAD	95%	98%	TIF	CP	EIL	Mean + 2 SD	Med + 2 MAD	95%	98%	TIF	CP
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
As	5	50	20	200	18.5	3.4	7.1	11.1	16.8	12.6	12	13	248	65	26	15	18
Ba			300		222	149	204	275	894	296	18	53	196	66	27	0	18
Cd	1	10	3	40	0.4	0.1	0.2	0.3	0.5	0.3	1	17	180	66	27	16	22
Co	20	100	50	200	21	14	19	24	91	31	3	49	171	65	27	0	6
Cr	100	200	400	200	186	44	93	139	149	155	7	21	250	66	27	24	22
Cu	100	150	100	2000	39	24	34	50	109	60	4	46	176	65	27	1	12
Hg	0.5	2	1	30	0.2	0.01	0.06	0.09	0.29	0.13	1	5	643	41	20	3	11
Mn			500	3000	1057	653	929	1288	4576	1110	313	47	192	66	27	0	37
Mo			40		1.9	0.4	0.8	1.4	2.0	1.4	0	13	236	64	26	12	26
Ni	50	100	60	600	50	21	37	56	121	70	24	33	217	66	26	5	13
Pb	60	200	600	600	76	14	20	28	53	33	1	6	180	66	26	9	17
Sn			50		7.3	1.2	1.6	2.1	3.9	2.7	2	7	202	66	27	11	17
V	100	150	50		101	62	86	118	198	94	325	37	175	64	27	6	40
Zn	200	250	200	14,000	84	55	71	93	254	120	3	38	187	66	27	1	15

provides these different possible threshold values at the Australian scale for all 59 analysed elements, including many emerging 'high-tech' critical elements such as Be, Dy, Er, Eu, Ga, Gd, Ge, Ho, Nb, Nd, Pr, Sm, Tb, Te, Tm, Y and Yb.

In general a statistical threshold, independent of how it is determined, will not identify areas that are 'clearly contaminated' or that 'must be explored' or where the element concentration is toxic. A geochemical threshold merely draws attention to a certain number of sites that show unusual element concentrations. Further action must then be decided upon on a case by case basis, requiring expert judgment. Depending on circumstances, the decision may well be 'no action required'.

A different approach is to define threshold values that are not (solely) based on statistical considerations of survey data but rather on toxicological considerations (e.g., DEC's (2010) EILs or HILs – ecological or health investigation levels). Unfortunately, different values will emerge depending on what is to be protected (i.e., crops, invertebrates, or humans) and the approach can even result in action levels well within the natural background range (see Mn and V in Fig. 4a,b). For a toxicological evaluation to be relevant it must explicitly account for the high natural variability of element concentrations across a continent (see maps in Fig. 2) or be carried out on a much more local scale (e.g., geological or ecological region). This is important, as there may be different biological communities tolerant to local conditions forming healthy ecosystems in different background areas; and, to be realistic and relevant, ecotoxicological studies should be undertaken on those species in appropriate ambient conditions. The result would be many different EILs depending on the region. Consequently a single toxicologically based EIL for a whole continent may be even more difficult to handle than a statistically derived threshold.

Action levels are based on a political decision and local experience, and often not so much on science. Reimann et al. (2014b Appendix A) present a table of soil guideline values defined in the different countries of the European Union. Differences between the guideline values in these countries can be a factor of 20 and more (e.g., for As: 10–200, Cd: 0.5–20, Cr: 30–1000, Hg: 0.5–80, Pb: 40–750). In Finland, the Ministry of the Environment (MEF, 2007) has defined lower guideline values (LGV), which, in terms of how they are derived, should be quite comparable to DEC's (2010) EILs. When such values exist the sites where they are exceeded can easily be identified. This blanket analysis, however, can result in a large part of any survey area emerging as above threshold (e.g., V in the current study, for which the Western Australian EIL is by a factor of two and three smaller than the Finnish threshold and LGV,

respectively; see Table 2). The same is true for the maps presented in Tóth et al. (2016) for Europe, where an unsuitable set of threshold values for the continent, as defined in a northern European country (Finland), was used to argue that a major contamination problem exists at the European scale. It should be noted that the Finnish documentation accompanying the table of threshold values clearly addresses the problem of a locally varying background, as it states: 'The background concentration is regarded as the assessment threshold in areas with a background concentration higher than the threshold value'. Thus one is back to the question of how to reliably determine a geochemical background.

Yet another approach is the site specific risk assessment as carried out by the European metals industry in the EU to meet REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) requirements (EC No 1907, 2006). This approach acknowledges that a site specific risk assessment has to be carried out because the spatial variation of soil parameters such as cation exchange capacity, total organic carbon, grain size (especially clay content) and pH will all have an impact on the availability of metals in soil. It thus requires that all these parameters be determined, in addition to the chemical element in question. Furthermore the calculation has to be carried out for each site and results in a new set of risk characterisation maps (e.g., Demetriades, 2011; Oorts and Schoeters, 2014; Birke et al., 2016).

All methods will deliver a number – but what does that number mean? In the end it is a value to which old or new results can be compared to study whether they are within a reasonable range and to identify 'unusual' results but nothing a sound political decision should be blindly based on. Ideally threshold or guideline value selection should include, or be put in the context of, 1) statistical differences, 2) toxicology, 3) compatibility at a continental or regional scale, 4) local factors such as geology and climate, and 5) land use.

4.3. Spatial distribution of the various threshold exceedances

A large number of samples with Mn or V values above the EIL threshold is observed (Fig. 4a,b). There is a striking spatial coincidence between these exceedances and the distribution of lithologies likely to naturally contain elevated concentrations of these elements, such as mafic rocks and sedimentary rocks (basalt, gabbro, ultramafic rocks, shale, greywacke and carbonate are noted for their elevated Mn and V concentrations; Reimann and Caritat, 1998). For instance for V, of the 325 occurrences above the EIL (50 mg/kg), 188 come from catchments that intersect a mapped mafic lithological unit, and an additional 77 come from sedimentary geological regions. Noting the likely under-

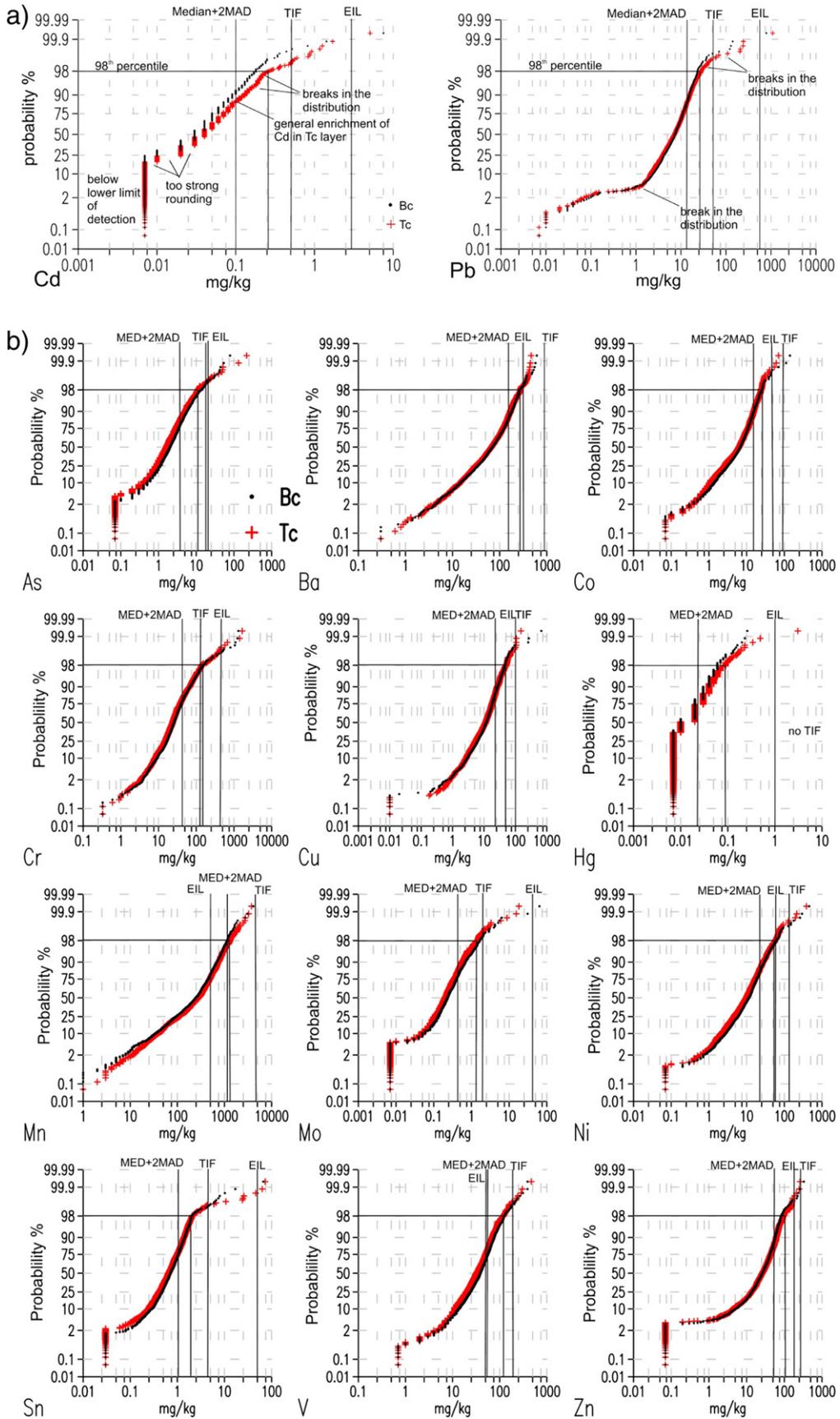


Fig. 3. Cumulative probability distribution diagrams for 14 elements ((a) Cd and Pb; (b) As, Ba, Co, Cr, Cu, Hg, Mn, Mo, Ni, Sn, V and Zn) in the coarse (<2 mm) fraction of NCSA's Top Outlet Sediments (Tc; red pluses) and Bottom Outlet Sediments (Bc; black dots) after aqua regia digestion (in mg/kg). Ecological investigation level (EIL), Median + 2 MAD and Tukey inner fence (TIF) are indicated by vertical lines; the 98th percentile is shown as combined horizontal and vertical lines. (Fig. 3SM in Supplementary material supplies CP diagrams for all 59 elements). Sources: DEC (2010), Caritat and Cooper (2011a).

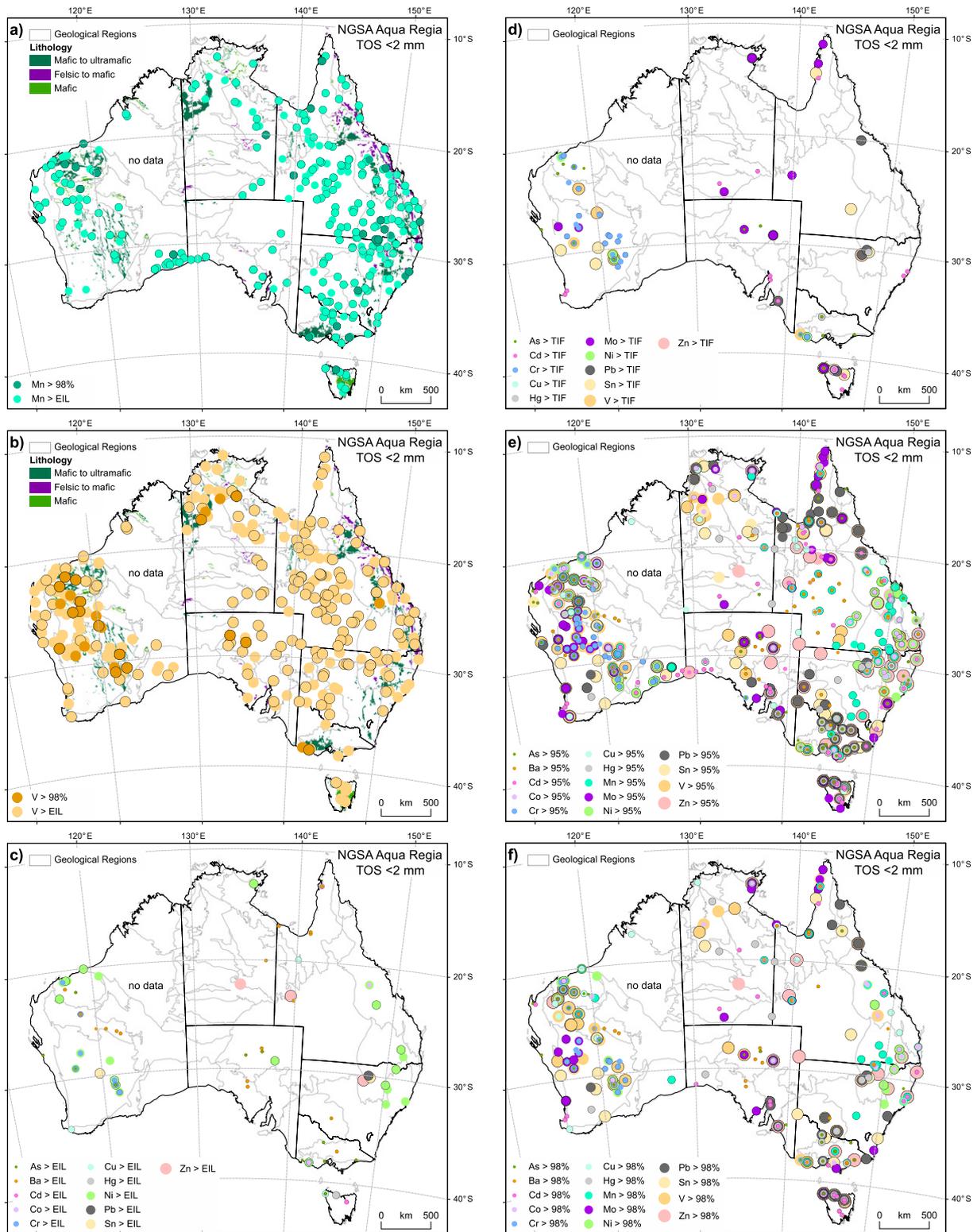


Fig. 4. Dot maps of Australia showing the location of samples exceeding the DEC (2010) EILs for (a) Mn, (b) V, (c) all other elements with at least one sample exceeding the EILs, (d) the TIF, (e) the 95th percentile, and (f) the 98th percentile of the distribution in the coarse (<2 mm) fraction of NGS's Top Outlet Sediments (Tc) after aqua regia (AR) digestion. A solid outline to the symbol indicates that concentration in Tc is greater than in the corresponding Bc. For the maps of Mn and V exceeding the EILs, a darker coloured symbol indicates where the concentration in Tc also exceeds the 98th percentile of the distribution. Geological regions are shown as grey polygons (refer to Fig. 1a). Sources: Blake and Kilgour (1998), Caritat and Cooper (2011a), DEC (2010).

representation of mapped outcrops of mafic lithologies in the continental-scale surface geology dataset, and the fact that additional samples with high Mn or V concentrations come from catchments immediately downstream from those containing the above lithologies, the vast

majority of these exceedances is attributed to natural, geological processes. The high proportion of sites exceeding the EIL thresholds for Mn and V indicates that these EILs are set too low for the natural conditions in Australia. In such a case, attempting to remediate these sites to

values below EILs would be both ruinous and futile. In these two maps (Fig. 4a,b) the samples that also have a concentration above the 98th percentile are additionally highlighted by a darker coloured symbol, indicating where the more outlying sites occur. Most of these sites are clearly related to geology. In Europe V was the element that best indicated the occurrence of basalts and the presence of volcanic activity (Reimann et al., 2014a).

Fig. 4c presents the location of the sample sites where the concentration for at least one of the 12 remaining elements is above the EIL (i.e., all except Mo). It shows that only few spatially isolated sites, as opposed to clusters or whole regions, have concentrations above DEC's (2010) investigation levels. This would be expected to change drastically if a contaminated site were studied at the local scale (e.g., tens to thousands of samples per km²). However, at the continental scale it emerges that

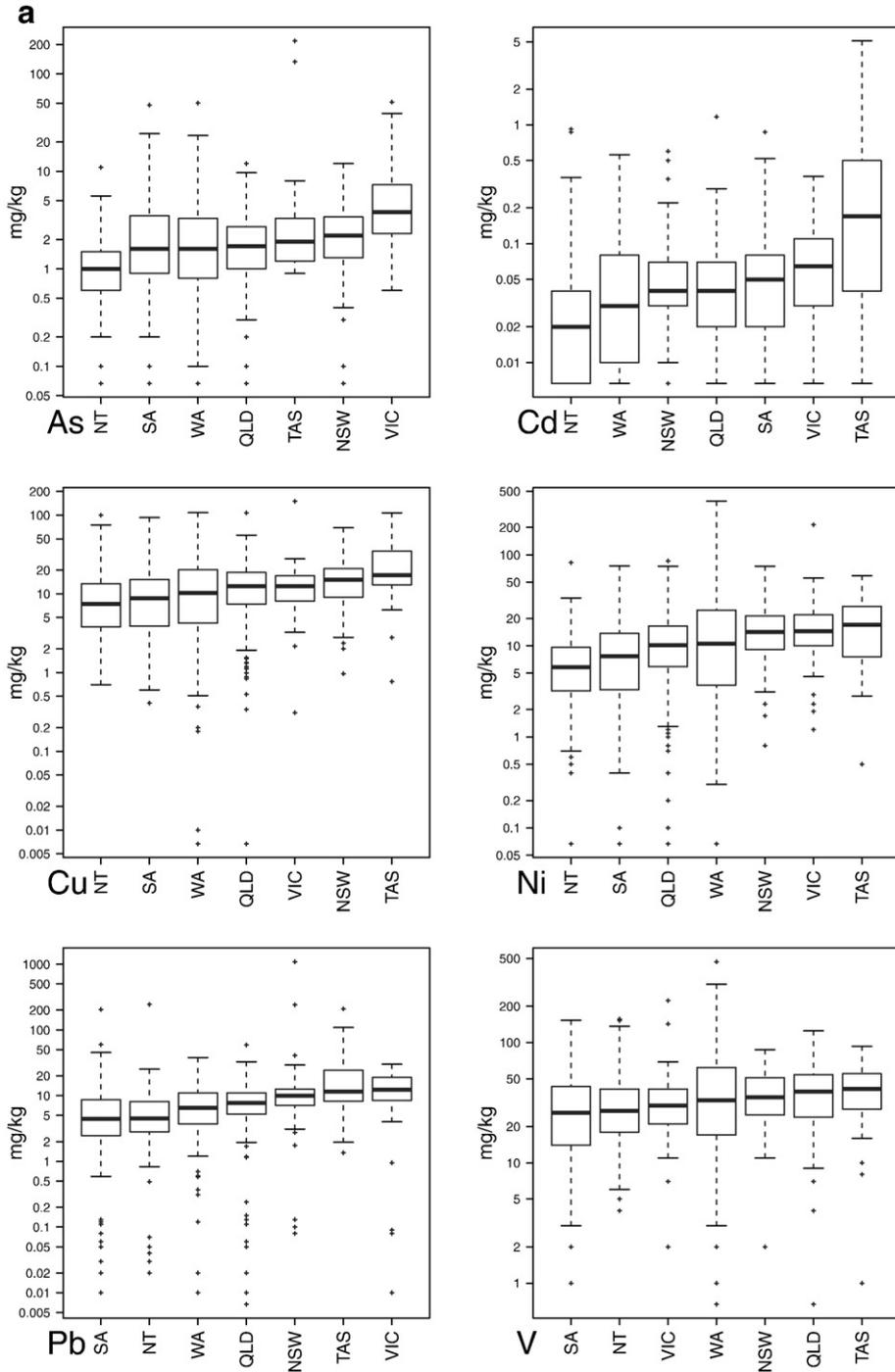


Fig. 5. Boxplots for six elements (As, Cd, Cu, Ni, Pb and V) in the coarse (<2 mm) fraction of NGSa's Top Outlet Sediments (Tc) after aqua regia (AR) digestion grouped by (a) State/Northern Territory and (b) by geological regions ordered by increasing median value. Only those geological regions with 10 or more samples were included in (b). Abbreviations for (a) are NSW = New South Wales, NT = Northern Territory, QLD = Queensland, SA = South Australia, TAS = Tasmania, VIC = Victoria, and WA = Western Australia. Abbreviations for (b) are ADE = Adelaide, ALF = Albany-Fraser, AMA = Amadeus, ART = Arunta-Tanami, CAN = Canning, CAP = Capricorn, CAR = Carpentaria, ERO = Eromanga, EUC = Eucla, GAW = Gawler, GEO = Georgina, McA = McArthur, MUR = Murray, OFF = Officer, OTW = Otway, PIC = Pine Creek, PIL = Pilbara, PIN = Pinjarra, PQL = Paleozoic-Queensland, PSE = Paleozoic-Southeast, SUR = Surat, TAS = Tasmania, VIC = Victoria, WIS = Wiso, and YIL = Yilgarn. Geological regions are shown as grey polygons in Fig. 1a. (Figs 5SMA and 5SMB in Supplementary material present the same information for all 59 elements). Sources: Blake and Kilgour (1998), Caritat and Cooper (2011a), DEC (2010).

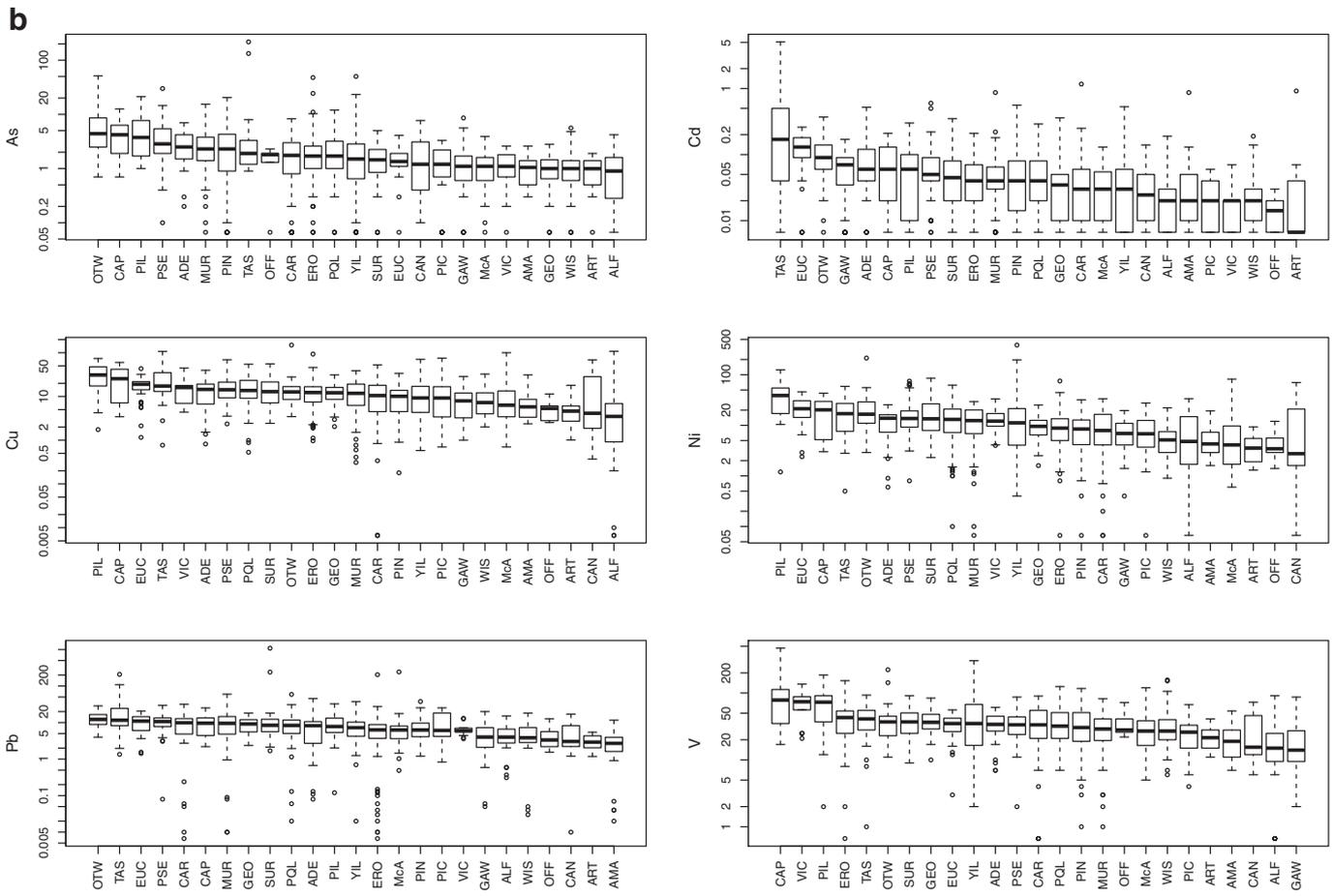


Fig. 5 (continued).

Australian soils as represented by catchment outlet sediments are generally below the EILs (except for Mn and V as discussed previously). No indication of systematic soil contamination via long range transport of PTEs is visible here or in any of the geochemical maps displayed in Fig. 2 or Fig. 2SM. The few high levels observed are most often due to

mineralisation or bedrock (e.g., Cu, Co, and Ni in the vicinity of mafic/ultramafic rock outcrops). In some cases these might be enhanced by human activities at a local scale (e.g., through mining). In general it would be very difficult to determine whether an observed high concentration is due to the presence of mineralisation in any one catchment or

Table 3
Comparison of median Top Outlet Sediment (TOS; 0–10 cm) coarse fraction (<2 mm) samples (Tc) for the whole NGS dataset (Aus) and for Tasmania (Tas) only, southernmost New Zealand (NZ) soil, and GEMAS Ap samples, as well as their various ratios for 20 elements including those with available EILs. Sources: DEC (2010), Caritat and Cooper (2011a), Reimann et al. (2014a, 2014b), Martin et al. (2015).

Element	Med Tc Aus (mg/kg)	Med Tc Tas (mg/kg)	Med NZ Soil (mg/kg)	Med GEMAS Ap (mg/kg)	MedTcAus/MedTcTas	MedTcAus/MedNZ	MedTcAus/MedAp	MedNZ/MedAp
Ag	0.012	0.025	0.037	0.038	0.5	0.3	0.3	1.0
As	1.6	1.9	3.7	5.5	0.8	0.4	0.3	0.7
Ba	67	59	54	62	1.1	1.2	1.1	0.9
Cd	0.04	0.17	0.06	0.18	0.2	0.7	0.2	0.3
Co	6.3	12.4	4.7	7.5	0.5	1.3	0.8	0.6
Cr	24	28	13	20	0.8	1.8	1.2	0.7
Cu	11	17	11	15	0.6	1.0	0.7	0.7
Hg	0.01	0.05	0.06	0.03	0.2	0.2	0.3	2.1
Mn	281	534	329	445	0.5	0.9	0.6	0.7
Mo	0.20	0.51	0.31	0.42	0.4	0.6	0.5	0.7
Ni	10	17	8	15	0.6	1.3	0.7	0.5
Pb	7	12	11	16	0.6	0.7	0.5	0.7
Sb	0.12	0.11	0.11	0.23	1.1	1.1	0.5	0.5
Se	0.06	0.16	0.40	0.35	0.4	0.2	0.2	1.1
Sn	0.65	0.80	0.80	0.72	0.8	0.8	0.9	1.1
Tl	0.08	0.06	0.08	0.12	1.3	1.0	0.7	0.7
U	0.5	0.8	0.7	0.8	0.6	0.7	0.6	0.9
V	32	41	34	25	0.8	0.9	1.3	1.4
Zn	26	47	47	45	0.6	0.6	0.6	1.0
Zr	3.2	1.2	0.7	1.8	2.7	4.6	1.8	0.4

enhanced by anthropogenic activities due to mining or smelting. None of the highly populated areas (e.g., Sydney, Melbourne, Brisbane, Perth or Adelaide, with populations ranging from 4.8 to 1.3 million; ABS, 2015) is marked by a large number of regional or even local anomalies. Only very few PTE values in excess of EILs correspond spatially to major infrastructure/industry centres: one Hg anomaly (Burnie, western north coast of Tasmania), one As anomaly (Anglesea, central south coast of Victoria), a second As anomaly (Portland, western south coast of Victoria), and one Ni + Cr anomaly (Port Walcott, on the coast of northwestern Western Australia). Although establishing a causative link would require more detailed information to be collected and analysed, it is noted that known industry (e.g., paper pulp mill, brown coal fired power plant, aluminium smelter, and iron ore shipping port, respectively) operates within the catchment area of these locations. Catchment outlet sediments may be more sensitive to contamination than the GEMAS topsoil samples because they are more representative of a whole catchment basin.

In addition to the EILs, DEC (2010) also defined 'health investigation levels' (HILs). These differ considerably according to land use. Separate classes exist for residential soil (class 'A'); residential soil with minimal opportunities for soil access (class 'D'); parks, recreational open space and playing fields (class 'E'); and commercial/industrial sites (class 'F'). Class 'E' is probably the best fit for the catchment outlet sediments discussed here, but even if the most vulnerable class 'A' is considered very few sites above the HIL emerge. These include 17 sites for Mn above the class 'A' level of 1500 mg/kg (only two sites above class 'E' level of 3000, none above class 'D' or 'F' levels of 6000 and 7500 mg/kg, respectively). The majority of these Mn exceedances appear to relate to geology, i.e., there are mafic/ultramafic igneous rocks in their vicinity, or within sedimentary basins. Note that for the European GEMAS survey (Reimann et al., 2014a) about 5% of all samples would report Mn concentrations above the HIL class 'E' level. In Australia exactly one site each exceeds both the class 'A' and the class 'E' level for the two PTEs As (100 and 200 mg/kg, respectively) and Pb (300 and 600 mg/kg, respectively). These two anomalies, which are the maximum values recorded for these two elements (218 mg/kg As and 1090 mg/kg Pb; see Table 1) are located in northern Tasmania (Arthur River catchment; mostly forested) and northern New South Wales (Barwon catchment; mostly dryland agriculture). These sites are not associated with industrial activity and are thought to potentially represent a local contamination source. Follow-up detailed investigation may elucidate the reason(s) for these concentrations being above the HILs.

Fig. 4d presents the location of the sample sites where the concentration is above the TIF for at least one element from the EIL list. No TIF exceedances were found in the dataset for Ba, Co and Mn (hence only 11 elements are plotted). In Western Australia (Pilbara, Capricorn and Yilgarn geological regions) sites with TIF exceedances are clearly related to geology. Chromium, Ni and V all point at the occurrence of mafic/ultramafic rocks here (see Fig. 1a) and possibly mineral deposits (see Fig. 1b). A few of the heavy industry localities noted previously for EIL exceedances, also have values >TIF, e.g., the bulk commodity cargo loading terminal of Port Walcott in northwestern WA and the paper mill town of Burnie in northern Tasmania, among a few other anomalies along that coast. Again no >TIF anomalies are associated with major population centres.

The last two maps present the locations of samples above the 95th percentile (Fig. 4e) and the 98th percentile (Fig. 4f) of the distributions for the same 14 elements. They document a substantially larger number of sites requiring further investigation, especially for the map of 95th percentile sites (Fig. 4e). Such a number of highlighted sites is almost impossible to deal with and follow up properly without some major prioritisation. In the more manageable 98th percentile map (Fig. 4f), three roughly north-south zones with a number of high element concentrations appear, the first comprising the Yilgarn, Capricorn, and Pilbara geological regions, the second running through central Australia, and the third running up the east coast; the latter two zones cut across

many geological regions. Because these three zones are still only comprised of individual sites separated by 'normal' sites, this does not suggest wholesale regional elevated concentrations. Interestingly some of the highly populated areas, e.g., the surroundings of Melbourne, are marked by a number of anomalies here. Still, each one of these would need to be followed up with at least a higher density geochemical survey before a determination on its cause and potential need for action could be taken. This map may be the most useful for the explorer looking for anomalies that may be due to the occurrence of mineralisation.

The number of exceedances reported here varies dramatically depending on the threshold chosen (Table 2). The largest number of instances of threshold exceedances were found in the case of Median + 2 MAD method (3253), followed by the 95th percentile (892), EIL (714, of which 638 are for Mn and V combined), Mean + 2 SD (385) followed very closely by the 98th percentile (367), CP (274), while the least instances were found for the TIF threshold (103), which is close to the EIL if Mn and V are not considered.

4.4. Comparison between states and the Australian background

Fig. 5 presents boxplots comparing the median and range of six key elements between the Australian States/Northern Territory (Fig. 5a) and between the geological regions (Fig. 5b). The grouping by State/Territory is useful when it comes to legislation that depends on State government policies (e.g., Environment Protection Act 1970 in Victoria) rather than Commonwealth (Federal) legislation (e.g., Environment Protection and Biodiversity Conservation Act 1999).

One of the surprising results of the European GEMAS project (Reimann et al., 2014a, 2014b) was the large difference in concentrations for many elements between the younger and less weathered soils of northern Europe compared to the older and more weathered soils of southern Europe. For many elements there was a factor of two to three times difference even for the median concentrations between northern and southern Europe (Reimann et al., 2014a). This indicates that for Europe it is not realistic to establish a single threshold value identifying 'unusually high' element concentrations at any one sample site. Despite being artificial to a large extent, a comparison of element concentrations for PTEs according to political borders was of importance for the European administration. In Europe the difference between countries is substantial – on average a factor of 5 and ranging from 2.5 to 133 for the median values (Reimann et al., 2014a). Such large differences prohibit the definition or use of a single threshold value. However, statistically derived background values have often been used in legislation to differentiate between 'natural background' and 'potentially contaminated sites'.

Comparing the analytical results of the six Australian States/Northern Territory via boxplots (Fig. 5a), the median Tc values vary between the States between a factor of 1.6 (Median V in Tasmania/Median V in South Australia) to 8.5 (Median Cd in Tasmania/Median Cd in Northern Territory), with the majority of elements showing a factor of 2–4 difference. This range is small compared to the variation of the country medians in Europe. In that context it is perhaps more meaningful to consider a single set of continental thresholds for Australia than for Europe. To some extent this is, however, a reflection of the large size of Australian jurisdictions compared to the geological variability. The highest medians for the six elements in Fig. 5a all come from Tasmania (Cd, Cu, Ni and V) or Victoria (As and Pb); the lowest are from the Northern Territory (As, Cd, Cu and Ni) or South Australia (Pb and V).

If the same boxplots are constructed by geological region (Blake and Kilgour, 1998), it becomes apparent that there is a more marked (and expected) variation in median (and range) values for the PTEs (Fig. 5b). This suggests that geological substrate (i.e., the ultimate source of clastic detritus) does control to a considerable extent the trace element composition of the overlying catchment sediments, consistent with the findings of Caritat and Grunsky (2013). In contrast to the

political boundary based boxplots in Fig. 5a, the median values in Tc by geological region (ignoring elements with >50% of values <LLD) range from 3.6 (median Sn in Eucla geological region/median Sn in Albany-Fraser geological region) to 637 (median Ca in Eucla geological region/median Ca in Officer geological region), with the median ratios for most elements being between 8 and 25. The highest medians for the six elements in Fig. 5b come from the following geological regions: Otway (As, Pb), Tasmania (Cd), Pilbara (Cu, Ni), and Capricorn (V); the lowest are from Albany-Fraser (As, Cu), Arunta-Tanami (Cd), Canning (Ni), Amadeus (Pb), and Gawler (V). An alternative grouping of the data could also be by ecoregions (DEE, 2016) rather than geological regions, from which various thresholds (98th percentile, TIF, CP) could be derived.

If threshold values are calculated State by State, as might be envisaged for environmental regulatory purposes, large differences emerge for some elements. For example for As a 98th percentile threshold would vary from 3.9 mg/kg in the Northern Territory to 184 mg/kg in Tasmania (compared with 11 mg/kg for the whole country, or 20 mg/kg for the EIL). This highlights the problems with the definition of a meaningful threshold (discussed in Section 4.2 above).

4.5. Comparison of Tc/Bc ratios

No geochemical threshold as defined herein can distinguish between natural and anthropogenic element provenance. It will only identify samples with an unusually high concentration of any analysed element in a given dataset. Other threshold values will emerge for other datasets or different areas. Many authors (e.g., Facchinelli et al., 2001; Massas et al., 2009; Yang et al., 2009) have suggested that the calculation of ratios of element concentrations observed in topsoil to those in the subsoil (e.g., the soil B or C horizon) from the same location may provide a good indication of contamination. Using this approach the subsoil is assumed to provide the local geogenic background while the topsoil will include an additional input of elements from anthropogenic activities. The Tc/Bc ratio for selected elements from the NGSa dataset is included in Table 1 (and Table 1SM in the Supplementary material for all elements). All median ratios are close to unity, with an average of 0.94. Maps of this ratio (not shown) are very noisy and do not point to any single dominant process (e.g., contamination) causing high values in the Tc/Bc ratio. Not unexpectedly the same is true for maps of the more elaborate element enrichment factors (see Reimann and Caritat, 2000, 2005). When considering the 98th percentile of the Tc/Bc ratio a few elements show a slight enrichment in the Tc sample, namely Hg (1.5), Cd (1.4), Pb (1.21), and Ag (1.16) (see also the CP diagrams in Fig. 3). This slight enrichment may be due to natural or anthropogenic factors which cannot be distinguished by the Tc/Bc ratio alone. For instance some elements, including those above, have a high affinity for organic matter (Goldschmidt, 1937), which is more abundant in Tc than in Bc. To apportion topsoil enrichment to natural processes or anthropogenic contamination, analysis of spatial (horizontal and vertical) variability, potential sources, and historic fluxes, among others, is required.

Reimann et al. (2015) have recently reported large enrichments for similar elements (Cd, Ag, Hg, Sb, Pb and Sn) in Norwegian forest soil far removed from likely contamination sources. Here the median top soil/median bottom soil ratios are 17 for Cd, 11 for Ag, 10 for Hg, 9 for Sb, 4 for Pb and 2 for Sn. These authors attribute the enrichment of these elements at the top of a soil profile to a natural process related to the strong affinity of the enriched PTEs to organic material. This explanation, however, does not necessarily apply to Australian soil. In the mostly hot and dry central Australian climate little to no organic matter accumulates or persists in the upper parts of the soil profile. This might explain the comparatively less significant enrichment of these elements in the Australian topsoil. It is instructive to compare the Tc samples from Tasmania (see State boxplots, Fig. 5a and Fig. 5SMa in the Supplementary material) with topsoils from similar climatic regions. In Tasmania climate and soil are in several aspects more

comparable to those of New Zealand (Martin et al., 2015) or Europe (Reimann et al., 2014a, 2014b) than to most of the mainland of Australia. Table 3 shows such a comparison for 20 elements including those commonly found enriched in topsoil. The samples from a cooler and wetter climate, e.g., Tasmania or New Zealand, are consistently enriched in PTEs such as Cd, Hg, As, and Pb compared to mainland Australia. This is in agreement with the original proposal by Goldschmidt (1937), published nearly 80 years ago, that certain elements have a natural tendency to accumulate with organic material at the top of soil profiles.

The more 'elaborate' (double ratio based) enrichment factors (EFs) do not provide any better results than the direct Tc/Bc ratios, something that has been repeatedly demonstrated in the literature (Reimann and Caritat, 2000, 2005; Sucharova et al., 2012). We have calculated EFs for all elements relative to the reference element Sc and plotted EF maps. These maps (not shown) are in our view noisy and more inconclusive than the single element distribution maps presented in Fig. 2.

5. Conclusions

Maps of 59 elements analysed after aqua regia digestion of the coarse fraction of the top layer of catchment outlet sediments (Tc) collected across Australia during the National Geochemical Survey of Australia can be used to display the background variation of these elements at the continental scale. At present ecological investigation levels (EILs), i.e., thresholds (the upper limit of the background variation) derived with toxicological assessment in mind, are established for but a few potentially toxic elements. In the future such levels will be needed for many more elements, including the critical elements of a 'high-tech' world. For Australia, at the continental scale, breaks in the cumulative probability (CP) distributions, the upper Tukey inner fence (TIF) or the 98th percentile of the Tc dataset can be used as geochemical thresholds for identifying sites that may need further investigation. The TIF values are often surprisingly close to the EILs for those elements where these were defined. Geochemical threshold values are provided here for 59 elements.

All methods of determining a threshold, be they statistical (CP, 98th percentile, TIF) or based on toxicological considerations (most often done in combination with statistical observations of real data variation), come with limitations on their universal application. Ultimately the question is which part of the ecosystem needs protection and where, and that question cannot be answered using a single concentration. To identify unusually high element concentrations in a given dataset the TIF approach is considered here as most easy and straightforward and delivers realistic estimates. Geochemical threshold values from the Australian dataset presented here can be used as a guide to 'what is high' in any other investigation where too few samples were collected to determine the local background for the area under consideration. As opposed to other places, e.g., Europe, it appears that single threshold values for the whole continent make reasonable sense in Australia, although regional studies confined to any given geological region would be well advised to use a threshold determined from that region's data subset.

Studying the distribution of the samples above the established EILs (DEC, 2010) shows that:

- (1) The EILs are unrealistically low for Mn and V, for which a high proportion of samples at the Australian scale (>300 of ~1300) exceed their respective EIL, and that the spatial distribution of these samples is clearly related to geology, and
- (2) for the other 12 elements for which EILs are defined, few sites exceed these levels at the continental scale and most of these can be explained by geological processes.

Analysis of the distribution of sample sites with one or more elements above the EIL reveals no indication of continental-scale contamination. Anomalies occur quite locally and may in some cases be related

to human activities (e.g., mining, heavy industry). Quite often they indicate natural anomalies and might identify areas warranting follow-up mineral exploration activities.

No geochemical threshold value, be it derived statistically or toxicologically, can be used to prove contamination at any scale. Similarly, neither the Tc/Bc (top coarse/bottom coarse) ratio nor the more elaborate enrichment factors are able to deliver any useful and reliable indication of contamination. Ratios of the topsoil results between different provinces and different geochemical surveys from other parts of the world indicate that certain PTEs (e.g., Ag, Cd, Hg, Mo, Pb, Se) are generally enriched in the more organic topsoils that form under cold and wet climatic conditions.

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