

Trace metal enrichment observed in soils around a coal fired power plant in South Africa

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A site assessment was conducted at a coal fired power plant in South Africa to determine whether surrounding soils were being enriched with trace metals resulting from activities at the power plant. It was found that deposition of fly ash from the flue stacks and the ash dump along with deposition of coal dust from the coal stock yard were the activities most likely to lead to such enrichment. Eighty topsoil samples were gathered and analysed for total metal content. Results were interpreted within the context of background values. It was found that concentrations of As, Cu, Mn, Ni and Pb exceeded local screening levels, but only As and Pb could be confidently attributed to anthropogenic intervention and actual enrichment.

Keywords: Trace metals; soil pollution; coal fired power plant.

1. Introduction

Coal fired thermal power plants are one of the largest anthropogenic sources of trace metals in the natural environment (Dragovic et al., 2013). Changes to the concentrations of heavy metals in soils is considered to be a very important indicator of contamination as soil can act as a sink for these metals (Freudenschuss et al., 2001). In this study, the nature and extent of possible enrichment of trace metals in soils that might arise from the various operations at such a power plant were investigated through an in situ site assessment.

Due to the complexities of the operations at a coal fired power plant, including coal handling, coal combustion and subsequent disposal of ash, it is important to holistically consider such a power plant's interaction with soil within the context of these various operations. Subsequently a holistic view of soil pollution at a coal fired power plant can be formed. Due to national and international similarities in the designs of coal fired power plants, it is expected that the contamination profiles and patterns observed within this study, would to some extent be mirrored at other sites, depending however on the composition of coal burnt and emission controls in place.

A study of fly ash from the Matla power plant, which is in the same region as the power plant being investigated here, showed that the fly ash contained toxic heavy metals such as Arsenic (As),

Antimony (Sb), Cadmium (Cd), Chromium (Cr) and Lead (Pb) (Ayanda et al., 2012)

Trace metal enrichment has been observed in soils around various sites exposed to the deposition of fly ash and coal dust. A few studies have been conducted in South and southern Africa which provide some indication on what the expected impact of coal power station emissions are likely to be. A study in Bloemfontein examined the impact of a coal fired power station on heavy metal deposition and showed elevated levels of Cd, Sb, Mercury (Hg) and localised contamination of As (Clark, Tredoux and van Huyssteen, 2015). Similarly a study at the Morupule Power station in Botswana showed increases in the concentration of Cr, Nickel (Ni), Zinc (Zn) and As in the surface soils for a distance of approximately 9km downwind of the power plant (which at 132 Mw capacity is much smaller than the standard coal power stations ~3.5 Gw in the South African Highveld region) (Zhai et al., 2009). Various studies outside of the southern Africa region have assessed the impact of coal power stations on soil concentrations of heavy metals. In studies conducted by Singh et al. (1995) and Praharaj et al. (2003) on soils around coal fired power plants in India, enrichment of trace metals in soils were observed and Raja et al. (2015) found high concentrations of Cd, Pb Cr and Ni. In both studies, a correlation was observed between the most heavily contaminated soils and the mean wind vectors. In Slovakia the levels of As in the soil in the near vicinity of the power station are raised in

comparison to the surrounding environment (Keegan et al., 2006). Similarly Dragović et al. 2013 observed an enrichment of trace metals in soils around a large coal fired power plant in Serbia. Within the Eordea Basin in Greece, it was found that the most enriched elements in the local soil were S, Chlorine (Cl), Copper (Cu), As, Selenium (Se), Bromine (Br), Cd and Pb which were attributed to power plant activities (Petaloti et al., 2006). Within the vicinity of a lignite burning power station in Southern Greece AS, Molybdenum (Mo), Se, Sb, Uranium (U) and Zn were found to be enriched in the samples influenced by power station emissions (Papaefthymiou, 2008). The specific trace metals expected to be enriched in soils is dependent on the type of coal being burnt, however enrichment of some or all of the following notable trace metals are often observed in soils around coal fired power plants: As, Cd, Cobalt (Co), Cr, Cu, Hg, Manganese (Mn), Ni, Pb and Zn (Singh et al., 1995; Praharaj et al., 2003; Dragović et al., 2013; Okedeyi et al., 2014).

South Africa's electricity sector is heavily reliant on coal, with approximately 92% of the country's electricity generation coming from coal (IEA, 2015). South African coals are typically bituminous coals that have higher ash content (i.e. non-combustible mineral content) than their counterparts in the northern hemisphere (Hancox and Götz, 2014). The results of this study will be discussed within the context of local legislative regulations pertaining to contaminated land.

2. Materials and Methods

2.1 The Study Area

Lands were assessed on and around a large coal fired power plant in the Mpumalanga province. The power plant has an installed capacity of 3654MW and annually sends out approximately 19000 GWh (2013-2016 average) onto the national grid. The first of the power plant's 6 turbine units became commercially operational in 1986. Approximately 11 000 000 Mg of coal is burnt annually resulting in approximately 2 814 900 Mg of ash being produced. Coal gets delivered to the power plant via truck or rail and subsequently gets stored at a 28 ha coal stockyard which is 3.4 km to the north of the main station precinct. From the stockyard, coal gets transported via conveyor systems to the boilers. The majority of ash produced by the power plant is captured by electrostatic precipitators and subsequently disposed via overland conveyor at its ash disposal facility. The ash disposal facility is located approximately 3 km east of the main station precinct. The size of the dump – including the active deposition area and the rehabilitated area, is

about 320ha. Fly ash not captured by the electrostatic precipitators is emitted from the power plant's flue stacks. The annual average particulate matter emissions (from 2013-2016) is approximately 15440 Mg per year.

2.2 Sampling

Stratified random sampling (STSI) was used as the sampling pattern. The STSI is a systematic design-based approach whereby the area is divided into a number of sub-regions, or strata, after which simple random sampling is conducted within each of the strata (Brus and De Gruijter, 1997). The stratification process typically divides the site into smaller strata based on specific properties of the stratum whereby the variance of a parameter within a stratum should, if accurately applied, be smaller than the variance between strata (Edwards, 2010). Primarily STSI was employed to reduce the error associated with simple random sampling or bias introduced with other traditional sampling schemes such as following an X or W pattern (Edwards, 2010).

Prior to the sampling phase, a detailed preliminary site assessment was conducted in order to decide on the most efficient stratification, based on identification of activities at the coal fired power plant that were deemed most likely to lead to trace metal enrichment of adjacent soils. From the preliminary site assessment the primary hazards and potential pathways of trace elements to soil as observed were:

- Deposition of windblown ash and coal dust and subsequent particle deposition onto adjacent land;
- Coal and ash handling processes within the main station precinct, notably the emergency ashing area and various associated activities that could lead to agitation, entrainment and subsequent deposition coal and ash dust.
- Deposition of particulate matter from the flue stack onto adjacent land – particularly farmland further to the east of the ash dump.

The study area was divided accordingly into four strata as seen in Figure 1: stratum 1 – farmland further to the east of the ash dump; stratum 2 – land directly adjacent to the ash dump; stratum 3 – land directly adjacent to the coal stock yard and stratum 4 – the main station precinct. In determining the dimensions and the location of stratum 1, deposition of particulate matter from the flue stacks was considered using air quality modelling studies which were previously conducted at the power plant and made use of the CALPUFF dispersion model. From the modelling studies, it was evident that the highest predicted ambient concentrations – for both emissions scenarios

considered – were generally found to the east of the power plant’s ash disposal facility. The assumption was made that these areas of maximum ground-level impact would correlate to areas of maximum deposition of pollutants. Therefore isopleths indicating maximum ambient concentrations of particulates, as obtained from the modelling run, were used to establish the geographical area of stratum 1.

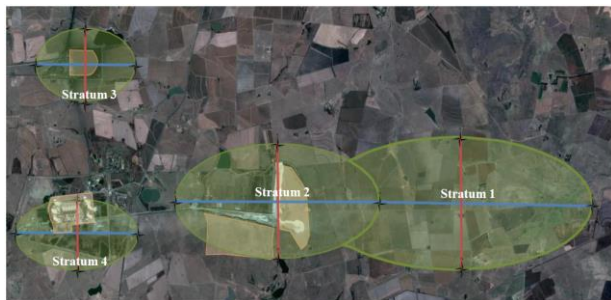


Figure 1: Overview of division of strata within study area

Dust fallout figures obtained from the power plant, based on monthly independent monitoring being conducted around the ash dump and coal stock yard, along with mean wind vectors, were used to determine the dimensions of strata 2 & 3. Pertaining to stratum 2, maximum dust fallout was observed at a sites located 1600m to the east and 2300m to the west of the ash dump’s eastern face. Monitoring sites directly to the north and south of the ash dump experienced comparatively little dust fallout. These observations determined the horizontally elongated ellipsoid shape of stratum 2. The dimensions of stratum 3 were similarly established, though maximum dust fallout was measured at sites closer to the coal stock yard which is likely due to mean differences between coal dust and fly ash particle size distribution. Stratum 4 was established by taking into consideration the various activities being conducted in the main station precinct – particularly to the south of the unit houses – that could lead to the agitation and entrainment of particulates. These activities include the emergency ash storage area, electrostatic precipitators and dust hoppers, coal silos and ash conveyors.

Twenty samples were randomly gathered within each stratum, resulting in 80 samples across the study area. To ensure randomness, Microsoft Excel’s random number generator function was used to select the intra-strata coordinates at which samples were gathered. Areas such as fence lines, roads, water channels, field edges, conveyor belts, buildings, areas directly beneath power lines, large rocks, and water bodies were avoided. If the randomly selected co-ordinates within a stratum fell upon such a location, coordinates were reselected.

Samples of approximately 100g were collected in April 2017, at a sampling depth of 0-15cm. The 0-15cm sampling depth was selected as the highest concentration of contaminants were expected within the first diagnostic horizon (A-horizon) as nutrient status diminishes with depth whereby dilution with deeper submerged nutrient- poor soil could occur (Herselman et al., 2005).

To avoid cross-contamination between samples the sampling equipment was cleaned between each sampling point. Prior to the collection of a sample, the area to be sampled was cleared of surface debris such as twigs, rocks and dried leaves. To avoid sample deterioration, samples were stored in dark and cooled conditions (below 5°C, but not allowed to freeze) on site and during transportation. This was achieved through the use of cold boxes and wet ice. For all samples, pre-cleaned glass bottles were used as sample containers. Upon completion of taking a sample, the bottles were filled to the brim and closed to allow minimum airspace

2.3 Analytical Methods

A portion of the soil sample (>20g) was transferred to a weighing dish and the wet weight was recorded after which the sample was dried at 60°C. Subsequently the sample was ground to achieve homogeneity. For analysis of total metals, a 0.5 g portion of the dried, homogenized sample was digested with dilute aqua regia (2.5 ml deionised water, followed by 7mL HNO₃, 0.5ml Hydrogen peroxide and 5mL HCL) and heated to approximately 95°C. The sample extract was diluted to 50ml and analysed by inductively coupled plasma optical emissions spectrometry (ICP-OES). The method for digestion was based on the US.EPA method 200.2 and the US.EPA method 200.7 and APHA 3120 were used for the analysis. The same extraction procedure was followed for Hg analysis. The sample was however not dried due to the volatility of Hg. The analysis for Hg content was conducted by coupled plasma mass spectrometry (ICP-MS) based on US.EPA 200.8. Instrument detection limits for selected priority metals were as follows: As - 1mg/kg; Cd - 0.1mg/kg; Cr(III) - 0.2mg/kg; Co - 0.5mg/kg; Cu - 2mg/kg; Hg - 0.1µg/kg; Pb - 1mg/kg; Mn - 1mg/kg; Ni - 0.5mg/kg; Pb - 1mg/kg and Zn- 1mg/kg.

2.4 Background Values and Soil Screening Values

Background values for selected trace metals were used as an indication of natural concentrations of elements that could be expected prior to contamination through anthropogenic activity. To establish a baseline for selected trace

metals (Cd, Co, Cr, Cu, Pb, Ni and Zn) across South Africa, Herselman (2007) analysed soil samples that were collected during the Natural Resources Land Type mapping project (consisting of approx. 4500 samples taken across the country) that was conducted in South Africa during the mid-1970s. The Natural Resources Land Type mapping project was conducted prior to the construction of the coal fired power plant under consideration, thus making these samples ideal for determining baseline concentrations. An arithmetic average of trace metal content (Cd, Co, Cr, Cu, Ni, Pb and Zn) of three samples taken in close proximity to the study area during the Natural Resources Land Type mapping project, are seen as uncontaminated background samples. For other metals of importance that were not included in the analysis of Herselman (2007), notably As and Mn, the median concentrations for rangeland in Mpumalanga, based on 514 samples, is used (Steyn and Herselman, 2006). These median concentrations for rangeland in Mpumalanga are considered acceptably representative as they are closely correlated to the arithmetic averages of the three samples taken during the Natural Resources Land Type mapping project. Background concentration as used along with their respective arithmetic standard deviations (a.s.d.) are: As-1.45mg/kg; Cu-34.01.±11.94mg/kg; Co-21.16.±16.80mg/kg; Cr-87.65.±39.08mg/kg; Mn-538mg/kg; Ni-64.41±54.10mg/kg; Pb-11.08±4.60mg/kg; and Zn-49.74±16.67mg/kg. The background values for As and Mn were obtained from a study by Steyn and Herselman (2006) that did not state the a.s.d.

As evident from the standard deviations expressed, soil across the study area is heterogeneous highly variable as the majority of the study area is underlain by dolerite and arenite (Lidwala Consulting Engineers, 2013). In instances where dolerites served as parent material for soils, an increase in background trace element concentration for most elements can be expected. In instances where arenite or shale served as parent material for residual soils, lower concentrations of trace elements are expected. Another reason for high background trace metal concentrations observed is the high incidences of clayey soils observed across the study area. This reasoning is based on the metal binding properties of clayey soils (Tack et al., 1997).

Results are discussed with reference to local legislation. The National Norms and Standards for Contaminated Land and Soil Quality (hence called the 'Norms and Standards') (DEA, 2014), published in terms of the National Environmental Management: Waste Act (59 of 2008) provides soil screening values (SSVs) for various trace metals. The conservative SSV1 for all land use protective of water resources was used to contextualize the

results. SSV1s provided are: As-5,8mg/kg; Co-300mg/kg; Cu-16mg/kg; Pb-20mg/kg; Mn-740mg/kg; Hg-0.93mg/kg; Ni-91mg/kg; Sn-150mg/kg; Zn-240mg/kg. It should be noted that the background concentrations of Cu and Ni exceed the SSV1 thresholds.

2.5 Statistical Methods

In determining whether enrichment of trace metals has occurred in soils, the mean difference (Δ) between observed and background concentrations of a trace metals were determined. Secondly, hypothesis testing was conducted whereby the null hypothesis was that trace metal concentrations observed in soils were equal to or less than their respective background concentrations. Prior to conducting a hypothesis test, the data distribution had to be determined, as certain methods for hypothesis testing such as the Student's t.test assumes normal distribution. For testing the data distribution across strata, the D'Agostino test (two- sided) was used for departures from normality, as advocated by the US.EPA (2001) for sample sizes greater than 50. For intra-stratum normality, the Shapiro-Wilks test was used as proposed by the US.EPA (2001) when the sample size is less than or equal to 50. The Shapiro-Wilk test calculates a W value which is dependent on the correlation between the measured data set and their corresponding normal values. To determine whether the difference between the sample concentrations and background concentrations were consistently, and significantly, larger than the background values, the Wilcoxon Rank Sum (WRS) test was used, as proposed by the US.EPA (2001) for non- normally distributed data. The assumption was made that any differences between the site concentrations and background values are attributable to anthropogenic intervention. The WSR test is preferable for this kind of analysis as it is considered robust with respect to outliers because analysis is done in terms of ranks of the data and it does not assume that the data is normally distributed. All statistical analysis was done using the R Foundation for Statistical Computing software (R Core Team, 2013).

For display purposes, results of STSI were interpolated across the strata by way of the Inverse Distance Weighted (IDW) function on ArcGIS software (ESRI, 2011). IDW is a deterministic and nonlinear interpolation technique that uses values from surrounding measured data points to predict values in unmeasured areas. The use of IDW is motivated by its robustness and simplicity in favour of variants of kriging as discussed by Babak and Deutsch (2009). With IDW, it is assumed that a data point has a localized influence on the predicted area, and that influence diminishes with

distance in accordance to Tobler's first law of geography (i.e. simply that things that are closer together are more alike than those that are further apart) (Tobler, 1970). Subsequently, greater weights are assigned to data points closer to an interpolated location, than those further away.

In terms of the power parameter - which determines the significance of measured points on interpolated values - the default value of 2 was used, therefore an inverse distance-squared relationship is established. Four (4) pseudo points were added to the data set using the mean value for each element so that the raster would cover the entire area of interest. In terms of the search radius, twenty (20) points were specified - which was deemed appropriate considering the relatively small surface areas of the respective strata. Furthermore, as IDW is a weighted distance average, it cannot create peaks or valleys as interpolated values cannot be lower than the lowest value in the observed data set, or higher than the highest value in the observed data set.

3. Results and Discussion

Numerous exceedances of the conservative SSV1 were observed for As, Cu, Mn, Ni, Pb – which was considered the first indicator of anthropogenic enrichment for these metals. Subsequently the mean difference (Δ) between the metal concentrations observed in samples and their respective background concentrations were determined. A positive difference was found for As, Mn and Pb across the study area, which indicative of enrichment. Average measured concentrations of Co, Cu, Cr(total), Ni and Zn where however found to be less than their background values across the study area, as can be seen in Table 1 below. Interestingly, a positive Δ was found for Co in stratum 1 which is indicative of enrichment specific to that stratum if not necessarily across the entire study area.

Table 1: Summary of Δ across study area and within specific strata \pm the a.s.d.

	Δ Total (mg/kg)	Δ Stratum 1 (mg/kg)	Δ Stratum 2 (mg/kg)	Δ Stratum 3 (mg/kg)	Δ Stratum 4 (mg/kg)
As	2.03 \pm 1.17	1.98 \pm 1.64	2.40 \pm 1.12	1.68 \pm 0.57	2.04 \pm 1.01
Co	-1.53 \pm 9.40	4.66 \pm 12.72	-1.24 \pm 8.93	-7.02 \pm 3.36	-3.06 \pm 5.95
Cr	-49.32 \pm 26.19	-20.11 \pm 34.57	-49.66 \pm 9.57	-67.27 \pm 5.38	-62.05 \pm 9.63
Cu	-15.03 \pm 13.28	-13.24 \pm 10.13	-15.10 \pm 14.06	-18.59 \pm 12.33	-13.52 \pm 16.13
Mn	362.59 \pm 471.31	527.15 \pm 578.36	347.45 \pm 527.33	182.50 \pm 303.18	375.25 \pm 381.79
Ni	-42.77 \pm 20.95	-36.71 \pm 28.07	-46.10 \pm 17.05	-49.92 \pm 9.38	-39.07 \pm 22.54
Pb	1.73 \pm 5.78	0.50 \pm 6.57	2.14 \pm 4.88	1.90 \pm 3.50	2.39 \pm 7.42
Zn	-32.20 \pm 11.18	-33.21 \pm 6.48	-37.03 \pm 4.83	-31.65 \pm 8.96	-26.87 \pm 17.71

Table 2: Delta values normalised against the mean background data

	Total (z-value)	Stratum 1 (z-value)	Stratum 2 (z-value)	Stratum 3 (z-value)	Stratum 4 (z-value)
As	0.50	0.32	0.84	0.40	0.58
Co	-2.41	-1.30	-2.51	-8.39	-4.07
Cr	-5.23	-3.12	-14.35	-28.79	-15.55
Cu	-3.69	-4.67	-3.49	-4.27	-2.95
Mn	-0.37	-0.02	-0.36	-1.17	-0.43
Ni	-5.12	-3.60	-6.48	-12.18	-4.59
Pb	-1.62	-1.61	-1.83	-2.63	-1.50
Zn	-7.33	-12.80	-17.95	-9.08	-4.33

In using the D'Agostino skewness test for the 80 surface samples taken across strata during STSI, and when considering selected trace metals, it was found that As, Co, Cr(total), Cu, Mn, Ni and Zn were not normally distributed. The only metal considered to be normally distributed across strata was Pb with a skewness of 0.309 and a p-value of 0.24, signifying the H_0 that data is not significantly different from the normal could not be rejected. In terms of inter-stratum distributions the Shapiro-Wilk test for normality was used. It was found that the data was not normally distributed and therefore the non-parametric Wilcoxon Rank Sum test at 0.95 confidence level was used to determine whether the difference between the site data and the background data was in fact significant. Subsequently it was found that the positive difference between sample concentrations and background concentrations as noted for As, Mn and Pb, were in fact highly significant with p-values of 1.09×10^{-14} , 1.21×10^{-9} and 7.83×10^{-3} respectively. This is deemed to indicate enrichment of these trace metals in soils.

When considering distributions of Cu and Ni concentrations in soils across the study area, as displayed in Figures 2-3, no clear dispersion pattern that could be linked to activities at the power plant is evident. Concentrations of Cu and Ni – though deemed naturally high – do not increase in areas around the ash dump or further east into adjacent farmland. Similarly, despite a positive Δ value being obtained for Mn, no identifiable distribution patterns were evident across the study area, notably adjacent to the ash dump where maximum deposition of fly ash would occur (Figure 4). Additionally the concentrations of Mn in the power plant's ash (315mg/kg) are much lower than the mean Mn concentrations found in soils across the study area of 898.55 \pm 471.31mg/kg.

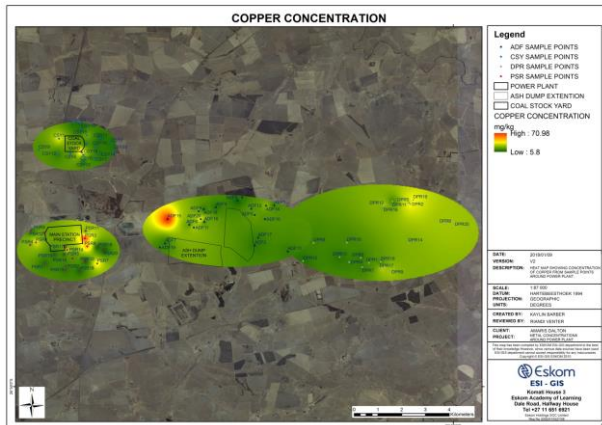


Figure 2: Overview of copper concentrations across the study area

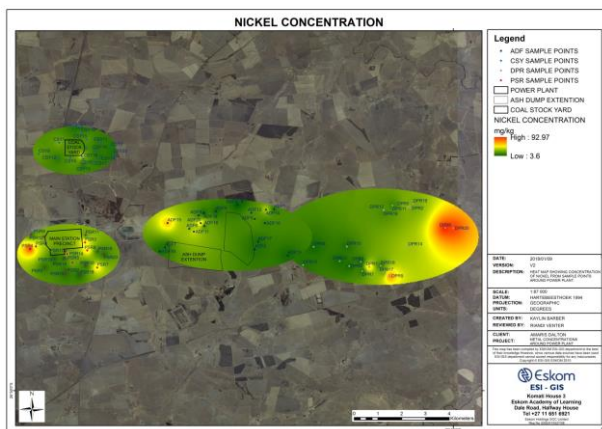


Figure 3: Overview of nickel concentrations across the study area

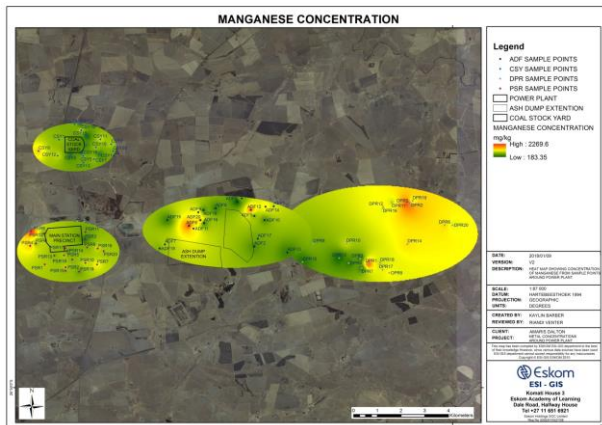


Figure 4: Overview of manganese concentrations across the study area

It could thereby be postulated that observed SSV exceedances of Cu, Mn and Ni concentrations in soils are in fact not anthropogenically caused, but is rather a reflection of naturally high background concentrations. This postulation would however be contradictory to various studies done pertaining to trace metal concentrations in soils around coal fired power stations, both locally and internationally

(Praharaj et al. 2003, Dracovic et al. 2013, Okedeyi et al., 2014). Conclusions made by such studies are, however, frequently dependant on calculation of an 'enrichment factor'. Fe is often used as a the normalizer element (Neto et al., 2006; Mediolla et al., 2008; Okedey et al., 2014) though in certain instances Al, total organic compounds or fractions of grain size could also be used (Liu et al., 2003). For this study however, a good fit normalizer element could not be found, and as such enrichment factor calculations weren't used.

It is argued that the reason for this enrichment not being evident in the results of this study is twofold. Firstly, any detectable signal of enrichment – whether in terms of Δ values or in terms of visible distribution pattern in IDW maps – was impossible to detect due to the already very high background values for these elements of Cu- 34.01 ± 11.94 mg/kg, Mn-538mg/kg and Ni- 64.41 ± 54.10 mg/kg, whereby incremental increases in these elements could not be distinguished. Secondly, the naturally heterogeneous distribution these elements in soils across the study area made detecting a signal for anthropogenic enrichment impossible with the data garnered from the number of samples collected.

When considering the distribution of As and Pb across the study area, as seen in Figures 5-6, it seems evident that higher concentrations of As and Pb were observed in close proximity to the ash dump (stratum 2). This observation would be expected if the source of As and Pb in soils is deposition of windblown ash. With particular reference to As, the perceived enrichment thereof in soil around the ash dump is deemed as partial confirmation of the statement made by Kazakis et al., (2017) that As can be seen as an indicator element for coal ash in soils. High concentrations of As and Pb are similarly evident towards the centre and south of stratum 1 further east of the ash dump. Based on modelling studies as discussed, it is believed that deposition from the flue stacks of the power plant would have been a contributing factor to trace metal concentrations in soils in Stratum 1. However, this relative hotspot of As and Pb concentrations may also in part be contributed to agricultural practices. Though information about specific agricultural practices around the study area was not available, various studies have observed trace metal enrichment in agricultural soils which could have resulted from application of various agrochemicals such as pesticides, fertilizers, herbicides, defoliants, inclusions to animal feeds and fungicides (Chen et al., 1997; Steyn and Herselman, 2006; Nziguheba and Smolders 2008). An alternative contributing factor to high trace metal concentrations observed in Stratum 1 is the underlying geology and soil type, notably instances where intrusive dolerites served as parent material and frequent clayey soils

observed, whereby an increase in trace metal concentrations are expected (Herselman, 2007). The elevated concentrations of As and Pb in soils in Stratum 1 is not solely attributed to deposition from the flue stacks as its localized nature is not aligned to the disperse distribution patterns that is expected had deposition from flue stacks, or the ash dump, been the primary source of As and Pb enrichment.

As and Pb is indicative of these metals partially originating from the same source. Though correlation does not necessarily imply causation, within the specific context of As and Pb concentrations in soils, it was similarly found by Chen et al. (1999) that correlation between these elements in soils may be attributed to anthropogenic intervention – specifically atmospheric deposition.

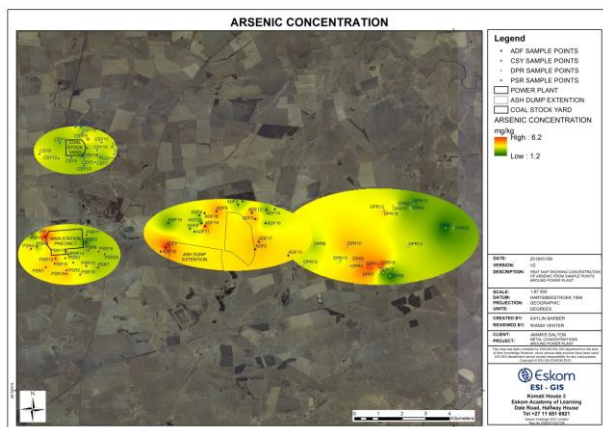


Figure 5: Overview of Arsenic concentrations across the study area

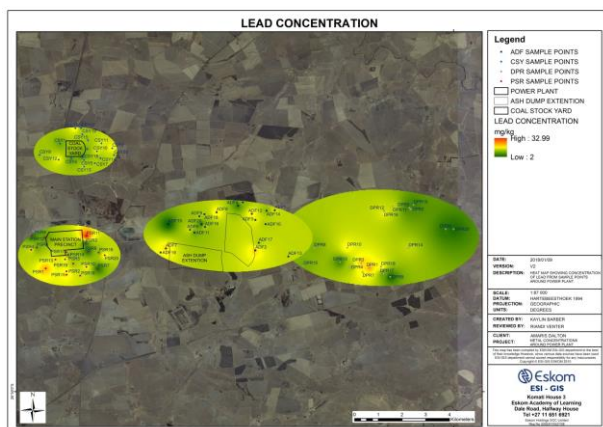


Figure 6: Overview of Lead concentrations across the study area

It was found that As and Pb concentrations in soils are highly significant and positively correlated at 0.95 confidence level, with a correlation coefficient value of 0.65 ($p = 1.15 \times 10^{-10}$) across the study area, based on the Pearson Correlation Coefficient. The inter-stratum correlation between Pb and As was found to be the strongest in Strata 1 and 2 with values of 0.93 ($p=4.648 \times 10^{-9}$) and 0.73 ($p= 2.37 \times 10^{-4}$) respectively. In Stratum 3 a correlation of 0.55 ($p= 0.018$) was observed and in Stratum 4 a correlation coefficient of 0.34 ($p=0.13$) was observed. Therefore, across the study area Stratum 4 was the only area where As and Pb were not significantly positively correlated if taking an alpha value of 0.05 as the cut off for significance. It is deemed that these strong correlations between

4. Conclusions

An integrated and holistic approach to a site assessment for contaminated land was taken at a coal fired power plant in the Mpumalanga province of South Africa. Various operations from which possible enrichment of trace metals could result were considered in designing a sampling strategy. Results were interpreted within the context of enrichment of trace metals when compared to respective background values and SSVs as provided by local environmental legislation. As far as could be determined from the literature consulted, this integrated method for a site assessment has never before been conducted at the site of a coal fired power plant. Based on the results of this study, the following conclusions can be made.

Various SSV exceedances of metal concentrations in soils, within the context of local legislation, were noted across the study area particularly As, Cu, Mn, Ni and Pb. It was attempted to determine if these exceedances were attributable to natural or anthropogenic sources. When considering SSV1 exceedances of Cu and Ni concentrations in soils and bearing in mind their distribution patterns in soils, the positive Δ obtained when considering their background concentrations and the significance of Δ , it is concluded that these exceedances are primarily due to high background concentrations of these elements in soils. Higher trace metal concentrations are attributed to pedogenic processes, with particular reference to underlying dolerite and high clay content of soils (Herselman, 2007). Furthermore, it is concluded that observed SSV1 exceedances of Mn are attributable to background concentrations (despite the positive Δ obtained therefore), based on the low concentrations of Mn (315mg/kg) found in the power plant's ash and the dispersion pattern of Mn concentrations around the ash dump. It is deemed that this distribution pattern is inconsistent with the disperse pollution pattern expected to arise from fly ash deposition. It was however noted from various peer reviewed sources on trace metal enrichment in soils around coal fired power plants that enrichment of Cu, Mn and Ni were to be expected. The postulated reason for this enrichment not being evident in this study is due to the already very high

background values of these elements which would disguise incremental enrichment expected from activities at the power plant. Therefore, though some anthropogenic enrichment of these elements in soils is not discarded, it is concluded that observed SSV1 exceedances of Cu, Ni and Mn concentrations are not primarily attributable to activities at the power plant.

When considering the observed distribution patterns of metals in soils across the study area, as displayed in IDW maps, and when considering the Δ values between background concentrations and metal concentrations in samples, along with the significance of these Δ s, it may be concluded that there has been enrichment of As and Pb concentrations in soils across the study area. Enrichment of As and Pb is particularly evident adjacent to the ash dump and within the station precinct where the respective Δ values were the highest. Lesser enrichment of As and Pb concentrations was also evident in the farmland further to the east of the ash dump and around the coal stock yard. Therefore it is postulated that observed enrichment of As and Pb in soils adjacent to the ash dump and within the station precinct is primarily due to deposition of windblown fly ash, which would be aligned with a significant body of literature on the subject (Sing et al., 1995; Praharaj et al., 2003; Dragovic et al., 2013; Okedeyi et al., 2014). Within the station precinct, deposition of coal dust and other industrial activities could also be contributing factors. In the adjacent farmland further east of the power plant, observed enrichment that is mostly attributed to ash deposition from the flue stacks and in part attributed to active agricultural practices which has been found in various studies to lead to an enrichment of trace metals in soils (Köleli, 2004; Steyn and Herselman, 2006). Observed enrichment of As and Pb around the coal stock yard is similarly attributed to deposition of coal dust along with active agricultural practices in the area.

It is clearly shown that the background concentrations of certain heavy metals in parts of South Africa are naturally high without the additional impact of anthropogenic inputs (Morrey et al., 1989; Herselman et al., 2005; Steyn and Herselman, 2006). Considering that some of these background concentrations are in exceedance of the legislated SSVs (DEA, 2014), determining active contamination of a site can be problematic. It is thereby suggested that further refinement of South African legislative tools are required whereby background concentrations, bioavailability of elements, a concise risk based methodology to site assessment and a partitioning coefficient that is representative of South African soils is to be used (Eijsackers et al., 2014; Papenfus et al., 2015).

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