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Mikkonen, H., Clarke, B., Dasika, R., Wallis, C., & Reichman, S. (2017). Assessment of ambient background concentrations of elements in soil using combined survey and open-source data. *Science of the Total Environment*, 580, 1410–1420. <https://doi.org/10.1016/j.scitotenv.2016.12.106>
Document Version: Accepted Manuscript

Published Version: <https://doi.org/10.1016/j.scitotenv.2016.12.106>

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Citation:

Mikkonen, H, Clarke, B, Dasika, R, Wallis, C and Reichman, S 2017, 'Assessment of ambient background concentrations of elements in soil using combined survey and open-source data', *Science of the Total Environment*, vol. 580, pp. 1410-1420.

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Version: Accepted Manuscript

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Link to Published Version:

<https://dx.doi.org/10.1016/j.scitotenv.2016.12.106>

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Assessment of ambient background concentrations of elements in soil using combined survey and open-source data

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Paper published in Science of the Total Environment: <https://doi.org/10.1016/j.scitotenv.2016.12.106>

This material should be cited as follows:

Mikkonen, H.G., Clarke, B.O., Dasika, R., Wallis, C.J., Reichman, S.M., 2017. Assessment of ambient background concentrations of elements in soil using combined survey and open-source data. Science of The Total Environment 580, 1410-1420.

Abstract

Understanding ambient background concentrations in soil, at a local scale, is an essential part of environmental risk assessment. Where high resolution geochemical soil surveys have not been undertaken, soil data from alternative sources, such as environmental site assessment reports, can be used to support an understanding of ambient background conditions. Concentrations of metals/metalloids (As, Mn, Ni, Pb and Zn) were extracted from open-source environmental site assessment reports, for soils derived from the Newer Volcanics basalt, of Melbourne, Victoria, Australia. A manual screening method was applied to remove samples that were indicated to be contaminated by point sources and hence not representative of ambient background conditions. The manual screening approach was validated by comparison to data from a targeted background soil survey. Statistical methods for exclusion of contaminated samples from background soil datasets were compared to the manual screening method. The statistical methods tested included the Median plus Two Median Absolute Deviations, the upper whisker of a normal and log transformed Tukey

boxplot, the point of inflection on a cumulative frequency plot and the 95th percentile. We have demonstrated that where anomalous sample results cannot be screened using site information, the Median plus Two Median Absolute Deviations is a conservative method for derivation of ambient background upper concentration limits (i.e. expected maximums). The upper whisker of a boxplot and the point of inflection on a cumulative frequency plot, were also considered adequate methods for deriving ambient background upper concentration limits, where the percentage of contaminated samples is less than 25%. Median ambient background concentrations of metals/metalloids in the Newer Volcanic soils of Melbourne were comparable to ambient background concentrations in Europe and the United States, except for Ni, which was naturally enriched in the basalt-derived soils of Melbourne.

Highlights:

- A framework was developed for collating background soil data from open-sources.
- Statistical methods for exclusion of contaminated results were validated.
- Background metal concentrations for basalt derived soils of Greater Melbourne.

Key words: Ambient background; soil; Upper Concentration Limit; Outliers; Open-source data; Median

Abbreviations: Limit of Reporting (LOR), Median plus two median absolute deviations (Med + 2MAD), cumulative frequency plot (CMF), generalised Wilcoxon (GW), upper whisker (UW)

1 Introduction

Guidance for land contamination assessment in England (DEFRA, 2012), Finland (Tarvainen and Jarva 2011), Italy (APAT-ISS 2006) and Australia (NEPC, 2013) have been revised to include consideration of ambient background concentrations in soil, when assessing environmental risk and the need for remediation. Therefore, knowledge of local soil conditions, including the expected range of background concentrations, is now required for undertaking environmental risk assessments.

Ambient background concentrations of metals and metalloids in soil can be highly variable, due to changes in mineral content, climate, land use, age, soil organisms, vegetation and topography (Jenny, 1941; Prabhakaran Nair and Cottenie, 1971, Reimann et al., 2009, Reimann et al., 2015).

Extensive soil surveys have been undertaken in Australia (de Caritat and Cooper 2011), Asia (Cheng et al., 2014; Ohta et al., 2005), Europe (Reimann et al., 2014, Salminen et al., 2004, Toth et al., 2016) and the United States of America (Smith et al., 2012), to assist in understanding the variability of background concentrations of metals and metalloids at a regional and continental scale (0.5–50 million km²). However, these surveys typically have a low sample density, insufficient for assessing local background variability. For example, the National Geochemical Survey of Australia Project (NGSA) included a sample frequency average of 1 sample site per 5500 km², (de Caritat et al., 2011).

The need for local scale (0.5–500 km²) soil knowledge for development of environmental policy has been recognized in England, resulting in the completion of high resolution soil surveys (1 sample site per 2 km² for rural areas and 4 sample sites per 1 km² in urban areas). These surveys have allowed for “normal background conditions”, defined as the 95th upper confidence limit of the 95th percentile of survey samples, to be estimated for different geological areas and land use domains (Ander et al., 2013). This dataset (Ander et al., 2013) has enabled environmental assessors to identify whether sites are contaminated compared to local conditions, assisting informed decisions for soil management and remediation.

However, undertaking high resolution soil surveys is expensive, time consuming and often logistically constrained due to land access restrictions. Where insufficient background survey results exist (as in Australia), open-sources of soil data, such as Environmental Site Assessment (ESA) reports, may provide useful soil information, which can be used to provide confidence in results from low resolution surveys and support an understanding of soil variability (McIlwaine et al., 2014). Environmental site assessments are undertaken across the world during the investigation, re-development and remediation of land. While ESAs are undertaken at potentially contaminated sites, there are a number of samples typically collected from areas of the sites that have not been impacted by point source contamination and can therefore be considered as representative of ambient background concentrations. In order to utilise open-source data, a method is required for identification of soil samples representative of ambient background concentrations and exclusion of samples impacted by contamination.

Several researchers have described statistical approaches for screening contaminated samples from soil datasets (Matschullat et al., 2000; Reimann et al., 2005; Rothwell and Cooke, 2015). Typically, statistical methods identify an upper concentration limit, above which results are considered “outliers” likely impacted by point source contamination (Dung et al., 2013; Matschullat et al., 2000; Redon et al., 2013). The statistically derived upper concentration limit is considered to represent the expected maximum of background concentrations.

To accurately understand background variability, anomalous results, “outliers”, should be reviewed to identify why each result is elevated; e.g. is the result elevated due to different parent material, laboratory error, or contamination? However, as background datasets are typically large and lacking detailed information on sample history there is often no validation or knowledge-based assessment of samples statistically identified as contaminated. Therefore, the estimated background upper concentration limit is little more than an artifact of the statistical method applied.

The accuracy of common statistical methods for derivation of background upper concentration limits have rarely been validated using real environmental data, particularly for datasets which include a high percentage of contaminated samples. Matschullat et al., (2000) assessed the suitability of three statistical methods for deriving background concentrations (the repeated mean plus 2 standard deviation (σ) technique, the 4 σ outlier test and the calculated distribution function). Matschullat et al., (2000) concluded that the calculated distribution function, which involves prediction of the distribution of the upper 50% of results based on the distribution of the lower 50% of results, and the repeated (iterative) mean plus 2 σ method provided realistic estimates of the range of background

concentrations. However, few background soil surveys have adopted these techniques. Reimann et al., (2005) discussed the strengths and weaknesses of commonly applied statistical methods including the mean plus 2 σ . Reimann et al., (2005) recommended the use of non-parametric methods including the upper whisker of a Tukey boxplot, the median plus 2 median absolute deviation and the point of inflection on a cumulative frequency plot. These methods are also described in the International Organisation of Standardisation guidance on determination of background values (BSI, 2011) and are commonly applied during background geochemical surveys (McIlwaine et al., 2014; Rothwell and Cooke, 2015).

The objectives of this study were to; (i) develop and validate a framework for collating and screening open-source environmental site assessment data, for the purpose of assessing local ambient background concentrations; (ii) use data collated from open-sources to support our understanding of ambient background concentrations of common contaminants As, Mn, Ni, Pb and Zn, in soils derived from Newer Volcanics (basalt) geology in Melbourne, Australia; and (iii) validate common statistical methods for screening contaminated samples from soil datasets for deriving expected maximum background concentrations.

2 Methods

2.1 Definition of Ambient Background Concentrations

The definition of ambient background concentrations is the sum of geogenic concentrations plus concentrations from diffuse anthropogenic contamination that has been introduced from non-point sources (Panno et al., 2006). However, there is lack of consistency on what constitutes diffuse contamination or a point source. For example, the definition provided by the International Organisation of Standardisation for guidance on determination of background values (BSI, 2011), indicates that application of substances through agricultural practices are considered background, whereas Australian policy (NEPC, 2013) suggests that inputs from agricultural activities are not considered background. In the current study, ambient background concentrations include human contributions of contaminants through diffuse inputs such as atmospheric deposition of Pb from the broad use of leaded fuels. However, Pb impacts directly associated with an adjacent road (within 25 m) were not considered representative of ABC. Consistent with background studies undertaken across Europe, broad application of fertilisers during typical agricultural practices (excluding horticulture and application of biosolids), were considered representative of ABC (Ottesen et al., 2013; Reimann et al., 2010; Saaltink et al., 2014).

2.2 The Study Area and Scope

The predominant exposed lithologies in Greater Melbourne, Victoria, Australia, include the Brighton Group Tertiary sediments to the South East, Silurian siltstone and sandstone to the North East and the Newer Volcanics to the North and West (VandenBerg, 1997). For the purpose of this research the Study Area was limited to soils overlying basalt of the Newer Volcanics, in Greater Melbourne, approximate area of 1700 km², as defined in Figure 1. The boundary of Greater

Melbourne was defined by the Australian Bureau of Statistics (Pink, 2011). The extent of the Newer Volcanics was based on the 1:250,000 geological survey of Victoria (VandenBerg, 1997).

Fig. 1. The Study Area, comprising soils derived from Newer Volcanics geology of Greater Melbourne, Australia.

The Newer Volcanics cover much of western Victoria, forming flat to undulating basaltic plains (Condon, 1951). The basalt plains include multiple layers of lava, deposited during the late Tertiary to Quaternary from eruptions at over 400 volcanic centres (Boyce, 2013). Soils weathered from the Newer Volcanics of Melbourne typically comprise heavy clays (Swartjes, 2011). Land uses in the Study Area predominantly included grazing and urban land uses (BOM, 2016).

The current study included a review of summary statistics for As, Mn, Ni, Pb and Zn. Lead and Zn were chosen because they are common contaminants associated with atmospheric deposition (Nicholson et al., 2003). Arsenic was selected as it is a common contaminant of concern; however background As concentrations are typically low, resulting in a high percentage of censored results which can complicate statistical analysis. Nickel was selected because grey literature indicated that Ni is naturally elevated in soils developed on the Newer Volcanics. Manganese was selected because geogenic concentrations can be highly variable, ranging by an order of magnitude for a single soil unit (Reimann et al., 2015).

2.3 Collation of Open-source soil data

Potential sources of ambient background soil data for the Study Area were reviewed. A summary of the identified open-source soil data repositories are provided in the Supplementary Information (SI 1).

Criteria were applied to systematically review open-data sources for suitable background soil information. The criteria were: (i) the dataset included samples collected from the Study Area; (ii) the data source included sample depth, location and chemical results for at least one of the selected elements of interest (As, Mn, Ni, Pb or Zn); (iii) sampling techniques were generally consistent with the Australian Standard “Guide to the investigation and sampling of sites with potentially contaminated soil - Non-volatile and semi-volatile compounds” (AS 4482.1-2005) (iv) analysis of metals/metalloids was undertaken using aqua regia digest methods or comparable techniques; and (iv) samples were representative of natural soil, rather than fill or waste.

In Melbourne, prior to environmental regulation, fill/waste from gasworks and other historical activities was used to fill low lying areas of the inner city. Fill soils were not considered representative of background conditions and were therefore excluded from this assessment.

Soil data presented in ESA reports for audited sites met the above criteria. The other reviewed open-sources of soil information did not meet the criteria outlined above and were therefore not included in this study (see supplementary information (SI 1) for further information).

Collated soil data were entered into a Microsoft Access database. Environmental data management software Esdat, 4.416, was used for the storage, categorisation and retrieval of background soil data. Where results were provided in portable document format (pdf), transcription errors were minimized by using a data extraction program, Able2Extract (Investintech.com Incorporated, Canada), to copy pdf tables into excel format, prior to importing data into the database.

2.4 *Manual Screening of Contaminated Samples from the Open-Source Dataset*

The open-source dataset consisted of natural soil samples collected from environmental assessment sites. Natural soil samples may contain point source contamination due to localized atmospheric deposition (such as from an adjacent smelter), spills, leaching of contaminants from overlying fill and/or from contact with contaminated surface water or groundwater. The reviewed ESA reports include descriptions of the site history; potential contaminants of concern, soil stratigraphy and field observations of indicators of potential contamination. Using this information it was possible to identify potentially contaminated samples and exclude these from the dataset.

Individual sample results for each element were interrogated to identify the presence of point source contamination. Elemental concentrations were separated into statistical domains, grouped by parent material and sample depth interval and sorted in ascending order. Starting with the highest concentration, each sample was reviewed for qualitative information that could indicate contamination, including the presence of a local source of contamination (such as an underground fuel storage tank), presence of another anthropogenic chemical input, such as polycyclic aromatic hydrocarbons, and/or visual evidence of contamination, such as black staining, or the presence of anthropogenic waste (i.e. brick rubble, tar or plastic), (Fig 2).

Fig. 2. Summary of the process applied for evaluation of elevated element concentrations, for open-source soil data

Based on the evaluation process (Fig. 2) each sample was categorised as one of the following;

- Representative: no evidence of point source contamination, inferred to be representative of background concentrations.
- Unreliable: low confidence in the data quality and/or a potential source of contamination was present.

For each element, samples were evaluated in descending order of concentration until five consecutive “Representative” samples, considered representative of background, were identified. Samples of lower concentration were then all considered to be representative of background concentrations. Samples categorized as “Unreliable”, were removed from the background dataset. Samples considered “Representative” were collated and are herein referred to as the “manually screened” open-source dataset.

2.5 Background soil survey- Soil sample collection and analysis

A targeted background soil survey was undertaken in the Study Area that provided a geochemical benchmark to which the manually screened open-source data could be compared. Soil samples were collected from 40 locations in the Study Area, mean sample density of 1 sample per 42 km². At each location, a topsoil sample (0 to 0.1 m) and sub-soil sample (collected between 0.3 to 0.6 m) was collected using a hand auger. The sub-soil samples were taken within the 0.3 and 0.6 m interval, but were limited to one soil horizon (e.g. where the B horizon was encountered at 0.4 m, the sample was collected from 0.4 to 0.6 m depth). Where rock was present at less than 0.3 m below the surface, sub-surface samples were collected immediately below 0.1 m, however these samples (n=2) were not included in the statistical assessment described in the current paper. The surface sample depth was consistent with the typical depth interval sampled during environmental site assessments and the depth of surface samples collected for the NGSA (de Caritat and Cooper, 2011). The sub-surface depth targeted the B-horizon, which can be naturally enriched in metals (Wrigley and van de Graaff, 2006).

To avoid point source contamination, as far as practicable, the soil survey locations were chosen using the following criteria:

- Minimum of 5 to 8 km downwind from active major industrial contamination point sources e.g. power stations or smelters
- Minimum of 200 m from highways
- Minimum of 25 m from rural roads
- Avoid proximity to road intersections
- Minimum of 100 m from buildings (this was not always possible, typically greater than 50 m from building, or clear separation was present, i.e. a fence or valley)
- Minimum of 50 m from the end rows or other areas where large amounts of fertilizer may have been deposited in agricultural sites
- Avoid atypical landscapes (such as hill crests), or excessively disturbed areas, such as mine dumps, landfills and construction sites.

These criteria are generally consistent with the procedures recommended by the International Geological Correlation Program (Darnley, 1995).

Samples were assessed for pseudo total Al, As, Mn, Ni, Pb, Ti and Zn concentrations, by inductively coupled plasma atomic emission spectroscopy following an aqua regia digest; HCl:HNO₃ (10:4) at 95°C for 30 minutes, followed by addition of hydrogen peroxide and heating for a further 30 minutes. Aqua regia was chosen for measuring pseudo- total metal concentrations because it is the standard method used in environmental assessment in Australia (NEPC, 2013) and internationally, e.g. the British Standard Institution (BSI, 1995), and thus produces results comparable to those collected by the environmental assessment industry.

Survey samples that reported elevated concentrations of As, Mn, Ni, Pb and Zn were manually screened using the same method applied to the open-source dataset (Fig. 2). All elevated results from the soil survey passed the manual screening and were considered representative of background, herein referred to as the “survey data”.

2.6 *Comparison of the manually screened open source data against the survey data*

Statistical comparison of the manually screened dataset with the survey data was undertaken to assess if the manual screening method had adequately removed samples impacted by point source contamination. The comparison was undertaken with particular emphasis of whether element concentrations in the manually screened dataset, which originated from potentially contaminated sites, were comparable to the survey samples which were deliberately collected from areas of low likelihood of contamination (i.e. located away from roads and buildings). Comparison of the distribution of the survey data and the manually screened data were undertaken using the Generalised Wilcoxon (GW) score test, using Minitab macro “GW.mac” (Helsel, 2012). The null hypothesis, that the median of the two datasets were the same, was assessed at a statistical significance level of 0.05. The GW method was chosen because it does not require assumptions to be made for results reported below the limit of reporting (LOR). For Mn datasets, where no results were below the LOR, the Kruskal and Wallis test was used rather than the GW method.

2.7 *Validation of statistical methods for exclusion of contaminated samples against the manually screened open-source dataset*

The background upper concentration limit was calculated using five commonly recommended statistical methods for the removal of results likely representative of contamination: (i) use of the point of inflection on a cumulative frequency plot (CFP), (ii) the Median plus two times the Median Absolute Deviation (Med+ 2MAD); (iii) the upper whisker (UW) of a box and whisker plot, (iv) the UW of a box and whisker plot after logarithm transformation and (v) the 95th percentile. These methods are described in more detail by Reimann et al. (2005) and Matschullat et al. (2000). To ascertain which statistical method best excluded samples identified as contaminated through the manual screening process, the upper concentration limit calculated by each of the statistical methods for each element was compared to the maximum concentration of the manually screened dataset.

Prior to analysis, the distribution of soil data for each element was assessed against normal, lognormal, Weibull and loglogistic distribution using the censqq macro (Helsel, 2012) in the statistical package Minitab 17 (Minitab, 2010). The censqq method was used because it allows for the assessment of data distribution on datasets that include censored results. The Anderson Darling test statistic was used to compare how well the data met each distribution (Stephens, 1974); the lower the Anderson Darling test statistic the better the data fits the selected distribution.

2.8 *Derivation of background summary statistics for Newer Volcanic soils of Greater Melbourne*

Summary statistics for the combined background dataset (the manually screened open-source data and survey data), were derived for surface (0 to 0.1 m) samples and sub-surface (0.3-0.6m) samples in the Study Area. Summary statistics were calculated using the “doBy”, “STatDa” and “gdata” libraries, with R statistical software, freely available at <http://cran.r-project.org/>.

Where results were reported below the LOR, substitution of half the LOR was adopted for calculation of summary statistics. Although some authors have criticized the use of substitution methods such as half the LOR (Helsel, 2012), Antweiler and Taylor (2008) compared the accuracy of a range of methods for managing censored results on an extensive range of environmental datasets and concluded that for the purpose of calculation of summary statistics, substitution of half the LOR was comparable to other non-parametric methods. A comparison of common censoring methods for derivation of the geometric mean, using data from this work, found similar results to Antweiler and Taylor (2008), data not presented.

Mean enrichment of element concentrations in surface soils compared to sub-surface soils, was calculated by dividing the mean surface soil concentration by the mean sub-surface soil concentration for each element.

In order to enable further interpretation of drivers of surface enrichment, normalised enrichment factors (Norm EFs) for surface soils at each individual sample location was determined, including normalisation with Al, to account for increases in metal concentrations due to increased clay content, equation (1).

$$\text{Norm EF} = \frac{([\text{Element}]_S / [\text{Al}]_S)}{([\text{Element}]_{SS} / [\text{Al}]_{SS})} \quad (1)$$

Where [Element] is the concentration of the element in the soil sample, [Al] is the concentration of the Al in the soil sample, subscript S refers to surface sample and subscript SS refers to the sub-surface sample (Blaser et al., 2000; Hernandez et al., 2003; Zoller 1974, Ducs 1975).

Sterckeman et al. (2006) showed that normalization with Al provided reasonable estimation of the pedo-geochemical background variability. However, Reimann and De Caritat (2005) showed that the choice of element utilized for normalisation of enrichment factors can cause conflicting results, particularly when assessing organic rich soils. In order, to assess influence of Al spatial variability on the EF normalisation results, normalisation with Ti, which is more immobile than Al (Reynders 1964), was also undertaken, to assess if consistent enrichment trends were observed. In the context of this study, enrichment factors were not used to prove anthropogenic contamination.

Calculation of the Norm EF was not possible for data from the manually screened dataset as not all samples included collection of both surface and sub-surface samples nor did all samples include analysis of Al or Ti.

3 Results and Discussion

3.1 Collation of Open-source soil data

Environmental site assessment reports from 122 individual sites within the Study Area were reviewed. Seventy-six of the environmental site assessment reports included surface and/or sub-surface samples of soils claimed to be representative of natural soil with analytical results for at least one of As, Mn, Ni, Pb or Zn (Table 1). A total of 268 surface (0-0.1 m) and 569 sub-surface samples (0.3-0.6m) were collated from the environmental site assessment reports. The count of results collated for each element is presented in Table 1. The count of results varied for different elements because samples were not assessed for a consistent suite of analytes, for example 268 surface

samples were assessed for As, Ni, Pb and Zn, whereas only 42 of the natural surface samples were assessed for Mn, which is a less common contaminant of interest (Table 1).

Table 1 Number of results for natural soil samples collated from multiple ESA reports within the Study Area, prior to screening (Open-Source dataset) and post manual screening of contaminated samples (Manually screened dataset)

Element	Depth Interval (m)	Open-Source (n)	Manually Screened (n)
As	0-0.1	268	194
As	0.3-0.6	513	395
Mn	0-0.1	42	27
Mn	0.3-0.6	92	58
Ni	0-0.1	268	194
Ni	0.3-0.6	536	429
Pb	0-0.1	259	185
Pb	0.3-0.6	528	406
Zn	0-0.1	268	194
Zn	0.3-0.6	535	416

Approximately 50% more sub-surface samples were collated than surface samples. The difference in the number of background surface and sub-surface samples was due to the broad presence of fill at the surface of many environmental assessment sites. Fill samples were excluded from the background dataset.

3.2 Manual screening of contaminated samples from the open-source database

Manual screening of elevated results from the open-source dataset resulted in removal of 27% of surface samples and 22% for sub-surface samples (Table 1). Point source contamination by Pb and/or Zn was the most common cause for removal of samples from the background dataset. Point sources of Pb contamination in the urban environment are common due to the use of Pb in paint, batteries, pipes, solder, ammunition and fuel (Laidlaw et al., 2014). Fuel can result in point source Pb contamination via spills and leaks. Similarly, sources of Zn contamination to soils are frequent in urban and industrial environments, including use in galvanized steel, paints, wood preservatives, fertilisers and pesticides (Nicholson et al., 2003). Given the dataset was collated from sites requiring environmental audit (often due to historical industrial activities) the high percentage of samples identified as contaminated was not surprising and highlights the importance of the manual screening process.

3.3 Review of data distribution

An assessment of data distribution was made prior to further statistical analysis of the manually screened data. The distributions of the data differed across elements (Table 2).

The element distributions were consistent with an increasing body of evidence suggesting that geochemical data do not often fit the default assumptions of normal or log-normal distribution (Reimann and Filzmoser, 2000). Therefore, data distribution should be determined for individual datasets or statistical methods that are least influenced by data distribution (i.e. non-parametric methods) should be used.

Table 2 Anderson Darling test statistic for manually screened open-source surface samples, under weibull, lognormal, loglogistic and normal distribution. The lowest Anderson Darling value is highlighted bold, to indicate the distribution of best fit.

Element	Anderson Darling Test Statistic			
	Normal	Lognormal	Loglogistic	Weibull
As	24.23	18.50	15.47	20.64
Mn	0.98	1.75	1.72	1.12
Ni	1.44	0.62	0.82	0.59
Pb	3.83	0.52	0.74	0.91
Zn	7.75	0.39	0.51	5.27

3.4 Validation of the Open-source data using Survey Data

To verify that the manual screening process adequately removed potentially contaminated samples from the open-source dataset, the distribution (Fig. 3) of concentrations of As, Mn, Ni, Pb, Zn of the manually screened open-source and survey datasets were compared (Table 3).

Fig.3. Cumulative frequency plots for As, Mn, Ni, Pb and Zn concentrations for the survey and manually screened datasets, for surface soils (0 to 0.1 m) and sub-surface soils (collected within 0.3 to 0.6m), of the Newer Volcanics of Greater Melbourne, Australia. Plots for As, Ni, Pb and Zn presented on logged scale. Vertical sections of plots indicate where results have been substituted for half the limit of reporting.

Table 3 Generalised Wilcoxon (GW) P-value results for manually screened data and survey data, for soils derived from the Newer Volcanics of Greater Melbourne, Australia

Element	Depth (m)	GW P value
As	0-0.1	0.59
As	0.3-0.6	0.83
Pb	0-0.1	0.26
Pb	0.3-0.6	0.24
Mn ¹	0-0.1	0.43
Mn ¹	0.3-0.6	0.02
Ni	0-0.1	0.13
Ni	0.3-0.6	0.00
Zn	0-0.1	0.24
Zn	0.3-0.6	0.09

Significant results ($P < 0.05$) shown in Bold

¹Kruskal and Wallis test was used rather than GW because no censored data were present in the Mn datasets.

The GW test indicated that there was no significant difference ($P > 0.05$) between As, Pb, or Zn concentrations for the manually screened dataset compared to the survey data (Table 4). However, the Ni and Mn concentrations in sub-surface soils of survey samples were significantly different ($P < 0.05$) from the manually screened dataset. In addition, visual comparison of Ni and Mn concentrations in surface soil indicates that although the medians of the datasets were similar, the distribution of results is not equal. For both Ni and Mn, the survey samples were positively skewed (greater number of samples with high concentrations), compared to the manually screened dataset. The difference in Ni and Mn concentrations may have been a result of sampling methodology differences. Although the manually screened data and survey data both included samples collected within the depth interval of 0.3 to 0.6 m below ground level, the survey samples were collected from a discrete interval within this depth range, targeting one soil horizon, typically the B horizon. Samples from the manually screened data were typically collected without consideration of soil horizon, and therefore may have include material associated with the A horizon or both A and B horizons. Manganese and Ni can accumulate in the B horizon of soils, due to leaching from the overlying A horizon, particularly in acidic conditions (Elias et al., 1981; Haque et al., 2015). During collection of survey samples, iron-manganese nodules were observed in the B-horizon of soils at some locations, further indicating accumulation and enrichment of metals in the B-horizon. As such, it was decided that the greater concentrations of Ni and Mn in the survey data compared to the open-source data was not due to contamination and that the data was representative of ambient background

concentrations in sub-surface soils. Therefore, following manual screening it was considered that information from open-source ESA reports could be utilised for assessment of ambient background concentrations.

3.5 Comparison of statistical methods for exclusion of contaminated samples with the manually screened dataset

Upper concentration limits of As, Mn, Ni, Pb and Zn were determined using five statistical methods for removing 'outliers' considered potentially 'contaminated'. The derived upper concentration limits were compared to the maximums of the original unscreened open-source dataset and the manually screened dataset (Table 4).

Table 4 Comparison of the maximum background concentration of the manually screened dataset with the maximum of the unscreened (Open-Source) dataset and upper concentration limits derived by the Median plus 2 Median Absolute Deviations (Med +2MAD), the upper whisker (UW) of a normally distributed boxplot and a log transformed (Ln) boxplot, the point of inflection on a cumulative frequency plot (CFP) and the 95th percentile, for surface soils (0 to 0.1m) of the Study Area (n=194). The percentage difference is shown in the parentheses¹.

Method	Upper Concentration Limit				
	As ²	Mn	Ni	Pb	Zn
Manually Screened (Max)	11	620	62	77	140
Open Source (Max)	21 (+91%)	820 (+32%)	81 (+31%)	1100 (+1329%)	7200 (+5043%)
Med + 2MAD	-	612 (-1%)	42 (-32%)	42 (-45%)	72 (-49%)
UW of Boxplot	-	710 (+15%)	51 (-18%)	55 (-29%)	140 (0%)
UW of Ln Boxplot	-	820 (+32%)	81 (+31%)	120 (+56%)	420 (+200%)
CFP	7 (-36%)	620 (0%)	43 (-31%)	64 (-17%)	154 (+10%)
95th percentile	10 (-10%)	710 (+15%)	42 (-32%)	97 (+26%)	1121 (+701%)

¹ A positive percentage difference indicates that this method over estimates the maximum background concentrations, whereas a negative percentage difference indicates an underestimation.

² The Med+2MAD and UW of the normal or Ln boxplot could not be calculated for As, because greater than 75% of the results were censored.

The estimated ambient background upper concentration limit varied between statistical methods and elements. The percentage differences between the maximum of the manually screened dataset (considered to be the control) and the calculated upper concentration limits are presented in Table

4. The upper concentration limit estimated by the Med+2MAD method, were 1 to 49% lower than the maximum background concentration of the manually screened dataset. Therefore the Med+2MAD method was conservative and likely to underestimate maximum ambient background concentrations. These findings are consistent with (Reimann et al., 2005) who suggested that the Med+2MAD method is likely to underestimate the upper concentration limit, where datasets include less than 20% contaminated results. The UW of a log transformed boxplot overestimated maximum ambient background concentrations, when compared to the manually screened dataset by 30% to 200%. For Mn concentrations, which were found to be normally distributed (Table 2), log transformation of the data resulted in no samples being identified as potentially contaminated; the upper limit of the log transformed boxplot was equal to the maximum of the unscreened dataset. These results highlight that errors in statistical interpretation can occur if the common assumption of environmental data being log normally distributed (Aide, 2005; Anderson and Kravitz, 2010; Hamon et al., 2004; Olszowey et al., 1995) is applied. The upper concentration limits derived from the observed point of inflection on a CFP and UW of a boxplot (normal distribution) were comparable (within 31%) to the maximum of the manually screened dataset. However, selection of the point of inflection was subjective. As the UW of a boxplot is based on the 75th percentile (Q3) plus $1.5 \times$ Inter-Quartile Range (Q3-Q1), this method will become more inaccurate (likely to overestimate ABC) when the percentage of contamination of the specified element exceeds 25%. For this dataset, 27% percent of surface samples were identified as contaminated. However, samples were not consistently contaminated with the same element, meaning typically less than 25% of samples were contaminated specifically with each element.

Where contamination is present in more than 5% of the samples, the 95th percentile method can over estimate background upper concentration limits, as shown for Zn, where the 95th percentile of the open-source dataset (1121 mg/kg) was over 8 times the maximum of the manually screened dataset of 140 mg/kg. Therefore, application of rigid statistical methods that assume only a small percentage of results are to be removed, such as the use of the 95th percentile, the 98th percentile, or the 95th upper confidence limit of the 95th percentile (Ander et al., 2013), are not suitable for open-source datasets compiled from potentially contaminated sites.

The percentage difference was used as a measure of error, however as the difference was dependent on the maximum of the manually screened data being a true representation of the maximum background concentration, the percentages shown (Table 4) provide an indication of the potential magnitude of error between different methods only; percentage differences would change for different datasets.

Due to variability in background conditions, an exceedance of the maximum of the manually screened dataset, would not conclude that the soil is contaminated from a point source, rather it would indicate that the result is not within the typical background range and therefore requires further consideration to confirm if the elevated result is due to the presence of contamination, mineralisation or, analytical or reporting error.

The findings of the current assessment suggest that when manual screening or other data interrogation approaches (e.g. multivariate analysis), are not practicable we suggest the use of the

Med+2MAD as a conservative method for deriving background upper concentration limits. The UW of a boxplot and the point of inflection on a CFP plot, are also considered adequate methods. However, the UW of a boxplot, will become less conservative when the expected percentage of contaminated samples is high (more than 25%).

3.6 *Background concentrations of As, Mn, Ni, Pb and Zn*

Given the manually screened dataset and the survey data were both considered representative of ambient background concentrations, the datasets were combined for derivation of summary statistics (Table 5).

The maximum background concentrations, reported in Table 5 include anomalous concentrations (results above the upper whisker of a boxplot) where no point source of contamination was identified. It could not be confirmed if the elevated results were due to an unidentified source of contamination or natural enrichment. Therefore, caution should be taken when applying maximum concentrations from background survey datasets for the development of screening criteria. Guidance for derivation of screening criteria from background survey data typically recommend not to use the maximum but rather more conservative values, such as the 95th percentile (BSI, 2011).

Table 5 Summary statistics for pooled background As, Mn, Ni, Pb and Zn concentrations (mg/kg) for soils developed on Newer Volcanic geology of Greater Melbourne, Australia

Element	Depth	Count	Min	Median	GeoMean	Mean	Stdev	75th	95th	Max	Mean Enrichment	Norm EF ¹	HIL A
As	0-0.1	234	<5	<5	<5	<5	<5	<5	6	11	-	-	100
As	0.3-0.6	431	<5	<5	<5	<5	<5	<5	6	18			100
Mn	0-0.1	67	11	377	291	403	258	573	809	1260	1.5	3.2	3800
Mn	0.3-0.6	94	3	210	152	274	238	450	670	871			3800
Ni	0-0.1	233	2	21	20	24	17	29	52	148	0.8	1.0	400
Ni	0.3-0.6	456	1	24	24	31	23	38	76	170			400
Pb	0-0.1	225	3	15	14	18	14	22	45	93	1.9	4.0	300
Pb	0.3-0.6	442	3	9	8	10	6	13	20	39			300
Zn	0-0.1	233	5	26	27	33	25	38	83	140	1.6	2.7	7400
Zn	0.3-0.6	452	2	16	16	20	14	25	52	97			7400

Minimum (min), geometric mean (Geomean), standard deviation (Stdev), 75th percentile (75th), 95th percentile (95th), maximum (Max) and 95th percentiles, Normalised Enrichment Factor (Norm EF), NEPM Human Health Investigation Level for residential land use (HILA A), (NEPC, 2013).

¹Norm EF calculated for survey samples only.

The mean enrichment for all data and mean Norm EFs for survey data are presented in Table 5. The Norm EF for each surface survey sample is presented in the supplementary information (SI2). It was not possible to confidently derive Norm EFs for As due to the high proportion of results (81%) less than the LOR. Trends of enrichment were consistent for Al and Ti normalised results (SI2).

Surface soils in the Study Area were enriched in Pb > Mn > Zn (Table 5). Mean Pb concentrations were almost 2 times that of subsurface soils. Ambient background concentrations of metals can become enriched in surface soils due to diffuse atmospheric deposition of contaminants (Boutron et al., 1994) and the broad application of fertilisers or soil amendments (Jiao et al., 2012). Enrichment can also occur in surface soils due to natural processes including nutrient cycling from vegetation particularly for elements essential to plant growth, such as Cu and Zn, (Blaser et al., 2000) and from natural atmospheric deposition and relocation of soil particulates, such as from sea spray or volcanic activity.

Sources of enrichment of metals/metalloids in soils of the Study Area are discussed in the following sections.

3.6.1 Lead

Enrichment of Pb has been reported in surface soils (Hernandez et al., 2003, Steinnes et al., 2005), snow (Planchon et al., 2003), ice cores (Eichler et al., 2011), tree rings (Zuna et al., 2011) and peat bogs (Martínez Cortizas et al., 2002, Shotyk et al., 2002). These studies cited atmospheric deposition of anthropogenic Pb associated with mining, burning of coal and/or the historic use of Pb in tetraethyl additives in fuel, as the predominant source of Pb enrichment. However, the magnitude of Pb enrichment from anthropogenic contamination in different media and different areas of the world is highly variable. For example peak concentrations of anthropogenic Pb in snow in Greenland were less than 0.1 mg/kg (Rosman et al. 1993); anthropogenic Pb added to remote sediments in Australia have been estimated to be approximately 5 mg/kg (Marx et al., 2016); and anthropogenic Pb measured in peat cores of Canada was approximately 45 mg/kg (Weise et al., 2002). It is likely that some of the Pb enrichment in the surface soil in the current study was due to diffuse anthropogenic sources as the Study Area was within an urban area.

Reimann et al. (2011), has shown that in remote areas, natural processes are the predominant cause of surface enrichment of Pb. Reimann et al. (2011) suggested that Pb enrichment in surface soils, particularly in remote forested areas, is largely a result of nutrient cycling by plants, whereby surface soils have become enriched in Pb due to accumulation and concentration of Pb in organic matter from leaf litter. Surface soil samples assessed in Greater Melbourne were collected from the A horizon. The role of translocation of Pb from subsoils to surface soils by plants in Victoria, where many native plants are not deciduous and soil O horizons are limited or not present at all, due to warm climates and low rainfall, has not been quantified.

The reported median Pb concentrations in surface soils of the Study Area (15 mg/kg) were equal to median Pb concentrations in soil (0- 0.15 m) from front gardens of new suburbs of Melbourne (developed post 1995) with low traffic (Olszowey et al 2005), and comparable to estimates of background Pb in the Sydney estuary catchment, Australia (16 mg/kg) (Birch et al., 2011).

On a regional scale, the median Pb concentration in surface soils (15 mg/kg) were significantly greater ($P=0.001$) than median Pb (12 mg/kg) in surface soils collected across Victoria ($n=51$) as reported by the NGSA (data available at). Higher Pb concentrations in soils of Greater Melbourne compared to soils of regional Victoria, is consistent with studies of surface Pb in Sydney (Birch et al., 2011) and New Orleans (Mielke 1994) which reveal diffuse enrichment of Pb around metropolitan areas.

Median sub-surface Pb in Greater Melbourne (9 mg/kg) was not significantly different ($P= 0.43$) to median Pb (11 mg/kg) concentrations in sub-surface soils collected across Victoria for the NGSA. However, the depth of sub-surface samples collected during the NGSA was from 0.6 to 0.8 m, immediately below the depth sampled during this work. In addition, median Pb concentrations in the Study Area were equal to median Pb reported by the Forum of European Geological Surveys (FOREGs), publically available at <http://www.gtk.fi/publ/foregsatlas/>, (for soil 0 to 0.2m), and only 1 mg/kg more than the geometric mean of background soils reported in the United States of America (14 mg/kg in soils collected at 0.2 m) (Shacklette and Boerngen, 1984).

Although collected across different depth intervals, the similarity of median background Pb concentrations between local soils derived from basalt and international studies is surprising. Further research into sources of surface Pb enrichment in Australian soils is required to quantify the influence of nutrient cycling and anthropogenic inputs of Pb to surface soils.

3.6.2 Zinc

Enrichment of Zn in surface soils of the Study Area, compared to subsurface soils (mean normalised EF of 2.7) was likely due to added diffuse contamination from atmospheric deposition, application of fertilisers, including as an impurity of super-phosphate (Riley et al., 1992) and nutrient cycling by vegetation (Blaser et al., 2000, Reimann 2011). As sample sites were deliberately located greater than 25 m from roads and greater than 200 m from highways, it is unlikely that Zn enrichment was associated with run off from roads, which has been reported to be the most common source of Zn contamination in urban surface soils (Birch et al., 2011). An inventory of sources of Zn added to agricultural soils of England and Wales found that Zn enrichment was predominantly due to additions from atmospheric deposition from multiple sources > application of livestock manures > application of sewage sludge > application of phosphate fertilisers (Nicholson et al., 2003). The survey sites in the Study Area were generally from parks, recreational open spaces and agricultural land used for grazing. Therefore, we consider that Zn enrichment at the soil surface is likely due to nutrient cycling by plants (Reimann et al., 2015), diffuse atmospheric deposition (including deposition of urban dust) and application of phosphate fertilisers.

3.6.3 Manganese

Comparison of mean Mn concentrations in surface soils and sub-soils indicated overall enrichment in the surface (mean enrichment of 1.5). However review of normalised EFs for individual results showed high variability on a location by location basis. Normalised EFs ranged from 0.1 to 25.8, with a mean of 3.3 (SI2), indicating inconsistency of sources and/or behaviour of Mn in surface soils across the Study Area. There are a number of possible sources of diffuse Mn contamination, including emissions from steel and iron foundries and coal combustion, which could cause diffuse

anthropogenic enrichment of Mn in urban surface soils (Luo et al., 2015). However, few studies have quantified diffuse atmospheric additions of Mn to soil; Herndon et al. (2011) reported that more than 50% of Mn in surface soils of Pennsylvania originated from atmospheric deposition from anthropogenic sources, including local influence from the iron industry and Luo et al., (2015) suggested that 80% of Mn variation in surface soils (0 to 0.05 m) of an urban area, of coastal south east China, was due to coal combustion. Dust storms have been reported as a natural source of Mn to soils of Eastern Australia (Gunawardena et al., 2013). Manganese is susceptible to mobilisation and leaching in acidic and/or reducing soil conditions (Carter et al., 2015). Therefore, differences in soil chemistry may have resulted in increased Mn depletion in some areas, compared to others. Further assessment would be required to verify sources of diffuse Mn inputs to the environment and quantify anthropogenic influence on background concentrations of Mn in the Study Area.

3.6.4 Arsenic

Median As concentrations in the Newer Volcanic soils were low (below the LOR of 5 mg/kg), as expected in soils derived from basalt (Koljonen, 1992). Given the low number of results greater than the LOR (less than 20%), enrichment factors for As were not calculated.

3.6.5 Nickel

Mean Ni concentrations in the Study Area were greater in sub-surface soils compared to surface soils (mean EF of 0.78). The Norm EF for Ni in survey samples was 1 when normalised using Al and 0.7 when normalised using Ti, indicating that Ni concentrations in the Study Area are likely driven by soil texture and parent material, rather than anthropogenic contamination (Blaser et al., 2000; Bourennane et al., 2010).

Median surface Ni concentrations (21 mg/kg) in the Study Area were not significantly different ($P=0.34$) to regional Ni (14 mg/kg) in surface soils, (NGSA). However, the sub-soils were significantly enriched with Ni (median of 24 mg/kg) compared to regional sub-soils (median 15 mg/kg).

Nickel enrichment is common in soils derived from basalt, such as the Newer Volcanic geology in Greater Melbourne, Australia. For example, the maximum Ni concentrations reported in the surface (148 mg/kg) and sub-surface soils of the current study (170 mg/kg) were comparable to mean Ni concentrations in gabbro basalt of Finland (130 mg/kg) and mean Ni concentrations in ocean ridge basalt (140 mg/kg) (Koljonen, 1992). The Newer Volcanics geology includes olivine and pyroxene basalts and olivine and iddingsite basalts (Condon, 1951). Mafic minerals such as olivine can yield up to 0.38% (3800 mg/kg) Ni (Simkin and Smith, 1970) providing a source of geogenic Ni enrichment in soils derived from the Newer Volcanics. Therefore, enrichment of Ni in soils of the Study Area compared to international background Ni concentrations is likely to be due to the mineralogy of the basalt derived soils.

3.7 Comparison to Human Health Investigation Levels

The reported range of ABC were well below the Australian screening criteria for protection of human health in low density residential environments, Table 5 (NEPC, 2013). However, recent research suggests that even low additions of Pb to soils may cause impacts to human health (Lanphear et al., 2005). Uncertainty around acceptable concentrations of Pb has resulted in Norway

remediating accessible soils at childcare centres to less than 100 mg/kg Pb (one third of the Australian HIL A criteria of 300 mg/kg) (Ottesen et al., 2008). Maximum background concentrations of Pb in the Study Area were below 100 mg/kg.

This study did not include assessment of “baseline” soils within Melbourne. It is likely that soils associated with fill or soils in close proximity to roads and buildings (particularly old roads or houses), are likely to have concentrations of Pb and Zn much higher than the ABC reported here (Birch et al., 2011). Therefore, the results presented here are not representative of soils which people are most frequently exposed to in Greater Melbourne (i.e. garden soils adjacent to their house or roadside soils). Rather, the results of this study provide an understanding of the ambient background conditions, which can be used to quantify added contamination from point sources to the environment.

4 Conclusions

A framework for collating and screening open-source environmental site assessment data, for the purpose of assessing local ambient background concentrations was developed. The methods outlined here have demonstrated that where sufficient sample information is available, open-source soil data can be successfully screened and used in merged datasets, to assess ABC of elements in soils. The concentrations of As, Mn, Ni, Pb and Zn in the Study Area, were consistent with our understanding of contaminant loading from diffuse sources and nutrient cycling and are considered representative of expected background conditions for soils derived from basalt. However, due to high variability in background conditions, an exceedance of the maximum reported range of background concentrations presented here, does not prove that the soil is contaminated from a point source, rather it would indicate that the result is not within the typical range of background and therefore requires further consideration to confirm if the elevated result is due to the presence of contamination, natural enrichment, analytical error and/or reporting error.

5 Acknowledgements

The authors would like to acknowledge the financial support of the Hazwaste Fund (project S43-0065) and the Australian Contaminated Land Consultants Association (ACLCA). The authors would like to thank the following; Darcy Dennis, Damien Carew and Stephen Lee for their assistance with soil sample collection; Rebecca Poole, Rebekah Russell and Jenny Trinh for their assistance with the collation of open-source data; Andrew Barker for his technical advice for data management; Rob Goudey of the Environment Protection Authority for advice on statistical methods and Golder Associates Pty Ltd for their technical support.

6 References

- Aide M. Geochemical Assessment of Iron and Vanadium Relationships in Oxidic Soil Environments. *Soil & Sediment Contamination* 2005; 14: 403-416.
- Ander EL, Johnson CC, Cave MR, Palumbo-Roe B, Nathanail CP, Lark RM. Methodology for the determination of normal background concentrations of contaminants in English soil. *Science of the Total Environment* 2013; 454-455: 604-618.
- Anderson R, Kravitz M. Evaluation of geochemical associations as a screening tool for identifying anthropogenic trace metal contamination. *Environmental Monitoring and Assessment* 2010; 167: 631-641.
- Antweiler RC, Taylor HE. Evaluation of statistical treatments of left-censored environmental data using coincident uncensored data sets: I. Summary statistics. *Environ Science and Technology* 2008; 42: 3732-8.
- Birch GF, Vanderhayden M, Olmos M. The nature and distribution of metals in soils of the Sydney estuary catchment, Australia. *Water, Air, & Soil Pollution* 2011; 216: 581-604.
- Blaser P, Zimmermann S, Luster J, Shotyk W. Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, Ni, Pb, and Zn in Swiss forest soils. *Science of The Total Environment* 2000; 249: 257-280.
- BOM. Melbourne Physical Information. 2016. Commonwealth of Australia, Bureau of Meteorology, Australian Government, 2013. Accessed at : http://www.bom.gov.au/water/nwa/2013/melbourne/contextual/physicalinformation.shtml#Land_use.
- Bourennane H, Douay F, Sterckeman T, Villanneau E, Ciesielski H, King D, et al. Mapping of anthropogenic trace elements inputs in agricultural topsoil from Northern France using enrichment factors. *Geoderma* 2010; 157: 165-174.
- Boutron CF, Candelone JP, Hong S. The changing occurrence of natural and man-derived heavy metals in antarctic and greenland ancient ice and recent snow. *International Journal of Environmental Analytical Chemistry* 1994; 55: 203-209.
- Boyce J. The Newer Volcanics Province of southeastern Australia: a new classification scheme and distribution map for eruption centres. *Australian Journal of Earth Sciences* 2013; 60: 449-462.
- BSI. British Standard 7755: Soil quality. Part 3: Chemical methods. Section 3.9 1995: Extraction of trace elements soluble in aqua regia. British Standards Institution, United Kingdom, 1995.
- BSI. Soil quality : Guidance on the determination of background values. International Organisation for Standardisation, 2011
- Carter MR, Gaudet BJ, Stauffer DR, White TS, Brantley SL. Using soil records with atmospheric dispersion modeling to investigate the effects of clean air regulations on 60 years of manganese deposition in Marietta, Ohio (USA). *Science of The Total Environment* 2015; 515-516: 49-59.
- Cheng Z, Xie X, Yao W, Feng J, Zhang Q, Fang J. Multi-element geochemical mapping in Southern China. *Journal of Geochemical Exploration* 2014; 139: 183-192.
- Condon MA. The geology of the lower Werribee River, Victoria. The Royal Society of Victoria. 63, Melbourne, Victoria, 1951, pp. 1-24.
- Darnley AG. International geochemical mapping — a review. *Journal of Geochemical Exploration* 1995; 55: 5-10.
- de Caritat P, Cooper M. National Geochemical Survey of Australia: The Geochemical Atlas of Australia. Commonwealth of Australia (Geoscience Australia), Canberra, 2011.
- DEFRA. Environmental Protection Act 1990: Part 2A, Contaminated Land Statutory Guidance. UK: Department for Environment Food and Rural Affairs (Defra). Accessed at <https://www.gov.uk/government/publications/contaminated-land-statutory-guidance>, 2012.
- Duce RA, Hoffman GL, Zoller WH. Atmospheric trace metals at remote northern and southern hemisphere sites. *Pollution or natural?* *Science* 1975; 187: 59-61.
- Dung TTT, Cappuyns V, Swennen R, Phung NK. From geochemical background determination to pollution assessment of heavy metals in sediments and soils. *Reviews in Environmental Science and Biotechnology* 2013; 12: 335-353.
- Elias M, Donaldson MJ, Giorgetta NE. Geology, mineralogy, and chemistry of lateritic nickel-cobalt deposits near Kalgoorlie, Western Australia. *Economic Geology* 1981; 76: 1775-1783.
- Eichler A, Tobler L, Eyrikh S, Gramlich G, Malygina N, Papina T, Schwikowski M. Three Centuries of Eastern European and Altai Lead Emissions Recorded in a Belukha Ice Core. *Environmental Science & Technology* 2012; 46: 4323-4330.

- Gunawardena J, Ziyath AM, Bostrom TE, Bekessy LK, Ayoko GA, Egodawatta P, et al. Characterisation of atmospheric deposited particles during a dust storm in urban areas of Eastern Australia. *Science of The Total Environment* 2013; 461–462: 72-80.
- Hamon RE, McLaughlin MJ, Gilkes RJ, Rate AW, Zarcinas B, Robertson A, et al. Geochemical indices allow estimation of heavy metal background concentrations in soils. *Global Biogeochemical Cycles* 2004; 18: GB1014.
- Haque KMS, Eberbach PL, Weston LA, Dyall-Smith M, Howitt JA. Pore Mn²⁺ dynamics of the rhizosphere of flooded and non-flooded rice during a long wet and drying phase in two rice growing soils. *Chemosphere* 2015; 134: 16-24.
- Helsel DR. *Statistics for Censored Environmental Data Using Minitab and R*: Wiley, 2012.
- Hernandez L, Probst A, Probst JL, Ulrich E. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Science of The Total Environment* 2003; 312: 195-219.
- Herndon EM, Jin L, Brantley SL. Soils Reveal Widespread Manganese Enrichment from Industrial Inputs. *Environmental Science & Technology* 2011; 45: 241-247.
- Jenny H. *Factors of soil formation: a system of quantitative pedology*. McGraw-Hill, New York, 1941.
- Jiao W, Chen W, Chang AC, Page AL. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: A review. *Environmental Pollution* 2012; 168: 44-53.
- Koljonen T. *Geochemical Atlas of Finland, Part 2: Till*. Espoo, Finland, 1992.
- Laidlaw MAS, Zahran S, Pingitore N, Clague J, Devlin G, Taylor MP. Identification of lead sources in residential environments: Sydney Australia. *Environmental Pollution* 2014; 184: 238-246.
- Lanphear BP, Hornung R, Khoury J, Yolton K, Baghurst P, Bellinger DC, et al. Low-level environmental lead exposure and children's intellectual function: An international pooled analysis. *Environmental Health Perspectives* 2005; 113: 894-899.
- Luo X-S, Xue Y, Wang Y-L, Cang L, Xu B, Ding J. Source identification and apportionment of heavy metals in urban soil profiles. *Chemosphere* 2015; 127: 152-157.
- Martínez Cortizas A, García-Rodeja E, Pontevedra Pombal X, Nóvoa Muñoz JC, Weiss D, Cheburkin, A. Atmospheric Pb deposition in Spain during the last 4600 years recorded by two ombrotrophic peat bogs and implications for the use of peat as archive. *Science of The Total Environment* 2002; 292, 33-44.
- Marx SK, Rashid S, Stromsoe N. Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives. *Environmental Pollution* 2016; 213: 283-298.
- Matschullat J, Ottenstein R, Reimann C. Geochemical background – can we calculate it? *Environmental Geology* 2000; 39: 990-1000.
- McIlwaine R, Cox SF, Doherty R, Palmer S, Offerdinger U, McKinley JM. Comparison of methods used to calculate typical threshold values for potentially toxic elements in soil. *Environmental Geochemistry and Health* 2014; 36: 953-971.
- Mielke HW. Lead in New Orleans soils: New images of an urban environment. *Environmental Geochemistry and Health* 1994; 16, 123-128.
- Minitab. *Minitab 17 Statistical Software*. Minitab, Inc. , State College, PA, 2010, pp. www.minitab.com.
- NEPC. *National Environmental Protection (Assessment of Site Contamination) Measure* National Environment Protection Council, Adelaide, Australia, 2013.
- Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers BJ. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of The Total Environment* 2003; 311: 205-219.
- Ohta A, Imai N, Terashima S, Tachibana Y. Application of multi-element statistical analysis for regional geochemical mapping in Central Japan. *Applied Geochemistry* 2005; 20: 1017-1037.
- Olszowey H, Torr P, Imray P. *Trace Element Concentrations in Soils from Rural and Urban Areas of Australia. Contaminated Sites Monograph Series No. 4*: Adelaide: Department of Human Services and Health, Environment Protection Agency, South Australian Health Commission, 1995.
- Ottesen RT, Birke M, Finne TE, Gosar M, Locutura J, Reimann C, et al. Mercury in European agricultural and grazing land soils. *Applied Geochemistry* 2013; 33: 1-12.
- Panno SV, Kelly WR, Martinsek AT, Hackley KC. Estimating Background and Threshold Nitrate Concentrations Using Probability Graphs. *Ground Water* 2006; 44: 697-709.
- Pink B. *Australian Statistical Geography Standard (ASGS) Volume 1 - Victoria Maps*. Australian Bureau of Statistics. Main Structure and Greater Capital City Statistical Areas, Belconnen, Australian Capital Territory, 2011.

- Planchon FAM, van de Velde K, Rosman KJR, Wolff EW, Ferrari CP, Boutron CF. One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land. *Geochimica et Cosmochimica Acta* 2003; 67, 693-708.
- Prabhakaran Nair KP, Cottenie A. Parent material-soil relationship in trace elements — a quantitative estimation. *Geoderma* 1971; 5: 81-97.
- Redon P-O, Bur T, Guiesse M, Probst J-L, Toiser A, Revel J-C, et al. Modelling trace metal background to evaluate anthropogenic contamination in arable soils of south-western France. *Geoderma* 2013; 206: 112-122.
- Reimann C, de Caritat P. *Chemical Elements in the Environment*. Berlin: Springer 1998.
- Reimann C, Filzmoser P. Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. *Environmental Geology* 2000; 39: 1001-1014.
- Reimann C, Filzmoser P, Garrett RG. Background and threshold: critical comparison of methods of determination. *Science of The Total Environment* 2005; 346: 1-16.
- Reimann C, Matschullat J, Birke M, Salminen R. Arsenic distribution in the environment: The effects of scale. *Applied Geochemistry* 2009; 24, 1147-1167.
- Reimann C, Matschullat J, Birke M, Salminen R. Antimony in the environment: Lessons from geochemical mapping. *Applied Geochemistry* 2010; 25: 175-198.
- Reimann C, Siewers U, Tarvainen T, Bitukova L, Eriksson J, Giucis A, et al. *Agricultural Soils in Northern Europe: A Geochemical Atlas*. Stuttgart: Schweizerbart Science Publishers, 2003.
- Reimann C, Smith, D B, Woodruff, L G, Flem, B. Pb-concentrations and Pb-isotope ratios in soils collected along an east–west transect across the United States. *Applied Geochemistry* 2011; 26, 1623-1631.
- Reimann C, Flem B, Fabian K, Birke M, Ladenberger A., Négrel P, Demetriades A., Hoogewerff J. Lead and lead isotopes in agricultural soils of Europe – The continental perspective. *Applied Geochemistry* 2012; 27, 532-542.
- Reimann, C., Birke, M., Demetriades, A., Filzmoser, P., O'Connor, P. *Chemistry of Europe's Agricultural Soils, Part A: Methodology and Interpretation of the GEMAS Data Set, 2014*, *Geologisches Jahrbuch Reihe B, Band B 102*. Schweizerbart Science Publishers, Stuttgart, 523 pp.
- Reimann C, Englmaier P, Fabian K, Gough L, Lamothe P, Smith D. Biogeochemical plant–soil interaction: Variable element composition in leaves of four plant species collected along a south–north transect at the southern tip of Norway. *Science of The Total Environment* 2015; 506–507, 480-495.
- Reynders J, J. A pedo-ecological study of soil genesis in the tropics from sea level to eternal snow, Star Mountains, central New Guinea. New Guinea, 1964.
- Riley M, M, Gartrell J, W, Brennan R, F, Hamblin J, Coates P. Zinc deficiency in wheat and lupins in Western Australia is affected by the source of phosphate fertiliser. *Australian Journal of Experimental Agriculture* 1992; 32: 455-463.
- Rosman KJR, Chisholm W, Boutron CF, Candelone JP, Görlach U. Isotopic evidence for the source of lead in Greenland snows since the late 1960s. *Nature* 1993; 362: 333.
- Rothwell KA, Cooke MP. A comparison of methods used to calculate normal background concentrations of potentially toxic elements for urban soil. *Science of The Total Environment* 2015; 532: 625-634.
- Saaltink R, Griffioen J, Mol G, Birke M. Geogenic and agricultural controls on the geochemical composition of European agricultural soils. *Journal of Soils and Sediments* 2014; 14: 121-137.
- Salminen R, Chekushin V, Tenhola M, Bogatyrev I, Fedotova E, Tomilina O, Zhdanova L, Glavatskikh SP, Selenok I, Gregorauskiene V, Kashulina G, Niskavaara H, Polischuk A, Rissanen K, *Geochemical Atlas of the Eastern Barents Region*, Elsevier Science, Amsterdam, 2004.
- Shacklette HT, Boerngen JG. *Element concentrations in soils and other surficial materials of the conterminous United States*. Washington DC: United States Government Printing Office, 1984.
- Shotyk W, Weiss D, Heisterkamp M, Cheburkin AK, Appleby PG, Adams FC. New Peat Bog Record of Atmospheric Lead Pollution in Switzerland: Pb Concentrations, Enrichment Factors, Isotopic Composition, and Organolead Species. *Environmental Science & Technology* 2002; 36, 3893-3900.
- Simkin T, Smith JV. Minor-Element Distribution in Olivine. *The Journal of Geology* 1970; 78: 304-325.
- Smith DB, Cannon WF, Woodruff LG, Riveria FM, Rencz AN, Garrett RG. History and Progress of the North American Soil Geochemical Landscapes Project, 2001 to 2010. *Earth Science Frontiers* 2012; 19.
- Steinnes E, Åberg G, Hjelmseth H. Atmospheric deposition of lead in Norway: spatial and temporal variation in isotopic composition. *Science of The Total Environment* 2005; 336: 105-117.

- Stephens MA. EDF Statistics for Goodness of Fit and Some Comparisons. *Journal of the American Statistical Association* 1974; 730-737.
- Swartjes FA. Dealing with contaminated sites : from theory towards practical application. In: Swartjes FA, editor. Springer, Dordrecht, 2011.
- Tóth G, Hermann T, Da Silva MR, Montanarella L, 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International* 88, 299-309.
- VandenBerg AHM. Melbourne SJ 55-5 Edition 2, 1:250 000 Geological Map Series. SJ 55-5. Geological Survey of Victoria, Melbourne, 1997.
- Wrigley RJ, van de Graaff RHM, and Lang S. Residential development on the New Volcanics – A case study of suspected barium contamination and soil amendment. *Australian Geomechanics* 2006; 41, 3, 107-113.
- Zoller WH, Gladney ES, Duce RA. Atmospheric Concentrations and Sources of Trace Metals at the South Pole. *Science* 1974; 183: 198. Zuna M, Mihaljevič M, Šebek O, Ettler V, Handley M, Navrátil T, Goliáš V. Recent lead deposition trends in the Czech Republic as recorded by peat bogs and tree rings. *Atmospheric Environment* 2011; 45, 4950-4958.

Supplementary Information 1

The identified open source soil data repositories included:

- Environmental Site Assessment reports for audited sites (EPA, 2016); statutory documents that are issued after a statutory environmental audit of a site has been conducted (<http://www.epa.vic.gov.au/our-work/environmental-auditing/environmental-audit-reports-online>).
- The National Geochemical Survey of Australia Project (de Caritat and Cooper, 2011), a nationwide, low resolution soil survey primarily undertaken for exploration purposes was completed in 2009, comprising samples from catchment sediments and floodplains across Australia, accessed via <http://www.ga.gov.au/about/projects/minerals/concluded/national-geochemical-survey>.
- Geological Survey of Victoria (DSDBI, 2014); a combined dataset of stream sediment and soil geochemical results collated from expired exploration and mining licenses issued since 1965. <http://www.energyandresources.vic.gov.au/earth-resources/geology-of-victoria/geological-survey-of-victoria/geochemistry>.
- Trace element concentrations in Soils from Rural and Urban Areas of Australia, (Olszowey et al., 1995); a targeted soil survey undertaken to assess baseline concentrations of trace elements in urban soils of Adelaide, Brisbane, Melbourne and Sydney, and the influence of traffic and old or new urbanization on metal concentrations. Data within report.

A summary of the reviewed sources and decision for inclusion in the assessment of background soil in the Study Area is provided in Table S1.

Supplementary Information 1

TableS1: Summary of review of data sources for inclusion within the background concentration database

Data Source	Summary of Scope	Quality Review	Data is Suitable?
Trace element concentrations in Soils from Rural and Urban Areas of Australia (Olszowey, Torr and Imray 1995)	<ul style="list-style-type: none"> • Surface soil samples (0 to 150 mm) generally collected from the front yards of residential properties within capital cities. • Rural soil samples collected in Queensland. • Samples were assessed for broad screen of metals. 	<ul style="list-style-type: none"> • No soil logs, soil texture, or underlying geology reported. • Sample locations are not provided. • Samples include topsoil within close proximity to houses and roads, unlikely representative of background concentrations. • Sample analysis undertaken prior to 1999. 	No Dataset does not include required sample details.
Geological Survey of Victoria Data available at: http://dpistore.efirst.com.au/categories.asp?cID=12 (Accessed April 2015)	<ul style="list-style-type: none"> • Dataset comprised over 72,000 stream sediment samples and 370,000 soil samples within Victoria. • Samples typically comprise of material collected from the weathering profile, at an approximate depth of 10-40 cm. • A few samples (not specified) were taken using a hand auger extending to a depth of 2m. • A total of 5711 soil samples and 2100 sediment samples were collected within the Study Area. 	<ul style="list-style-type: none"> • GPS coordinates for sample locations are provided. • No soil logs provided. • No distinction between samples from fill or natural material. • Sample depths not specified for each location. • Sample analysis undertaken prior to 1999 using varied analytical methods, including perchloric acid, hydrofluoric acid digest and aqua regia digest. 	No. Dataset does not meet quality objectives, however, due to the large dataset this data was added to the database for comparison purposes only.
The National Geochemical Survey of Australia Project (de Caritat and Cooper 2011) Data available at: http://www.ga.gov.au/about/what-we-do/projects/minerals/concluded/national-geochemical-survey Accessed 01 April 2015	<ul style="list-style-type: none"> • Dataset comprised samples collected at 0-10 and 60-80cm from 1315 locations across Australia. • Analysis of metals was undertaken at 51 locations within Victoria • 2 of the 51 locations were from sediments within the Study Area. 	<ul style="list-style-type: none"> • GPS coordinates for sample locations are provided. • Field descriptions and sample depths provided. • Sample analysis was undertaken post 1999 using aqua regia digest on the <2 mm fraction. • Likely parent material of sample not specified. 	No. Data meets data quality objectives, however, samples are likely representative of recent alluvium rather than the targeted parent materials of this study.
EPA Audit Reports Audit reports available at: http://www.epa.vic.gov.au/our-work/environmental-auditing/53v-reports-certificates-statements-of-environmental-audit Accessed April 2015.	<ul style="list-style-type: none"> • Many of the reports include soil data, collected from natural material, from sites that may have been contaminated. 	<ul style="list-style-type: none"> • Over 2500 audit reports are publically available, within the study area. • There is a large number of Audit reports completed post 1999. • Sample depth, location and chemical concentrations are typically reported in tables and on soil logs. The data is currently not collated into any single publically available database. 	Yes. Data evaluation method developed to exclude contaminated samples from the dataset and rank data quality.

Supplementary Information 1 references

de Caritat P, Cooper M. National Geochemical Survey of Australia: The Geochemical Atlas of Australia. Commonwealth of Australia (Geoscience Australia), Canberra, 2011.

DSDBI. GeoVic-Explore Victoria Online Energy and Earths Resources. 2014. Department of State Development Business and Innovation, <http://www.dpi.vic.gov.au/earth-resources/exploration-and-mining/tools-and-resources/geovic> 2014.

Olszowey H, Torr P, Imray P. Trace Element Concentrations in Soils from Rural and Urban Areas of Australia. Contaminated Sites Monograph Series No. 4: Adelaide: Department of Human Services and Health, Environment Protection Agency, South Australian Health Comission, 199

Supplementary Information 2

Table S2a: Normalised Enrichment Factors for Survey Samples, where both surface (S) and subsurface (SS) samples were collected, based on normalisation with Al.

Location	Pb(S)	Pb(SS)	EF	Mn (S)	Mn (SS)	EF	Ni (S)	Ni (SS)	EF	Zn (S)	Zn (SS)	EF	Al (S)	Al(SS)
BH003	18	10	2.9	171	76	3.7	22	37	1	31	28	1.8	17500	28600
BH004	31	12	3.8	238	138	2.5	27	29	1.4	118	40	4.4	11500	17000
BH005	20	7	2.1	56	282	0.1	22	45	0.4	24	10	1.8	16700	12400
BH014	31	8	6.5	130	12	18.1	8	12	1.1	26	7	6.2	7670	12800
BH015	23	8	14	11	29	1.8	2	10	1	12	12	4.9	3950	19200
BH016	9	9	0.9	377	437	0.8	65	78	0.7	41	33	1.1	18800	16400
BH017	17	6	2.3	1260	871	1.2	84	92	0.7	62	45	1.1	23300	18600
BH020	12	2.5	5.8	770	701	1.3	73	87	1	82	74	1.3	32600	39100
BH021	8	5	1.7	659	556	1.2	66	63	1.1	48	39	1.3	36800	38800
BH079	12	7	3.1	87	22	7.3	6	18	0.6	15	6	4.6	6480	11900
BH081	11	7	2.7	38	2.5	25.8	6	8	1.3	12	2.5	8.1	5740	9740
BH082	46	9	9.2	730	413	3.2	28	42	1.2	125	26	8.6	13600	24400
BH084	14	7	1.8	82	18	4.0	15	17	0.8	20	7	2.5	15200	13300
BH090	12	7	2.3	1040	785	1.8	93	128	1.0	51	38	1.8	26300	35400
BH091	14	2.5	2.1	910	360	0.9	148	108	0.5	83	16	1.9	27100	10100
BH102	93	13	17.3	272	651	1	22	82	0.6	90	54	4	9250	22400
BH108	19	5	5.6	79	54	2.2	8	14	0.8	20	7	4.2	7940	11700
BH109	16	7	3.3	153	122	1.8	18	33	0.8	22	14	2.3	11700	17000
BH110	13	7	4	34	89	0.8	7	20	0.8	17	11	3.4	7600	16500
BH111	26	12	2.9	427	309	1.8	15	18	1.1	59	24	3.3	9750	13000
BH117	12	7	2.3	193	325	0.8	18	52	0.5	24	25	1.3	17200	23200
BH118	16	11	3.4	25	16	3.6	6	9	1.5	11	9	2.8	11200	26000
BH119	8	6	1.7	832	495	2.1	34	36	1.2	63	19	4.2	23100	29100
BH120	2.5	9	0.1	670	376	0.6	62	11	1.9	74	21	1.2	31800	11000
BH121	6	14	0.4	435	862	0.4	41	23	1.5	29	22	1.1	24600	21200
BH218	16	8	4	556	360	3.1	52	113	0.9	22	23	1.9	20100	39800
BH219	8	6	2.9	510	389	2.8	20	43	1	23	32	1.6	9680	21000
BH220	64	9	15.3	494	146	7.3	32	56	1.2	30	41	1.6	24600	52800
BH221	17	12	2.9	703	616	2.3	12	44	0.6	12	17	1.4	13900	28200
BH222	12	8	3.9	442	235	4.8	23	45	1.3	19	16	3.1	13000	33400
BH225	15	10	1.8	554	487	1.4	28	57	0.6	24	25	1.2	30900	37500
BH226	13	9	1.8	357	234	1.9	52	60	1.1	34	39	1.1	42200	51200
BH237	16	28	0.5	618	638	0.8	12	8	1.2	16	8	1.6	9620	7790
BH238	14	10	1.5	123	93	1.4	6	8	0.8	14	10	1.5	14500	15600
BH239	9	2.5	6.3	704	619	2	32	50	1.1	46	58	1.4	13800	24000
BH240	11	12	2.3	136	532	0.6	15	65	0.6	13	22	1.5	14000	34900

Location	Pb(S)	Pb(SS)	EF	Mn (S)	Mn (SS)	EF	Ni (S)	Ni (SS)	EF	Zn (S)	Zn (SS)	EF	Al (S)	Al(SS)
BH241	11	11	2.8	336	671	1.4	18	53	1	9	23	1.1	10100	28600
BH242	14	6	3.7	819	325	4	23	40	0.9	17	8	3.4	19200	30800
Mean			4.0			3.2			1.0			2.7		

Table S2b: Normalised Enrichment Factors (EF) for Survey Samples, where both surface (S) and subsurface (SS) samples were collected, based on normalisation with Ti.

Location	Pb(S)	Pb(SS)	EF	Mn (S)	Mn (SS)	EF	Ni (S)	Ni (SS)	EF	Zn (S)	Zn (SS)	EF	Ti	Ti(SS)
BH003	18	10	2.1	171	76	2.6	22	37	0.7	31	28	1.3	120	140
BH004	31	12	2.3	238	138	1.5	27	29	0.8	118	40	2.6	160	140
BH005	20	7	1.3	56	282	0.1	22	45	0.2	24	10	1.1	90	40
BH014	31	8	2.6	130	12	7.2	8	12	0.4	26	7	2.5	60	40
BH015	23	8	3.4	11	29	0.4	2	10	0.2	12	12	1.2	60	70
BH016	9	9	1.0	377	437	0.9	65	78	0.8	41	33	1.2	290	290
BH017	17	6	2.3	1260	871	1.2	84	92	0.7	62	45	1.1	480	390
BH020	12	2.5	5.5	770	701	1.3	73	87	1.0	82	74	1.3	3380	3900
BH021	8	5	2.1	659	556	1.5	66	63	1.4	48	39	1.6	360	470
BH079	12	7	1.7	87	22	4.0	6	18	0.3	15	6	2.5	30	30
BH081	11	7	2.0	38	2.5	19.0	6	8	0.9	12	2.5	6.0	40	50
BH082	46	9	7.8	730	413	2.7	28	42	1.0	125	26	7.4	280	430
BH084	14	7	1.2	82	18	2.7	15	17	0.5	20	7	1.7	50	30
BH090	12	7	1.2	1040	785	0.9	93	128	0.5	51	38	0.9	1550	1040
BH091	14	2.5	0.6	910	360	0.3	148	108	0.1	83	16	0.5	2710	270
BH102	93	13	11.9	272	651	0.7	22	82	0.4	90	54	2.8	360	600
BH108	19	5	2.2	79	54	0.8	8	14	0.3	20	7	1.6	70	40
BH109	16	7	2.9	153	122	1.6	18	33	0.7	22	14	2.0	80	100
BH110	13	7	1.2	34	89	0.3	7	20	0.2	17	11	1.0	90	60
BH111	26	12	3.4	427	309	2.1	15	18	1.3	59	24	3.8	90	140
BH117	12	7	11.5	193	325	4.0	18	52	2.3	24	25	6.4	70	470
BH118	16	11	1.0	25	16	1.0	6	9	0.4	11	9	0.8	60	40
BH119	8	6	0.4	832	495	0.4	34	36	0.3	63	19	0.9	750	200
BH120	2.5	9	0.0	670	376	0.2	62	11	0.7	74	21	0.5	1280	170
BH121	6	14	0.5	435	862	0.6	41	23	2.1	29	22	1.6	210	250
BH218	16	8	1.5	556	360	1.2	52	113	0.3	22	23	0.7	470	350
BH219	8	6	3.3	510	389	3.2	20	43	1.1	23	32	1.8	400	980
BH220	64	9	5.7	494	146	2.7	32	56	0.5	30	41	0.6	260	210
BH221	17	12	1.0	703	616	0.8	12	44	0.2	12	17	0.5	190	130
BH222	12	8	0.7	442	235	0.9	23	45	0.2	19	16	0.6	410	190
BH225	15	10	1.0	554	487	0.8	28	57	0.3	24	25	0.6	120	80
BH226	13	9	2.2	357	234	2.3	52	60	1.3	34	39	1.3	80	120
BH237	16	28	0.4	618	638	0.7	12	8	1.1	16	8	1.5	260	190
BH238	14	10	1.5	123	93	1.5	6	8	0.8	14	10	1.5	100	110

Location	Pb(S)	Pb(SS)	EF	Mn (S)	Mn (SS)	EF	Ni (S)	Ni (SS)	EF	Zn (S)	Zn (SS)	EF	Ti	Ti(SS)
BH239	9	2.5	5.7	704	619	1.8	32	50	1.0	46	58	1.2	700	1100
BH240	11	12	0.6	136	532	0.2	15	65	0.1	13	22	0.4	200	120
BH241	11	11	1.2	336	671	0.6	18	53	0.4	9	23	0.5	250	290
BH242	14	6	1.3	819	325	1.4	23	40	0.3	17	8	1.2	330	180
Mean			2.6			2.0			0.7			1.8		