

Using Elemental Analyses and Multivariate Statistics to Identify the Off-site Dispersion from Informal e- waste Processing.

Stephen M Mudge ¹, Katrine A. Pfaffhuber ², Julius N. Fobil ³, Evert A. Bouman ¹, Hilde T. Uggerud ², Rebecca J. Thorne ^{1,4}

¹ IMPACT, Norwegian Institute for Air Research (NILU), Instituttveien 18, 2007 Kjeller, Norway.

² MILK, Norwegian Institute for Air Research (NILU), Instituttveien 18, 2007 Kjeller, Norway.

³ Department of Biological, Environmental & Occupational Health Sciences, School of Public Health, University of Ghana, Accra, Ghana.

⁴ Institute of Transport Economics, Norwegian Centre for Transport Research, Gaustadalléen 21, 0349 Oslo, Norway

Abstract

Electronic waste (e-waste) is informally processed and recycled in Agbogbloshie in Accra (Ghana), which may be the largest such site in West Africa. This industry can lead to significant environmental contamination. In this study, surface dust samples were collected at a range of sites within Accra to establish the offsite consequences of such activities. Fifty-one samples were collected and analysed for 69 elements by ICP-mass spectrometry after nitric acid digestion. The data indicated a significant enrichment in metals associated with

solder and copper wire at the site itself and a downwind dispersion of this source material to a distance of approximately 2.0 km. Chlorine and bromine were also elevated at this site as residues from polyvinyl chloride combustion and flame retardants respectively. The elemental composition indicated that only low technology electrical equipment was being treated this way. Multivariate statistical analyses by principal components analysis and polytopic vector analysis identified three sources contributing to the system; i) burn site residue dispersing within 2 km from the source site, ii) marine matter on the beaches alone and iii) the baseline soil conditions of the city of Accra. Risk ratios and hazard quotients developed from the measured concentrations indicated that copper was providing the greatest risk to inhabitants in most cases although nickel, vanadium, chromium and zinc also contributed.

Keywords

Agbogbloshie; Metals; Polytopic Vector Analysis (PVA); Principal Component Analysis (PCA); e-waste recycling; risk ratio

Introduction

Waste electronic and electrical equipment (WEEE or e-waste) is generated at a significant rate across the globe ¹. The export of such waste from developed to less developed nations is restricted under the Basel Convention ². Despite this, there is a significant transfer of such waste to locations like Agbogbloshie in Accra, Ghana where the metals are recovered by low technology methods for future use ³. E-waste may contain a diversity of elements that, once recovered, have a significant resale value. These include gold, silver, copper, some of the

platinum group elements (PGM) and the rare earth elements (REEs) ⁴. The methods of recovery employed in Ghana are relatively simple (the burning off of plastics to release the metals) and may lead to significant atmospheric contamination. Health studies ⁵ also indicate that the burners may be exposed to dioxins, mercury and heavy metals.

Previous studies of the metal contaminants present in the soil at the e-waste site have indicated significant enrichment of elements associated with electronic components and a number of these can also be quantified in hair from workers and residents near the reprocessing site ⁶. The stable isotopes of lead indicated that there may be several sources of this element, including food and soil, which also contribute to these hair samples.

Another study ⁷ analysed metals from the Agbogbloshie site and calculated the risk factors to workers. In this study, the risk factors were shown to exceed the US EPA cancer risk value ⁸; recommendations were subsequently made for governmental intervention to improve the conditions. In a study using a portable X-ray fluorescence device, elevated concentrations were measured across the site itself ⁹ and hazard quotients indicated that the concentrations exceeded the 1.0 threshold on the recycling site. Of the nine metals analysed, Pb, Cu, As and Sb posed the greatest risk.

Along with metals, a number of organic contaminants can be found at the same location. For example, studies have shown enhanced polybrominated diphenyl ethers (PBDEs) ¹⁰; these compounds are usually present in electronic equipment as a flame retardant. In addition to bromine, chlorine may also be present in a number of forms; this is due to the thermal decomposition of PVC (polyvinyl chloride) plastic in both the e-waste and covering

the wire that is burned to release the copper ¹¹. Other organic compounds may be in the e-waste itself or formed during the thermal decomposition processes.

The pathway between the source of contaminants at Agbogbloshie and receptors in wider city of Accra is through the atmospheric transport of gases, vapours and particles. Airborne particulate matter (PM) is both a vector for contaminant transport and has a significant impact on human health compared to other common air pollutants such as ground level ozone and carbon monoxide and reductions have benefits to health ¹². Particulate matter may comprise a heterogeneous mixture of solid and liquid particles suspended in air that varies continuously in size and chemical composition in space and time. The chemical composition of PM is diverse and includes nitrates, sulphates, elemental and organic carbon, organic compounds (*e.g.* polycyclic aromatic hydrocarbons), biological compounds (*e.g.* pollen and bacteria) and metals (*e.g.* iron, copper, nickel, zinc and vanadium). Various elements are found in different size ranges of atmospheric particles. Elements such as Al, Si, Ca, Fe, Na, Mg and K are mainly associated with the coarse particulate matter (>3µm) in ambient air. Ba, Be, Cr, Sn, Ni, Sr, U, and V are found in an intermediate range of about 1-5 µm whereas As, Sb, Se, Cd, Pb and Zn are present dominantly in the fine fraction (0.3-0.8 µm) ^{13, 14}. This is relevant both due to the negative health effects of PM and the potential for long-range transport. The principal aim of this investigation was to determine the extent of offsite metal contamination derived from the Agbogbloshie e-waste burning site, by taking dust samples as a proxy for atmospheric fallout. This will use the multi-element chemical signature associated with the source(s) to quantify the dispersion into the city of Accra.

Experimental

Many of the elements of interest, such as those with human health implications, are principally in the solid phase and will settle out of the atmosphere relatively quickly at a rate dependent on the particle density and meteorological conditions. Atmospheric sampling to intercept the airborne particles was not feasible over such a large area and within a sensible timescale. Samples at the burn site itself were taken from the surface of the soils. These “soils” contained residues from the burning of e-waste as well as fragments from the source materials. Samples were collected along three major transects downwind of the burning site at Agbogbloshie (Figure 1). An additional transect along the strandline of the beach was also sampled to investigate the movement of contaminants through river discharge and longshore drift towards the east. All the sampling locations can be seen in Figure 1 and Figure 2.

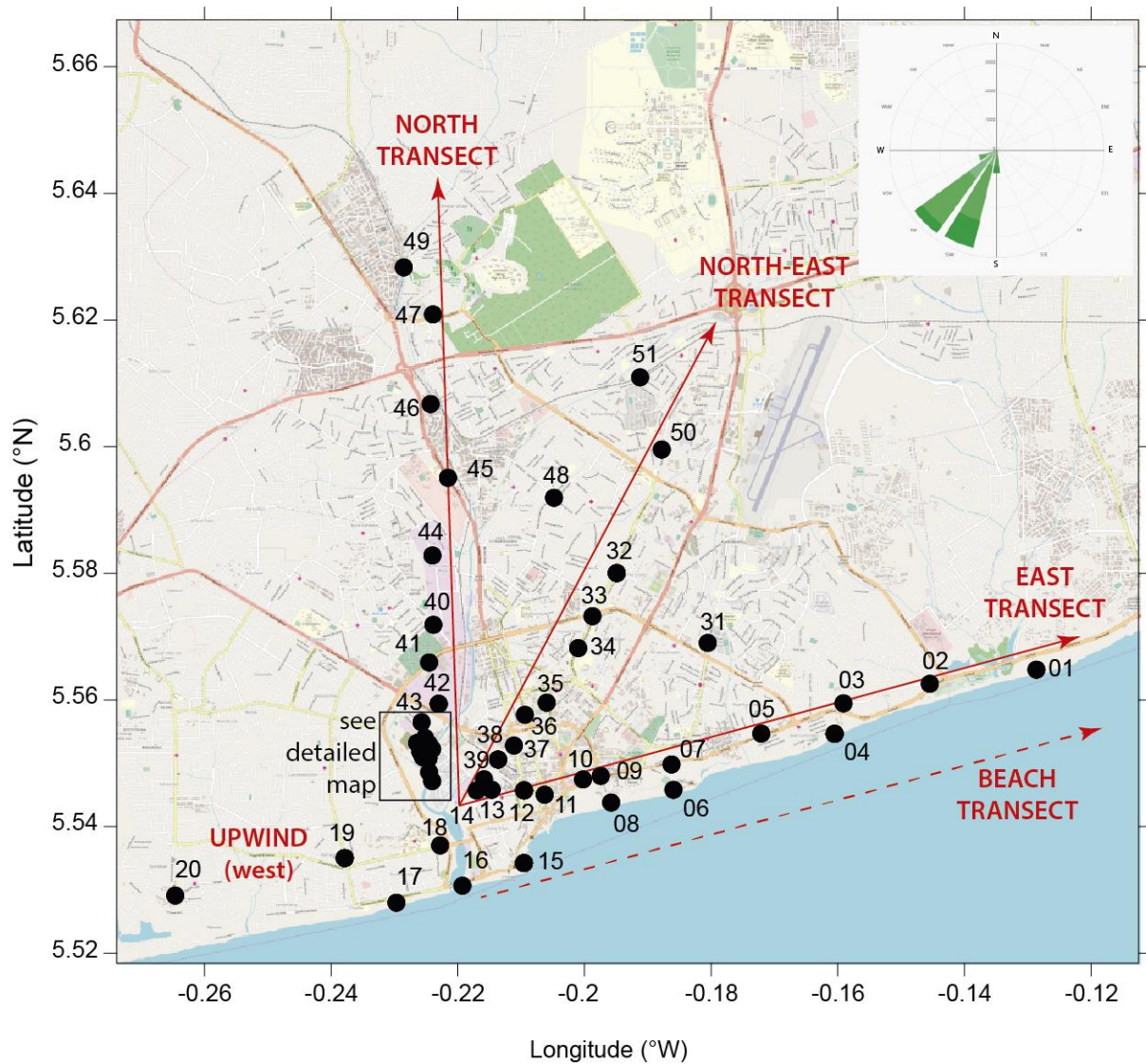


Figure 1. The location of the sampling transects away from the Agbogbloshie (burn) site. The wind rose for Accra airport is shown in the top right corner. Details around the burn site can be seen in Figure 2. Background map from OpenStreetMap and its contributors.

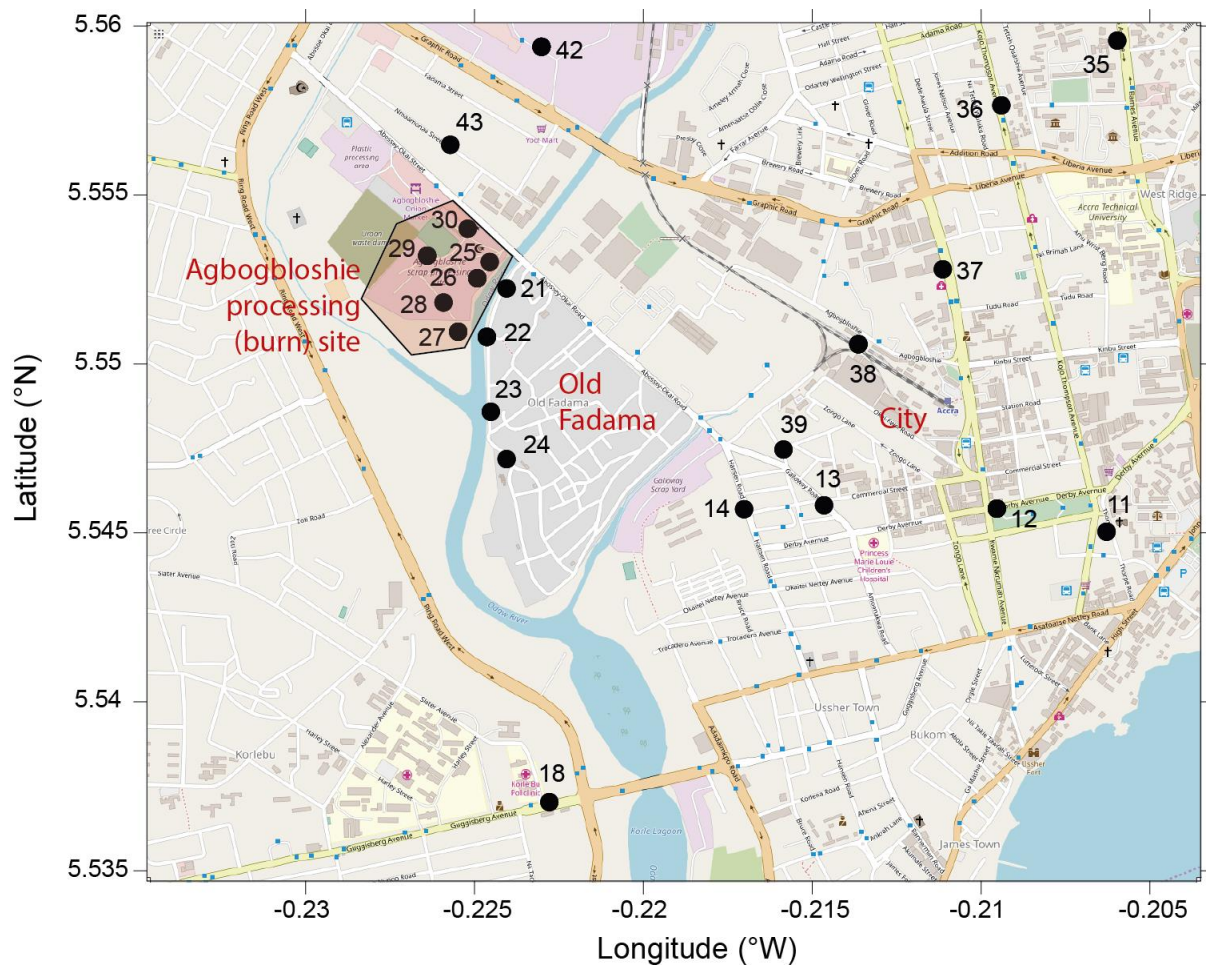


Figure 2. Sampling locations around the e-waste processing site at Agbogbloshe. Old Fadama is principally residential with the city centre to the east of this location. Background map from OpenStreetMap and its contributors.

A number of approaches may be used to determine the contribution from any one source within the samples. In a mixing approach, known chemical signatures are mixed together in different proportions until the best fit to the observed data is obtained. This relies on having samples of all sources appropriate to the system to mix together. An alternative approach is unmixing where the environmental data are used to determine what the original sources must have been to give rise to the observed conditions¹⁵. In this study, polytopic vector analysis (PVA), an unmixing approach, was used to determine (a) the most appropriate

number of discrete sources within the dataset, (b) the chemical composition of these sources and (c) the contribution that each source makes to every sample.

Since the primary wind direction is from the south and west¹⁶, three transects were chosen that ran to the east, the north east and the north of the site. The Agbogbloshie processing site is located towards the western side of Accra and is, therefore, upwind of the majority of the residential districts. A further short transect was sampled towards the west to determine the upwind condition and a final transect was sampled along the shoreline, primarily to the east of the outlet from the Korle Lagoon and Odaw River. In total, 51 sites were sampled including the burn site and the adjacent residential area of Old Fadama (Figure 2). The location of each site was recorded with a GPS and photographs were taken at each location to provide context when considering the results.

Dust was sampled from hard surfaces along the three city transects using a fine brush taking care to avoid resuspension into the air. Samples were collected from hard surfaces such as roadsides and regions contaminated with local soils were avoided. The dusts were double sealed into plastic bags and stored at room temperature until analysed. In addition to the dust samples in the city, surface samples were collected from the upper surfaces on the Agbogbloshie waste site. These latter materials were not soils in the true sense of the word and were comprised of mixed matter from many sources.

Digestion of the samples was performed with a closed-vessel microwave technique system (UltraCLAVE, Milestone, Italy). The choice of nitric acid for digestion was a compromise as

this produces the greatest number of elements in solution that can be quantified in an ICP-HR-MS analysis and it better reflects the potential (bio)-availability of these elements within the human lung. Since we are also primarily interested in the chemical signatures and not the total concentration, a consistent approach such as this was used. Approximately 0.1 g of each sample was weighed accurately on a Mettler PG503 balance and 5 ml nitric acid (HNO₃, s.p.) and 3 ml deionized water was added. The samples were digested according to a 65 min. temperature programme, with stepwise heating to 250°C and a holding time of 30 minutes at 250°C. After cooling, the digests were quantitatively transferred to polypropylene tubes and diluted to a total volume of 50 ml with deionized water.

A total of 69 elements were quantified in the 51 samples with 11 of these samples being extracted three separate times. The 11 pseudo-replicate analyses were to establish the degree of homogeneity of the samples and the repeatability of the analysis. In total, 73 separate analyses were completed:

- For determination of Hg, aliquots of 25 ml were diluted with deionized water to 50 ml after addition of hydrochloric acid (HCl, s.p.) to a total concentration of 0.5% (v/v), and analysis was performed on an Agilent 7700x series ICP-MS octopole reaction system. Indium was added to the sample line as an internal standard at a constant rate of approximately 1 µg.ml⁻¹.
- For determination of the remaining 68 elements (from Li to U), aliquots of 1.0 ml, 0.1 ml and 0.01 ml, respectively, were diluted to 10 ml using deionized water or 1% HNO₃ for a total acid matrix of 1%. Rhenium (at 1 ng.ml⁻¹) was added as an internal standard.

Analyses were performed on an ICP-sector field-MS (Element2, Thermo Fisher Scientific, Bremen, Germany).

- All elements, including Hg, in all samples, were quantified by external calibration using multi element mixtures from Teknolab AS and Spectrascan all made from high purity NIST traceable primary element solutions of 99.99% or better. All calibration solutions (except for Hg) were prepared in nitric acid solutions free of chloride to avoid common Cl molecular ions in the ICP-MS, at a nitric acid concentration of 1% to match the matrix of the samples. For Hg, calibration solutions were prepared from a single element high purity NIST traceable standard from Spectrascan, and HCl was added to matrix match the samples. An analysis programme containing the 68 target elements was designed using appropriate resolutions for each element to avoid expected interferences such as polyatomic ions and doubly charged species. The strength of ICP-HR-MS is that most of the serious molecular ion problems encountered in classical quadrupole ICP-MS are removed when appropriate instrument resolutions of 4000 and 10000 are used. Additionally, to reduce risk of matrix interferences and signal suppression due to matrix effects the analytes were determined in diluted samples.
- Procedural blanks were produced using the same reagents and microwave extraction but without any sample in the Teflon extraction tubes. These samples were used to determine the limits of quantification for the dust sample extracts ($LoQ = 10 * \text{Standard Deviation of the procedural blank}$).
- Quality control (QC) samples were used to check the recovery and external calibration procedures. Certified reference materials (BCR 176R, fly ash and MODAS-2, bottom sediment (Institute of Nuclear Chemistry and Technology, IChTJ, Poland)) were digested

alongside the samples to check the efficiency of the digestion. Results from analysis of CRMs are presented in supplementary information. Blank samples were run after highly concentrated samples to check for appropriate washout and carry-over between samples. All samples, standards, blanks, QC-samples and CRM had rhenium (or indium for Hg) added as an internal standard at a concentration of 1 ng.ml^{-1} in a HNO_3 acidified matrix of 1% (v/v).

The dispersion of the elements from the burn site was investigated through a number of multivariate statistical methods such as principal components analysis (PCA), the projection to latent structures through partial least squares (PLS) and polytopic vector analysis (PVA)¹⁵. In each case, the data were converted to proportions as this removes the concentration effect and enables the underlying chemical signature to be determined. PCA and PLS were performed with SIMCA-P from Umetrics and PVA was conducted using software from Dr Robert Ehrlich.

Instrumental Variability

As part of the calibration of the ICP-MS, quality control standard solutions of known concentration were routinely analysed as part of the quantification procedure. These results also provide a measure of the variability associated with the instrument. For the major metals in solution, the coefficient of variability was 6% for replicate analyses.

Results

Concentrations

The concentrations of individual elements measured across all samples ranged over many orders of magnitude, as anticipated from the crustal abundances of each ¹⁷. The measured concentrations are presented in the Supplementary Information and as a box and whisker plot and these superficially mirror the expected crustal abundances, also presented on the same figure ¹⁸. The enrichment or depletion relative to these crustal abundances were calculated from the mean concentration for each element across all samples. Several elements were enriched (Figure 3.) and these are the ones that can be linked to a potential presence in electrical wastes. Table 1 lists the correspondence of these enriched elements to various potential sources such as wiring, solder and catalytic converters. The mean, median, range and standard deviation for each element can be seen in Table 2.

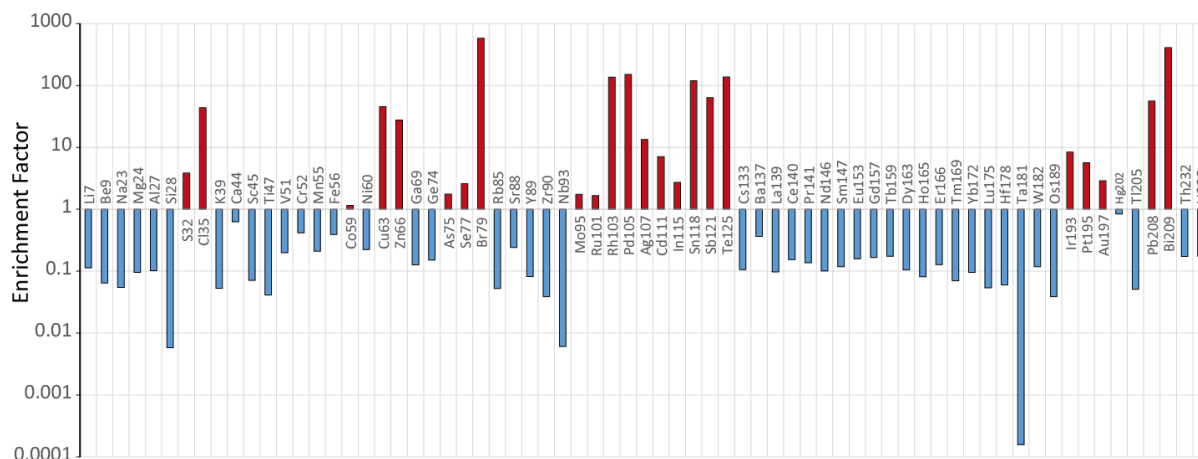


Figure 3. The enrichment (red) or depletion (blue) of each element relative to the crustal abundance (84th Edition CRC Handbook). Note that the Y-axis is on a log₁₀ scale.

Table 1. The potential origin of elements that were enriched relative to the expected crustal abundance. The change in composition of tin-lead solder to lead-free solder was in response to the 2006 European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS). While this was directed at electronic goods and solder in the EU, it had a global effect and led to a reduction in the amount of lead in most consumer goods worldwide.

Element	Potential reason for enrichment at Agbogbloshie
Chlorine	Combustion residue of chlorine-containing plastics such as PVC
Copper	Wiring and newer (lead-free) solder
Zinc	Newer solder and galvanised items
Bromine	Flame retardants
Palladium	Catalytic converters
Silver	Electronic circuit boards and newer solder
Cadmium	Older rechargeable batteries (NiCd)
Indium	Newer solder
Tin	Solder
Antimony	Flame retardants and newer solder
Iridium	Spark plugs
Platinum	Catalytic converters
Gold	Edge connectors on printed circuit boards
Lead	Older solder
Bismuth	Newer solder

Table 2. The Limit of Quantification (LoQ = 10 * St Dev of the procedural blank), mean, median, standard deviation (St Dev), coefficient of variation (CoV), minimum and maximum concentrations (mg.kg⁻¹) for all elements. These data were calculated using results from all 73 analyses including replicates. The number of samples with concentrations below the LoQ is also shown. Elements with MR were analysed at medium resolution (4000) and HR were at high resolution (10000). The remaining elements were measured at low resolution (300).

Element	LoQ	Mean	Median	St Dev	CoV (%)	Minimum	Maximum	n<LoQ
Li7	0.002	2.3	1.5	2.0	86.2	<0.002	8.3	3
Be9	0.0002	0.18	0.14	0.2	97.6	<0.0002	1.0	2
Na23	1.4	1284	792.1	1417.7	110.4	49	9124.7	0
Mg24(MR)	0.5	2236.3	1776.4	1918.9	85.8	11.9	12139.1	0
Al27(MR)	1.1	8380.1	6851.1	6517.9	77.8	73.8	32658.5	0
Si28(MR)	4.2	1642.9	1684.2	644.7	39.2	<4.2	3198.3	1
S32(MR)	1.5	1345.4	341.	3446.0	256.1	163.6	20084.9	0
Cl35(MR)	20	6345.4	609.2	23586.1	371.7	57.2	121052	0
K39(HR)	0.9	1109.5	859.	873.5	78.7	79.9	5641.8	0
Ca44(MR)	13	26046.3	11037	40950.6	157.2	3345.7	207444	0
Sc45(MR)	0.004	1.6	1.4	1.3	82.5	<0.004	6.2	2
Ti47(MR)	0.06	233.6	218.7	154.5	66.2	5	895.6	0
V51(MR)	0.002	23.9	20.7	20.1	84.1	0.8	124.7	0
Cr52(MR)	0.04	42.4	35.8	37.0	87.4	<0.04	213.6	2
Mn55(MR)	0.009	199.6	152.5	179.7	90.0	6.9	1099.6	0
Fe56(MR)	0.9	22118.4	18217	22220.2	100.5	355.3	124016	0
Co59(MR)	0.002	28.8	3.5	117.6	407.9	0.1	651.5	0
Ni60(MR)	0.05	18.7	8.5	42.2	226.0	0.9	339.2	0
Cu63(MR)	0.04	2739	31	13654.6	498.5	1.4	109803	0
Zn66(MR)	0.9	1929.4	108.2	7254.7	376.0	17	40301.9	0
Ga69(MR)	0.0003	2.4	2.2	1.5	62.9	0.1	8.0	0
Ge74	0.0002	0.23	0.19	0.2	94.8	<0.0002	1.3	2
As75(HR)	0.002	3.2	2	3.7	116.0	0.4	19.0	0
Se77(MR)	0.04	0.13	0.09	0.1	102.0	<0.04	0.6	5
Br79(MR)	1.3	1391.4	1416.8	624.0	44.8	499.3	2754.0	0
Rb85	0.002	4.7	3.9	3.5	74.9	<0.002	16.7	1
Sr88	0.06	89.3	44.9	101.7	113.9	13.1	414.9	0
Y89	0.0002	2.7	2.3	1.6	57.7	0.2	8.5	0
Zr90	0.2	6.4	5.9	3.8	59.0	0.4	19.4	0
Nb93	0.005	0.12	0.12	0.1	52.8	0.005	0.4	0
Mo95	0.02	2.1	1.2	2.2	106.5	<0.02	8.7	3
Ru101	0.0003	0.002	0.0	0.0	445.2	<0.0003	0.1	63
Rh103	0.0001	0.14	0.008	0.6	447.5	<0.0001	4.9	6
Pd105	0.001	2.3	1.9	1.9	83.2	0.4	14.3	0
Ag107	0.01	1	0.27	1.8	177.9	0.024	8.8	0
Cd111	0.001	1.1	0.21	2.7	249.0	0.002	14.6	0
In115	0.001	0.68	0.02	3.6	537.7	0.004	29.4	0
Sn118	0.5	273.1	1.3	1613.8	591.0	<0.5	13116.6	13
Sb121	0.003	12.8	0.24	59.9	469.4	<0.003	378.2	5
Te125	0.003	0.14	0.08	0.2	176.4	0.033	1.6	0
Cs133	0.0005	0.32	0.27	0.2	56.9	0.1	1.0	0
Ba137	0.015	154.8	60.4	298.8	193.0	2.5	1506.1	0
La139	0.0003	3.8	3	2.6	68.0	0.3	11.6	0
Ce140	0.0006	10.2	7.8	8.3	80.9	0.7	44.8	0
Pr141	0.0001	1.3	1.0	0.8	64.5	0.1	3.6	0
Nd146	0.0004	4.2	3.5	2.7	64.2	0.3	12.4	0
Sm147	0.0001	0.83	0.76	0.5	59.4	0.1	2.4	0
Eu153	0.0001	0.32	0.22	0.3	95.3	0.02	1.4	0
Gd157	0.0002	1.0	0.85	0.6	62.8	0.1	2.9	0

Element	LoQ	Mean	Median	St Dev	CoV (%)	Minimum	Maximum	n<LoQ
Tb159	0.0001	0.21	0.19	0.1	57.1	0.02	0.6	0
Dy163	0.0001	0.55	0.48	0.3	55.0	0.1	1.5	0
Ho165	0.0001	0.11	0.09	0.1	54.5	0.01	0.3	0
Er166	0.0001	0.44	0.42	0.3	56.2	0.03	1.2	0
Tm169	0.0001	0.04	0.03	0.0	62.6	0.0005	0.1	0
Yb172	0.0001	0.31	0.28	0.2	56.9	0.02	0.8	0
Lu175	0.0001	0.04	0.04	0.0	58.0	0.002	0.1	0
Hf178	0.01	0.18	0.17	0.1	57.9	0.01	0.5	0
Ta181	0.008	0.0003	0	0.0	600.0	<0.008	0.0	71
W182	0.1	0.15	0.12	0.1	50.5	0.1	0.5	0
Os189	0.0002	0.0001	0	0.0	368.1	<0.0002	0.0	62
Ir193	0.001	0.008	0.005	0.0	173.7	<0.001	0.1	19
Pt195	0.0001	0.03	0.02	0.0	149.8	<0.0001	0.2	13
Au197	0.0001	0.01	0	0.0	309.5	<0.0001	0.2	44
Hg202	0.0001	0.07	0.01	0.2	245.2	<0.0001	0.9	3
Tl205	0.0001	0.04	0.03	0.0	75.5	0.002	0.2	0
Pb208	0.015	783.2	16.6	3015.0	385.0	0.4	16743.3	0
Bi209	0.12	3.5	0.0	24.0	690.9	<0.12	205.4	43
Th232	0.013	1.7	0.69	5.0	302.1	<0.013	41.2	12
U238	0.0001	0.47	0.37	0.6	129.3	0.1	5.0	0

As an example representative element for the solder in the recycled e-wastes, the spatial distribution of tin is presented in Figure 4. High concentration values were found at the burn site and lower concentrations were measured upwind of the site and towards the ends of the downwind transects. All of the elements listed in Table 1 have the same general spatial distribution pattern as tin and further examples of the spatial distribution can be seen in the SI. More detail of the distribution around the burn site and city centre can be seen in Figure 5. It is worth noting that the concentrations of metals varied considerably across the burn site, indicating the diverse source materials and the heterogeneous nature of the distribution of these materials in the soils and dusts. The fragmented remains of printed circuit boards could be seen in the soils during collection (Figure 6) at Agboglobshie. It was clear that many different electronic components were randomly strewn across the site.

As suggested by the PCA (see below), the elements exhibited distributions across the sampled area according to their source. Those elements that were associated with the processing of e-waste followed the similar distribution as tin in Figure 4 and Figure 5. A further example (Pb208) is included in the SI. Those elements associated with the local geology and general city contamination followed a different pattern with no specific point source in the area. Those elements associated with the marine source were only enriched along the beach transects. Example figures are included in the SI.

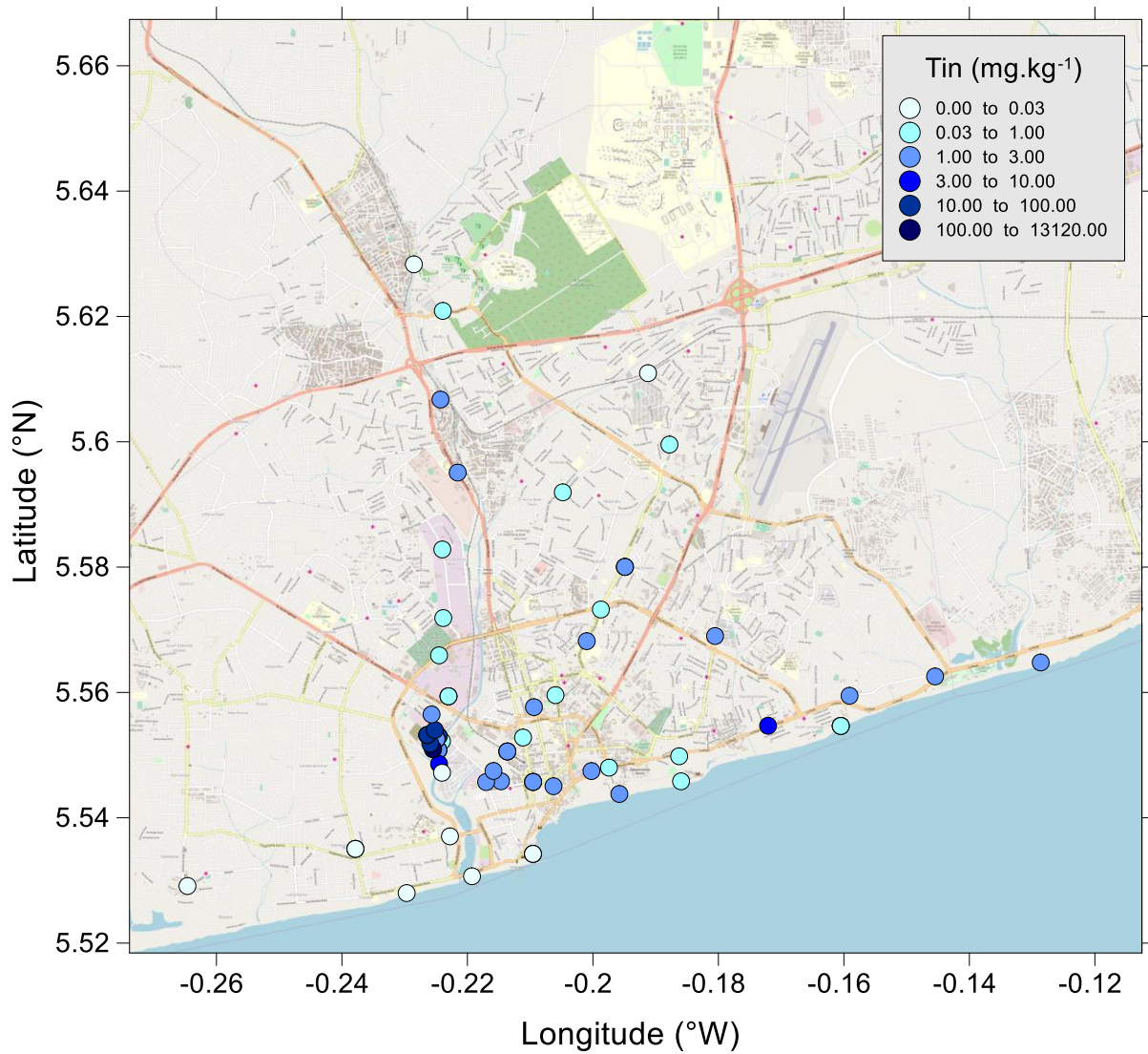


Figure 4. The spatial distribution of tin (Sn118) in the dust samples collected across Accra. The data are presented in six classes with intervals to indicate the gradients across the region. Pseudo-replicate samples from the same location are stacked and only the C sample of each is visible in this figure. Background map from Open Street Map and its contributors.

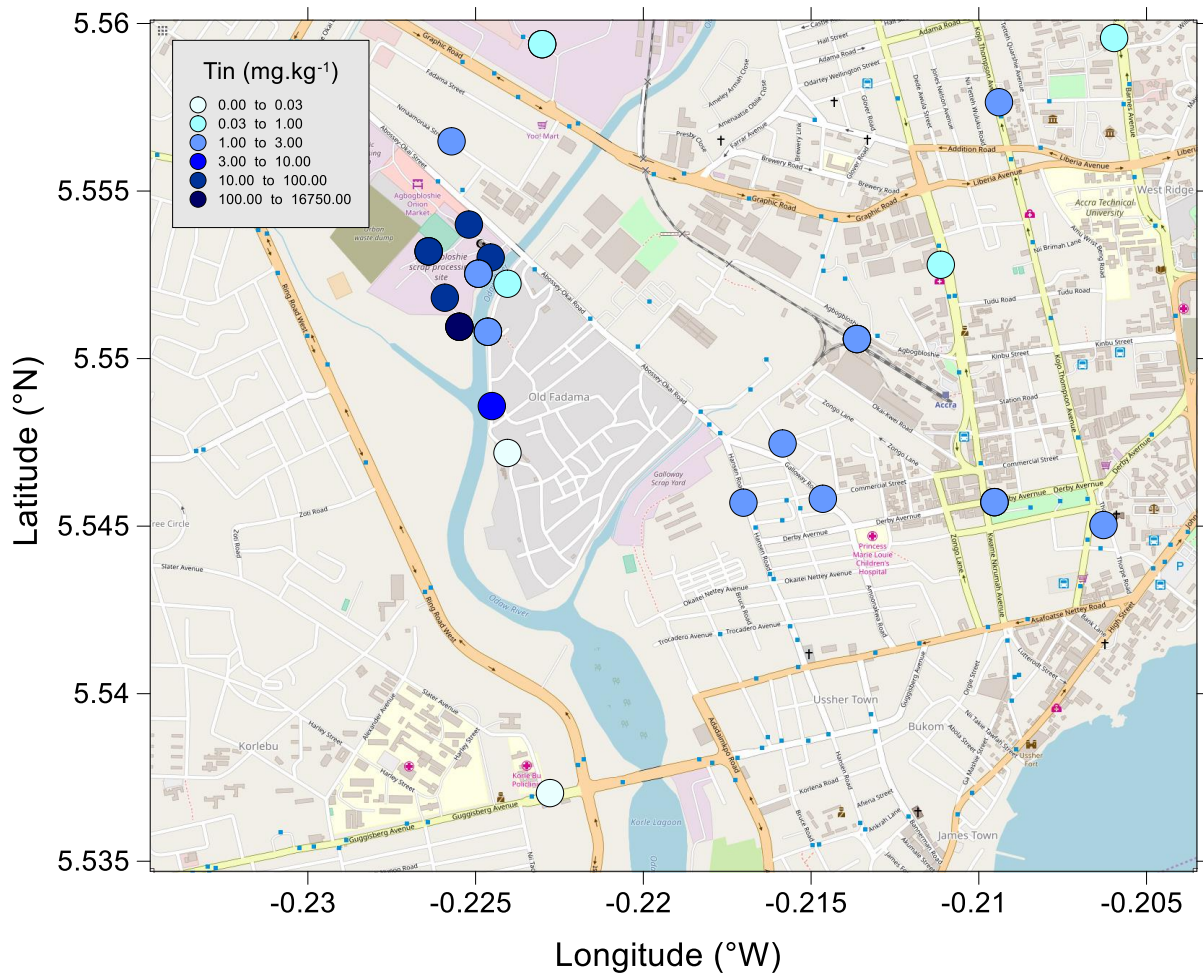


Figure 5. The distribution of tin in the city centre, Agbogbloshie burn site and Old Fadama. The data are presented in six classes with the same class intervals as Figure 4. Background map from Open Street Map and its contributors.



Figure 6. The soil surface at the Agbogbloshe e-waste processing site. Numerous fragments of electronic components and circuit boards are evident along with soldered joints.

Principal Components Analysis (PCA)

In order to determine which of the metals were co-varying and which sites had similar chemical compositions, PCA was conducted on the normalised data. The normalisation procedure (expressing the concentrations as a proportion of the total concentration) removes the concentration effects and allows the chemical signatures to be compared. The results of these analyses using all 69 elements can be seen in Figure 7 and Figure 8. The scores plot (Figure 7) shows that the 11 pseudo-replicates (repeat analyses of three

subsamples from a single field sample) cluster together fairly well although the fact they are not more closely clustered does suggest there is a degree of heterogeneity in these samples. This heterogeneity is more apparent in the samples from the burn site (26, 27 and 29) than those from the city and transects. In general, the samples from the burn site project into the upper left quadrant of the figure and are separate from the shoreline (marine) samples (lower left) and the samples taken along the transects and within the city centre. The marine samples aggregate together quite tightly, more so than the burn site samples. The samples from within the city may show a tendency from left to right in the figure, indicating a change in chemical composition.

The distribution of the sample sites in the scores plot is governed by the distribution of the elements shown in the loadings plot (Figure 8). In this figure, elements that behave the same chemically or have the same source (and, therefore, co-vary) will aggregate together. The right-hand side of the figure is dominated by the REEs and related transition metals, while the upper left contains those elements associated with the e-waste. These are the same elements that were relatively enriched compared to the crustal abundance in **Error! Reference source not found.** in the Supplementary Information and Table 1. Many of these metals are found in the lead-free solders, although lead is also part of the group as some of the e-waste may have been produced before the move to reduce lead in solder took effect. Another element of interest within this broad group is mercury that may be associated with button batteries, switches and lamps. The elements to the lower left are enriched in the marine samples collected from the top of the strand line along the beaches. Elements that cluster near the centre of the figure will have a small effect on the loadings as their values

are close to zero. This may be because the concentrations are low and close to the limit of detection or because they are randomly distributed in all samples and are not associated with any particular source.

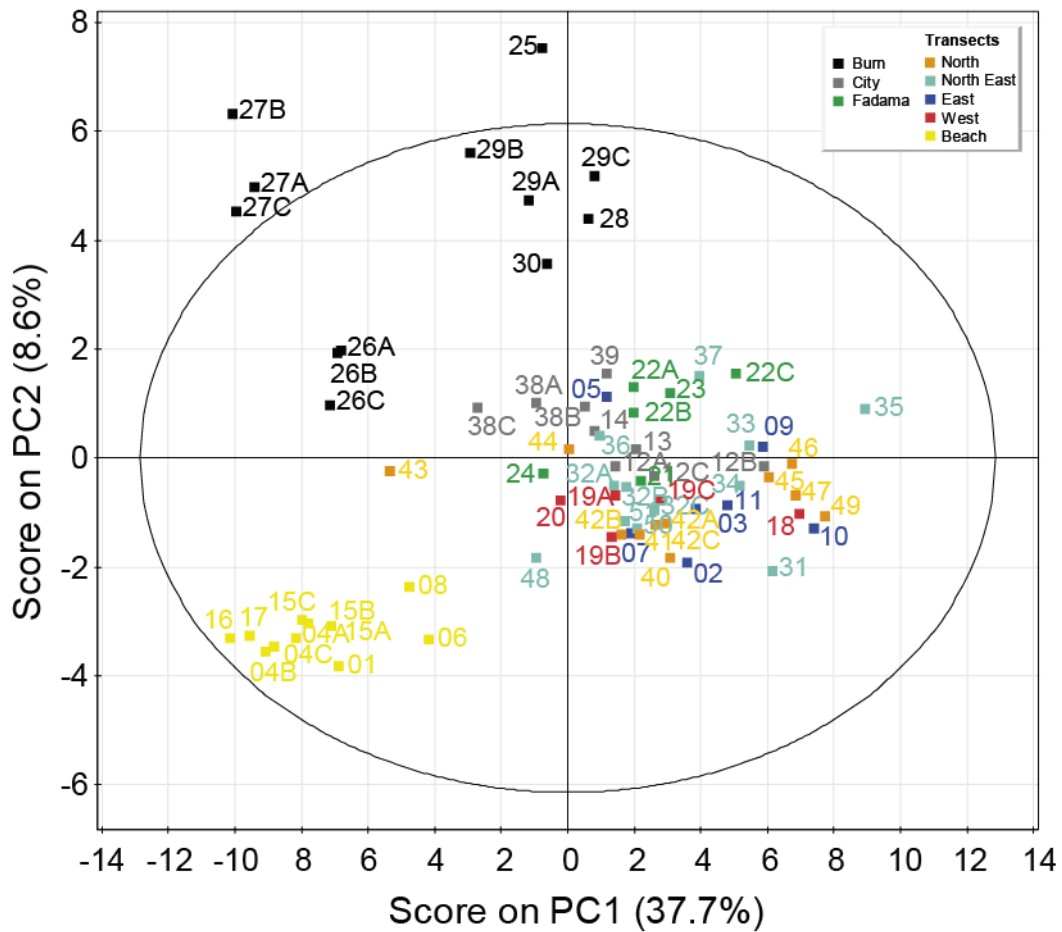


Figure 7. The scores plot for all 73 analyses of 51 samples. Pseudo-replicates are denoted by the A, B and C suffix. The samples are colour-coded according to their location within the Accra sampling campaign.

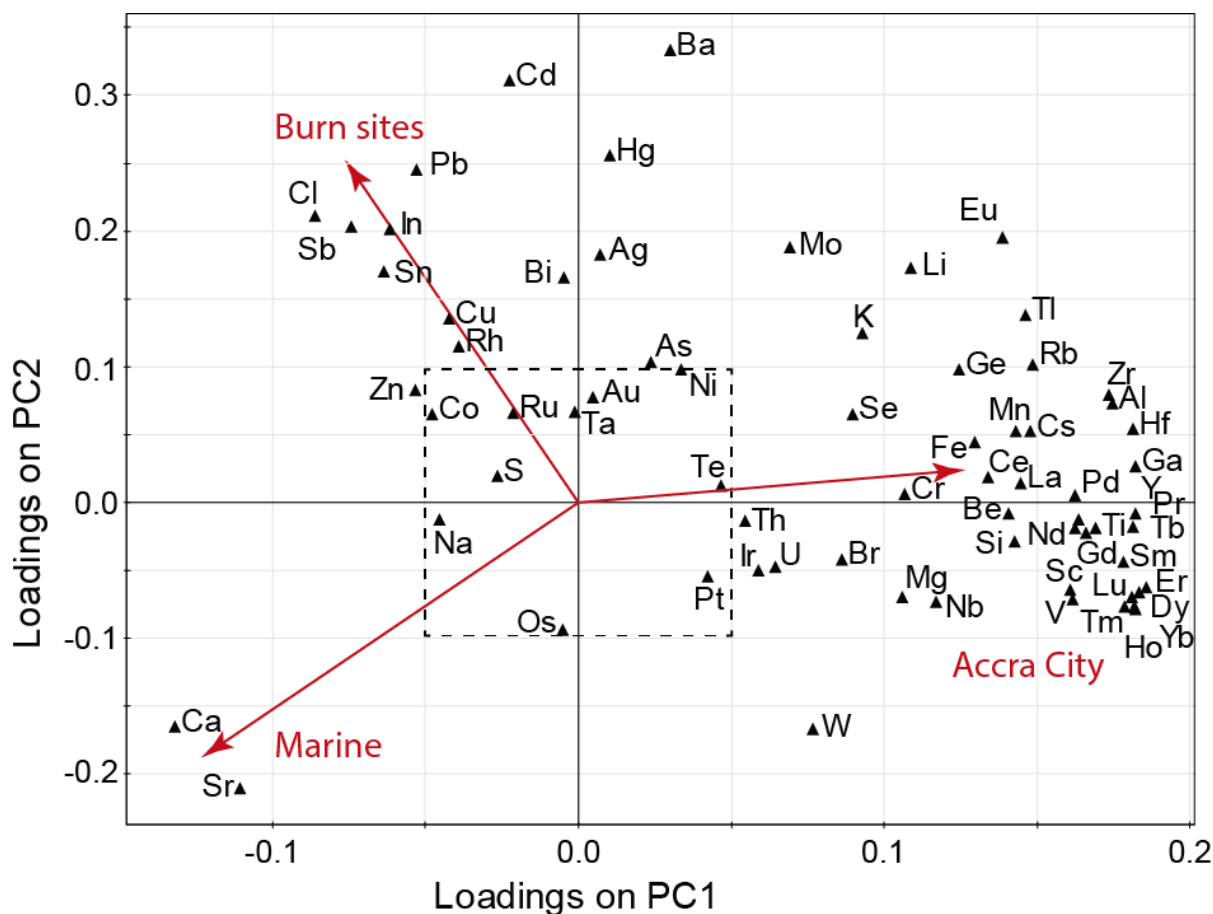


Figure 8. The loadings plot for all 69 elements analysed. The arrows indicate the different locations from the scores plot. The dashed box around the centre encloses those compounds that have a small influence on the principal component (PC) loadings.

Source Apportionment

Polytopic vector analysis (PVA) was carried out to determine the least amount of potential sources, also called end members, explaining the measured elemental concentrations. One of the outputs from the PVA model is the amount of variance explained for each element for each run solution. The model was run with 2 to 10 end members (EMs) and the individual fits to each element are present in Figure 9. This figure shows the following features:

1. Two elements (Ca and Fe) are well explained (>80% of the variance) with just two EMs indicating they probably only have two sources in the system.
2. A substantial number of elements have a significant improvement in their explained variance when the number of EMs is increased from two to three. This includes most of the REEs, Sr and V, which increase to ~80% of the variance explained with three EMs. This indicates these elements may have three sources in the system.
3. There are a number of other large improvements in fit, most notably, at from five and six EMs. Smaller improvements in fit are obtained with even more EMs.
4. Many of the heavier elements including Pt, Au, Th and U are poorly explained even after 10 EMs have been fitted.
5. The mean fit rises from 21% at 2 EMs, 37% at 3 EMs, 42% at 4 EMs, 51% at 5 EMs and 58% at 6 EMs. These mean fits are relatively small compared to other systems and may be due to poorly explained elements reducing the mean. One of the issues with all unmixing models is determining the correct number of EMs that cover all of the actual sources, whilst not attempting to fit the noise in the data ¹⁹.

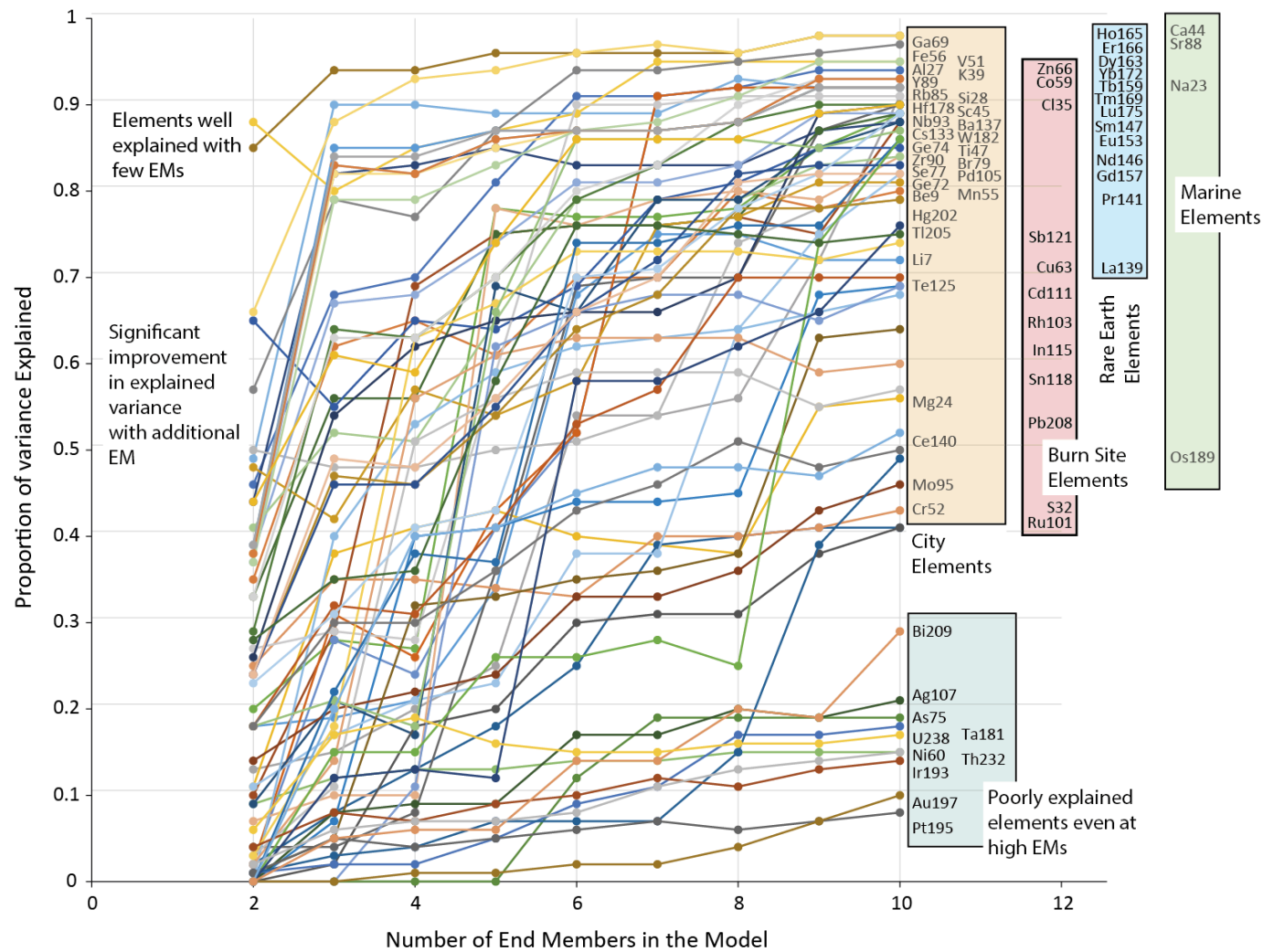


Figure 9. The proportion of variance explained for each element as the number of end members (EMs) in the PVA model is increased.

Before proceeding to determine the composition and contribution for each EM, the number of elements was reduced to remove those elements that might be considered as randomly distributed within the system and not associated with any particular source. These contribute to the noise in the system and reduce the overall predictability of the model. Four different approaches were used to determine which of the elements should be removed.

1. The dataset was examined and the elements with more than 50% of the samples exhibiting concentrations below the limit of detection were removed. In this case, only four elements fitted this category (Ru, Ta, Os and Au) and there was little improvement in the overall model as a result.
2. The coefficient of variation for each element was considered (see Table 2) and a decision made on whether high values indicated either significant enrichment at the burn site above a “normal” baseline condition in the other samples or low and a random variability in the entire dataset. Having considered these, it was determined that excluding elements through this approach would not be robust and objective.
3. The PCA loadings were considered (Figure 8) and the ten elements near the origin with loadings between -0.05 and +0.05 on PC1 and -0.1 and +0.1 on PC2 were removed. The PVA model was rerun and there was an improvement in the fits and the clarity in terms of the number of end members but not sufficiently to warrant pursuing this approach further.
4. The initial fit for each element in the PVA end member plot (Figure 9) was considered and all elements that failed to have 50% of their variance explained

within ten EMs were deemed to be due to “noise” or due to a random distribution in the samples. In this case, 14 elements were removed leaving 55 elements in the analysis. Many of these elements were the same as those that had been considered under the other schemes. Notably, most of the heavy elements (Pt, Au, Th, U and Ir) were removed and not used in the further PVA models. This multi-criteria approach improves the confidence that these elements are not contributing significantly to the overall chemical composition of the sources.

The PVA unmixing model approach was rerun with the reduced dataset and the results showed that the variance for all elements were explained to 50% or greater after 10 EMs. The scree plot of the mean explained variance indicated two possible end member solutions; one with three sources and a second with six. Both models were run and the data compared. In the three end member solution, the end members could be identified, on the basis of their geographical distribution and chemical composition, as the baseline soils of Accra, the marine environment and the burn site. The six end member solution also had the baseline soils and marine environments but divided the burn site source into four reinforcing the heterogeneous nature of the soils on this site (Table 3). In this case, the first three end members all had representative samples within the dataset that contained greater than 90% of that one pure source (*i.e.* they had a chemical composition close to that of one of the sources). For sources 5 and 6, the typifying samples only had a 36% contribution from those sources indicating that it was most probably a mixture of several different sources. It was, therefore, determined that the three end member solution would

be the most appropriate for this system and the results of this model are correspondingly discussed below.

The chemical composition of the three end members can be seen in Figure 10. The elemental composition indicates that only a few elements in each case have a concentration above 1% in each source (note, the y-axis is on a \log_{10} scale); the source may also include a range of elements at lower relative concentrations. For EM1, iron, silicon and aluminium make the greatest contribution to composition and are typical of minerals in soils. This corresponds with observations made during sampling of some red soils, which may be associated with an enrichment in iron. The REEs also make their greatest contribution in this source. Overall, these elements are typical of local baseline soils and are widely distributed through the city. The second end member is comprised of a small number of elements typical of the marine environment; calcium from shells and tests, sodium and chlorine from salt, as well as bromine and strontium. The high contributions from this source are only along the marine transect. The third end member contains many of the elements identified as being enriched at the burn site relative to the crustal abundance and are typically present in e-waste. The enrichment in chlorine is most likely due to the residues from burning chlorine containing plastics such as PVC while bromine may be present due to the presence of flame retardants. The antimony may also derive from this source.

Table 3. The quantity of explained variance in the six end member solution indicating the typifying samples according to the PVA output. Any negative values have been entered as zero and the sum of the explained variance (Total) can exceed 1.0 due to this. The cells are coloured from green to red on the basis of their value. Old Fadama is a residential area adjacent to the burn site at Agbogbloshe (Figure 2).

Location	Sample ID	EM1	EM2	EM3	EM4	EM5	EM6	Total
City Baseline	GH31	0.918	0.086	0.000	0.000	0.042	0.029	1.076
Marine	GH16	0.016	0.954	0.046	0.000	0.030	0.000	1.045
Burn	GH27B	0.017	0.032	0.915	0.000	0.036	0.014	1.015
Burn	GH26C	0.013	0.011	0.050	0.825	0.068	0.033	1.000
Old Fadama	GH24	0.277	0.344	0.007	0.000	0.360	0.048	1.035
Burn	GH28	0.360	0.112	0.174	0.024	0.000	0.350	1.020

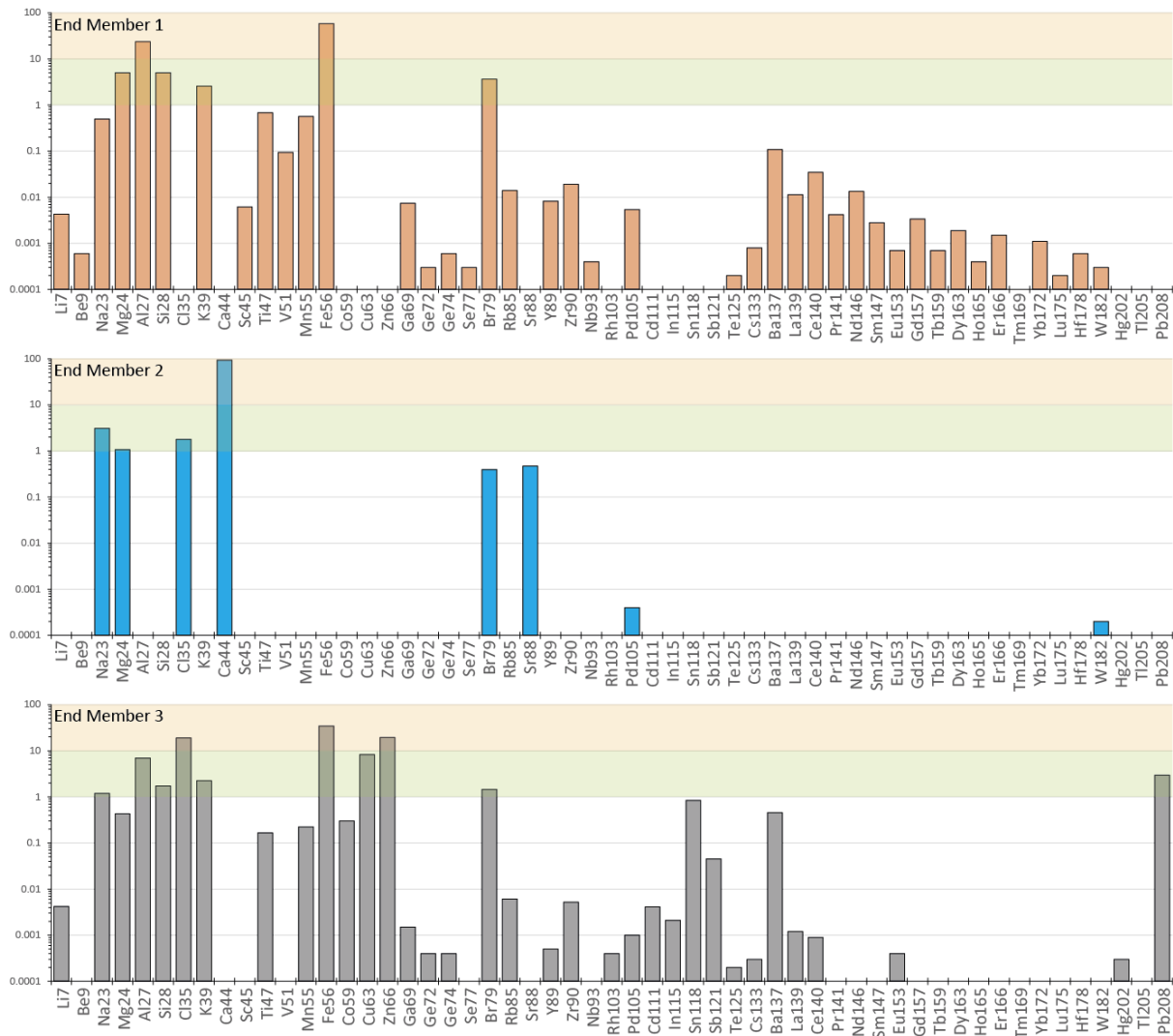
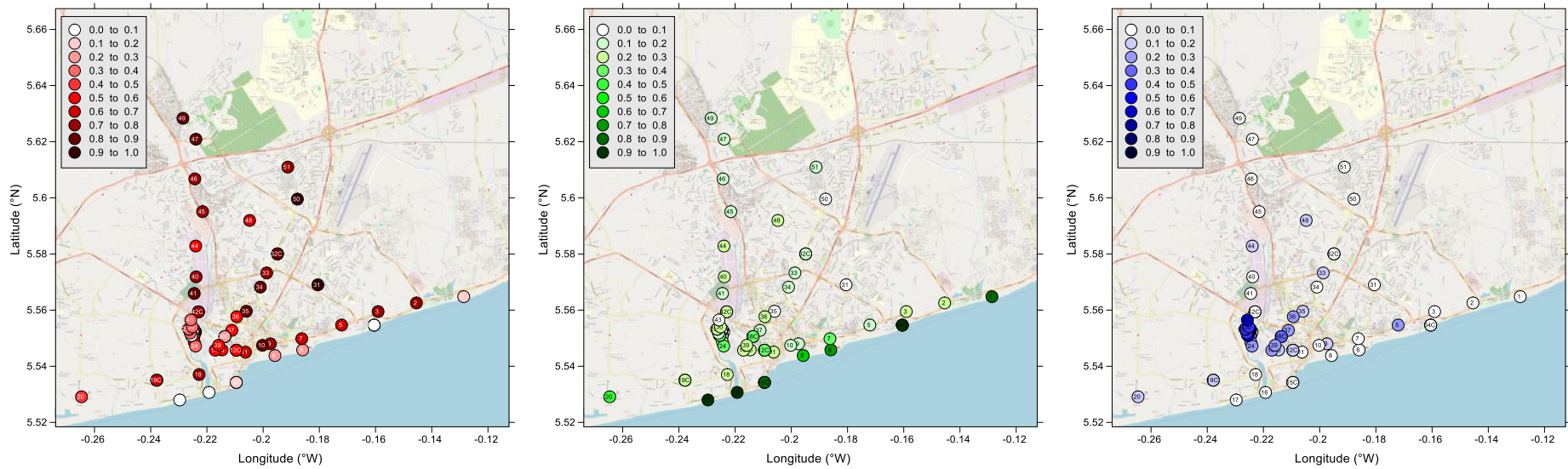


Figure 10. The elemental composition of each of the three end members from the PVA model. Bars in the green region are present at an abundance of >1% and those in the pale orange region at >10%. The y axis is on a log₁₀ scale.

The distribution of the three end members at the sites within Accra can be seen in Figure 11. End member 1, which is typical of the baseline soils, is the major source to all samples in the three transects downwind of the burn site as well as the one upwind to the west. EM2 is only present to any significant degree along the shoreline and it make little to no contribution to the samples within the city. This suggests there is little sea to land transfer

of contaminants at this location. EM3 has its origin at the burn site and there are measureable contributions in the dust samples to the east (downwind) of the source. An enlargement of the central region around the burn site, showing the EM3 distribution, can be seen in Figure 12. Although the values at the burn site may exceed 80%, the contribution this source makes to the samples from the city is small with samples containing between 20 and 40% to the east. The maximal range of influence from this source for these elements is between 1.5 and 2.0 km. No enrichment was seen in the upwind samples.



The baseline soils

The marine component

Burn site residues

Figure 11. The contribution from each end member to the dust samples across Accra. Background map from Open Street Map and its contributors.

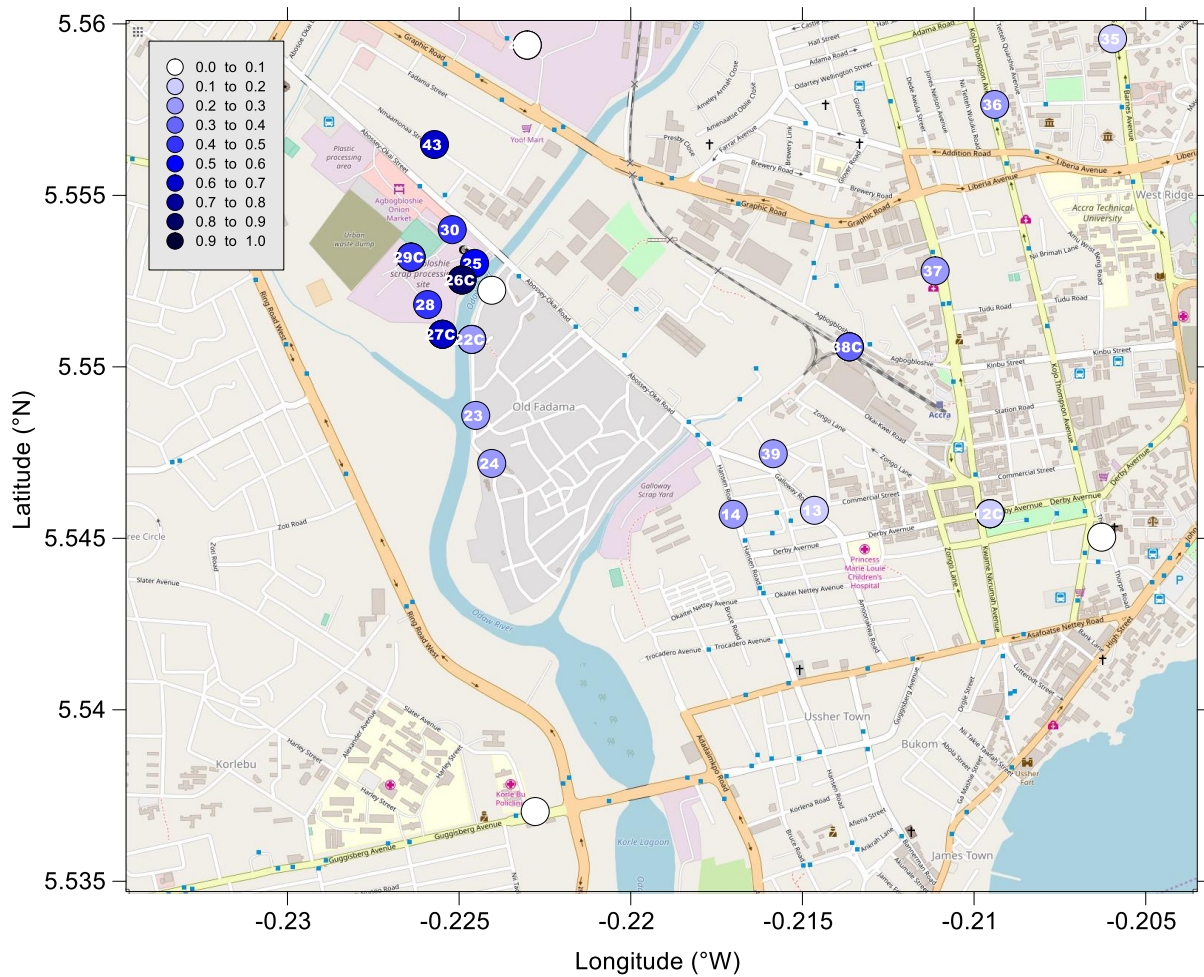


Figure 12. Contributions from EM3 at samples collected at and around the burn site. Higher values may be present as replicates were analysed at several sites but the spots are stacked as they are from the same location. Background map from Open Street Map and its contributors.

Variability

Pseudo-replicate (Intra-sample) Variability

Eleven samples were chosen for three separate sub-sample analyses (with separate digestions and analysis) to assess the homogeneity of the samples. At least one sample from each transect was chosen for pseudo-replicate variability testing, along with three taken from within the Agbogboshie processing site. The results indicated that intra-sample variability existed, with a mean coefficient of variation (CoV) across all metals and all pseudo-replicates of 30% (median of 21%). Elements present at the lowest concentrations

tended to have the greatest coefficient of variability although this was not a statistically significant trend. The larger CoV values were driven partly by values close to the limit of detection. The CoVs exhibited a log-normal distribution (Figure 13). The relatively high values indicate the heterogeneous nature of many of the samples as the elements appear to be concentrated in discrete particles rather than being surface bound.

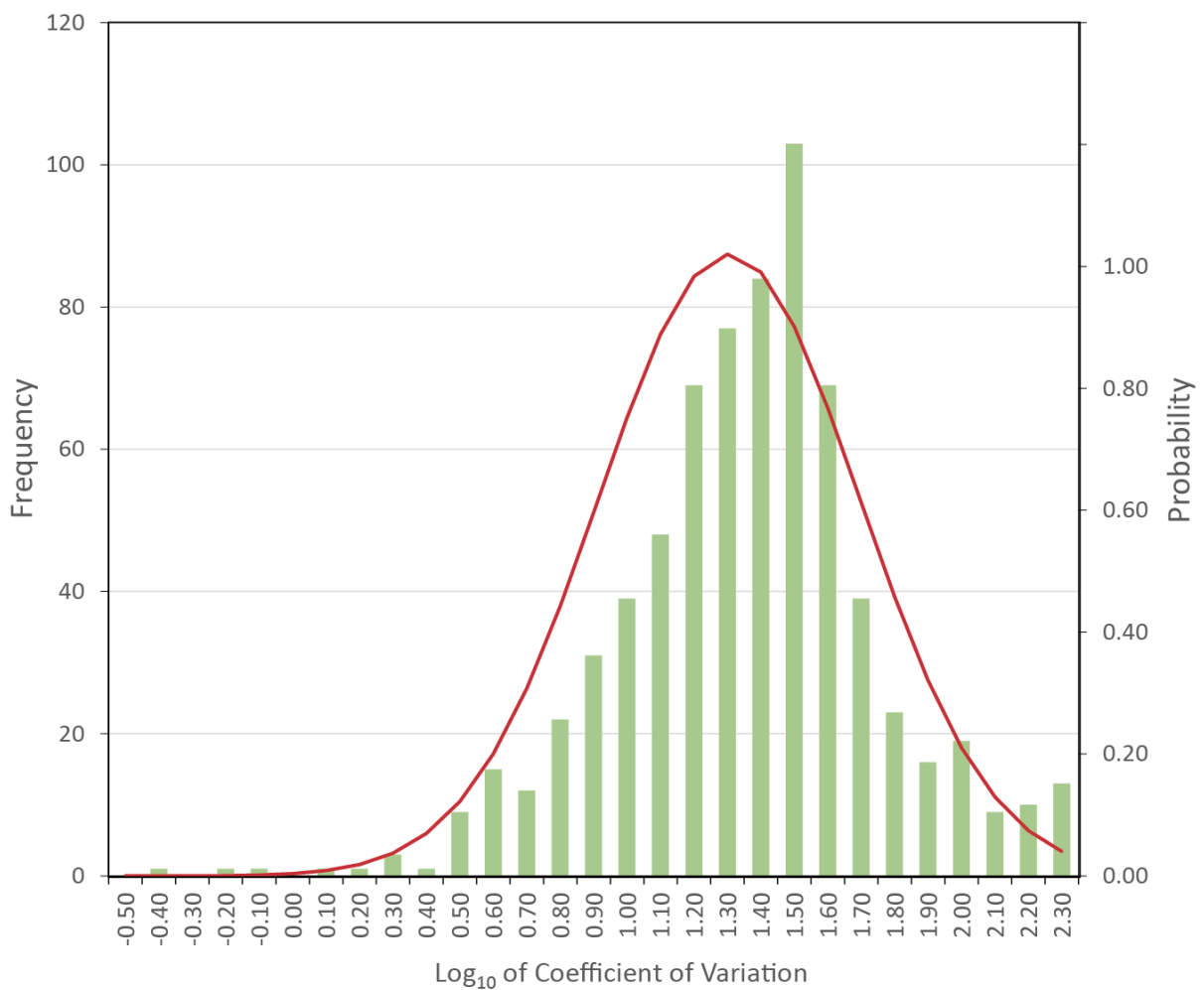


Figure 13. The distribution and probability for the CoV expressed on a log₁₀ scale. The data includes all metals and all replicates.

Discussion

Overall, the elemental concentrations measured in this work are in line with other studies that have focused on the burn site⁶. The elemental composition of the samples from the burn site was reflective of the materials used in electronic items (Table 1). Many of the metals in these samples are common in solder. Solder for electronic circuit boards typically used to contain a mixture of 63% tin and 37% lead but, due to the toxicity of the lead, it has been replaced with a number of alternative metals including copper, silver, bismuth, indium, zinc and antimony²⁰. Although tantalum was excluded from the multivariate statistical analyses due to its low abundance and occurrence in samples, it was present in two samples at the burn site possibly due to its use in capacitors. The chlorine is likely to have been derived from the PVC and bromine from flame retardants. Some of the antimony may also be associated with flame retardants²¹.

REEs that are typically present in newer high technology equipment such as mobile telephones, high density magnets and display equipment²² were essentially absent in the burn site residues, indicating that only low technology equipment was processed at the Agbogbloshie burn site. This conclusion is supported by observations made when sampling that the bulk of the waste was relatively low technology items with many white goods (*e.g.* fridges and freezers) and vehicles. The burners were principally interested in recovering the copper and it appeared as if the wiring looms from old vehicles were being stripped out and the PVC coatings burned off. The newer, high technology, equipment was potentially being removed from the waste stream before it reached Agbogbloshie and was recycled

elsewhere. Items within the waste stream that could potentially be reused or repurposed were also removed and were available for sale on the streets of Accra.

The burning aspect of metal recovery was conducted on a designated area of the Agbogbloshie site (site 27 on the maps, see Figure 2), with the insulation from fridges and freezers used as fuel. Sheets of expanded polyurethane (PU) foam were actively removed from white goods and used on the burn site for this purpose. The wire stripped from vehicles along with printed circuit boards was placed on the burning foam to remove any plastic components and release the metals. The burning took place at ground level and there was no significant rise in the smoke plume (Figure 14). The use of the PU foam as a fuel and combustion of PVC may give rise to a wide range of nitrogen and chlorine-containing inorganic and organic compounds^{23, 24}.



Figure 14. The burning of e-waste at Agbogbloshie. PU foam used as fuel can be seen near the central fire and bundles of wire stripped from vehicles is being brought to the burners in baskets.

Accra is a busy city with much commerce taking place on the streets. As a consequence, the city streets are relatively dusty with a range of additional potential sources of elements. The concentrations of elements in these city dusts are not dissimilar to the crustal abundances overall, but the REEs are relatively depleted and several elements that can be directly related to the e-waste are enriched. These same elements are also diagnostic of the burn site residues in the PCA and their occurrence can be linked to the nature of the e-waste.

Other studies have also identified Cu, Cd and Pb as indicative of these informal e-waste processing sites (*e.g.* Israel ²⁵ and China ²⁶) and more developed European processors ²⁷. Copper is present at an elevated concentration in the e-waste materials and is generally the target of the recycling community. The remaining elements are generally not recovered.

Human health may be at risk from a wide and diverse range of elements and compounds. The exposure routes will also vary but, in general, will encompass inhalation of gases and fine particles as well as the ingestion of food items. The risk to human health from exposure to the elements measured in this study is difficult to quantify without measurement of a number of exposure factors and blood markers, not performed within this study. Thus, as a proxy for risk, a ratio was developed using the maximum permissible concentrations (MPC) in soils ²⁸. The ratios were calculated at each site and for each metal with an MPC value. For those samples with three (pseudo)-replicates, the mean value was calculated. At several sites, more than one element had a risk ratio greater than 1; since there was no clear approach as to how to combine these risks, the element exhibiting the highest risk was presented.

Results for the risks are shown in Figure 15; in this figure, the colour of the spot is indicative of the element that gave the highest risk and the size of the spot is relative (\log_{10} scale) to the value of the ratio. The greatest risk is from copper, with greatest risk ratios at the burn sites at Agbogbloshie. It is clear that there are some effects of these dusts in the city leading to an increased human health risk, which is to be expected given the dispersion patterns observed in the PVA. What is less explainable is the presence of a few elevated values towards the end of the transects. These are due to nickel at site 05, zinc at sites 03, 34 and 36 and, more unusually chromium at site 50. The source of these elements at these locations is not clear.

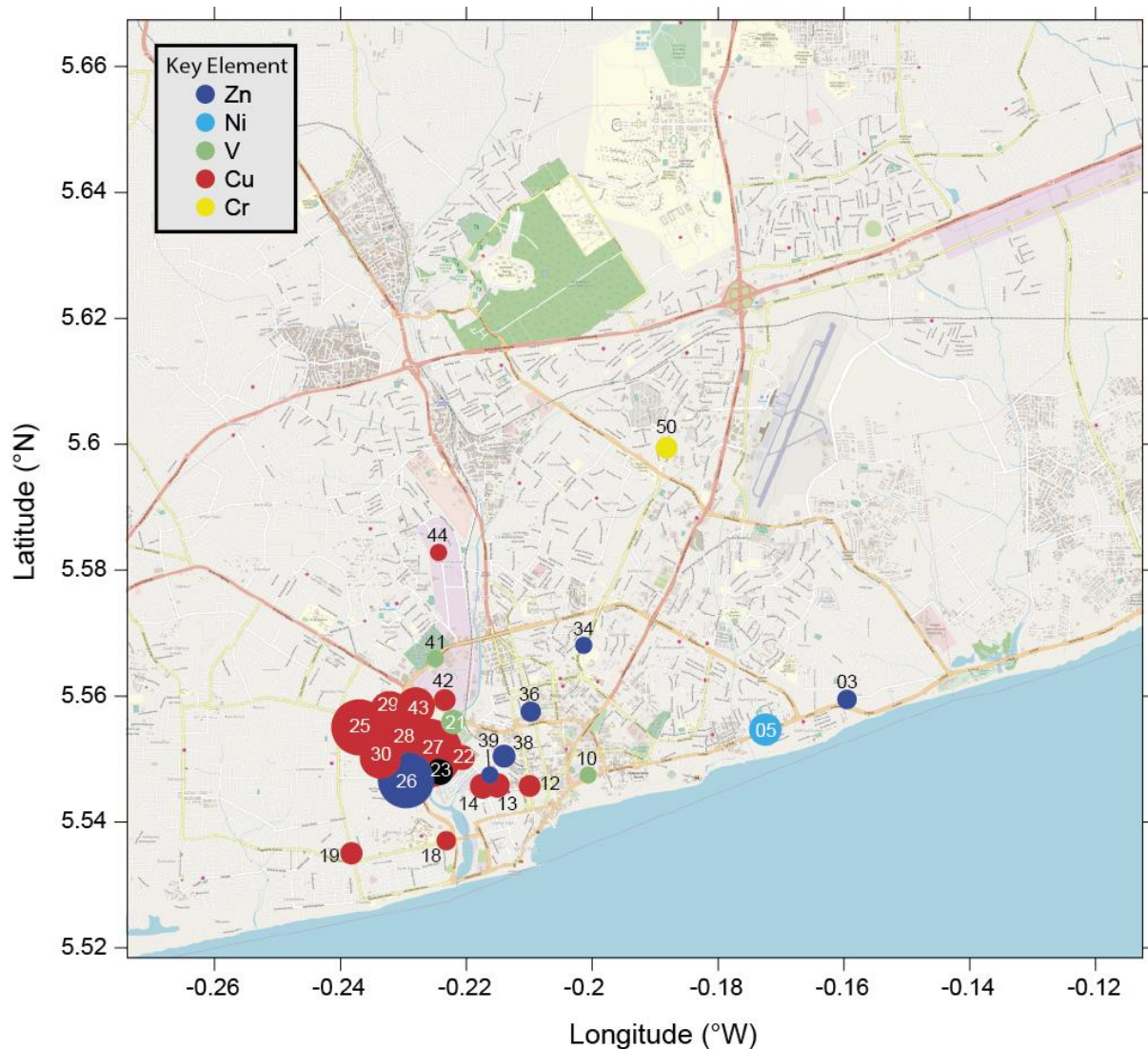


Figure 15. The "risk ratio" based on the measured concentrations and maximum permissible concentrations in soil. Only values greater than 1.0 are shown and in the case of more than one element exhibiting elevated values, the highest value is shown (since this poses the greatest risk to human health). The sample spots have been repositioned to enable all those around the Agbogbloshie waste site to be seen. The spot size is scaled according to the \log_{10} of the risk compared to 1 (reference size is sample 10). The highest risk is seen at site 27 (maximum value in 27C = 2745) and the mean risk ratio is 1192. Background map from Open Street Map and its contributors.

In addition to the ratios developed above, the hazard quotient approach of the US Environmental Protection Agency⁸ was also used. This is the same approach used by Itai and co-workers⁹. The concentrations were applied to the following equation using the coefficients from Itai et al.:

$$HQ_{oral} = \frac{(C \times IRS \times EF \times ED)}{(RfDO \times BW \times AT \times 1000000)}$$

Where C is the concentration of the element (mg.kg⁻¹);

IRS is the soil ingestion rate (100 mg.day⁻¹);

EF is the exposure frequency (number of days per year exposed to the dusts = 365 days per year);

ED is the exposure duration and 30 years has been used here to be consistent with ⁹;

RfDO is the chronic oral reference dose (mg.kg⁻¹.day⁻¹);

BW is the body weight of the exposed person and 62 kg has been used; and

AT is the average time of exposure (ED x 365 days per year).

The RfDO values used were from Itai *et al.* ⁹.

Results showed that the greatest hazard quotient was for copper (17.7) at the burn site. All values in excess of 1.0 were at the Agbogbloshie site, and not in the city, except for copper at site 44. Other elements that exceed 1.0 include Pb, Sb and Zn. These data are consistent with those of Itai *et al.* ⁹ although the values calculated here are greater than their reported quotients. This may be due to our sampling of the surface dusts that may have a greater surface area compared to bulk soils.

Overall, there are significantly elevated metal concentrations and associated risks with the soils and dusts on the Agbogbloshie e-waste processing site. This is not unexpected given the nature of the activities that are performed on site. Out of the elements analysed here, a significant number exceed the nominal MPC but copper, the target of e-waste recovery at

Agbogbloshie, leads to the greatest risk. It must be stressed that this does not include the considerable potential for organic compounds present with e-waste or formed during the combustion of the plastics on site²⁹. It appears as if the dispersion of the elements measured here from the burn site do not penetrate far into the city and the major zone of exposure is within 2.0 km of the site in an easterly direction.

The chemical composition of the marine samples from the shoreline are different from those at the e-waste site and the city, which indicates that materials from the waste site do not enter the river and are washed out into the sea. This correlates with observations made during sampling, that there was a considerable amount of plastic litter on the shoreline but little to no matter from the e-waste site. The majority of the transect samples also indicate a baseline composition unaffected by the waste site.

Conclusions

The type of e-waste being processed was of a low technology level and included discarded white goods and end-of-life vehicles. This was reflected in the chemical composition of the elements found in surface samples taken from the burn site, with the major components related to both tin-lead solder (Sn, Pb) and lead-free solder (Sn, Cu, Ag, Bi, In, Zn and Sb). Other elements found from samples taken on-site included chlorine potentially derived from the burned plastic residue and bromine from flame retardants.

The mechanism of processing e-waste at Agbogbloshie involves low temperature combustion of waste PU foam as a fuel, with little thermal lift in the generated smoke. This

means that the dispersion of these elements is rather limited, and the subsequent contributions can only be quantified up to 1.5 km from the site in a downwind (easterly) direction. The risk to human health from these elements is elevated at the burn site itself and in samples within a relatively short distance of the combustion. For copper, risk ratios up to 2745 and hazard quotients up to 17.7 were calculated. Other elements presenting elevated risk are zinc, nickel, vanadium, chromium, antimony and lead.

Analysis of the entire dataset by a range of multivariate statistical methods indicated that ~15 elements had no specific association with any one source in the region and were poorly explained. Of the four approaches used to identify which elements could be removed to improve source discrimination, the most appropriate was excluding the elements that had <50% of the variance explained after 10 end members had been fitted in PVA. The number of potential sources within the city is most likely to be three; the baseline soils of Accra, the marine environment and the burn site. For the burn site, however, there are a number of potential sources as the area is not homogeneous and elements may be resuspended and dispersed from each.

Acknowledgements

The authors would like to acknowledge the extensive assistance with sampling from Sylvia Akpene Takyi, Lawrencia Kwarteng, Abigail Adoley Addison and George Yeboah from the University of Ghana. The work was also facilitated by Nice One (James Town), Awal (burn site) and John Morcher to whom we are indebted.

Conflicts of Interest

There are no conflicts to declare.

References

1. M. Favot and L. Grasseti, E-waste collection in Italy: Results from an exploratory analysis, *Waste Management*, 2017, **67**, 222-231.
2. M. Man, R. Naidu and M. H. Wong, Persistent toxic substances released from uncontrolled e-waste recycling and actions for the future, *Science of The Total Environment*, 2013, **463-464**, 1133-1137.
3. E. A. Yu, M. Akormedi, E. Asampong, C. G. Meyer and J. N. Fobil, Informal processing of electronic waste at Agbogbloshie, Ghana: workers' knowledge about associated health hazards and alternative livelihoods, *Global Health Promotion*, 2016, **24**, 90-98.
4. C. P. Baldé, F. V., V. Gray, R. Kuehr and P. Stegmann, *The Global E-waste Monitor*, Bonn/Geneva/Vienna, 2017.
5. D. Cazabon, J. N. Fobil, G. Essegbey and N. Basu, Structured identification of response options to address environmental health risks at the Agbogbloshie electronic waste site, *Integr. Environ. Assess. Manag.*, 2017, **13**, 980-991.
6. T. Tokumaru, H. Ozaki, S. Onwona-Agyeman, J. Ofosu-Anim and I. Watanabe, Determination of the Extent of Trace Metals Pollution in Soils, Sediments and Human Hair at e-Waste Recycling Site in Ghana, *Arch. Environ. Contam. Toxicol.*, 2017, **73**, 377-390.
7. S. Obiri, O. D. Ansa-Asare, S. Mohammed, H. F. Darko and A. G. Dartey, Exposure to toxicants in soil and bottom ash deposits in Agbogbloshie, Ghana: human health risk assessment, *Environ. Monit. Assess.*, 2016, **188**, 9.
8. US-EPA, *Exposure factors handbook*, Springfield, VA., Washington, DC, 2011.
9. T. Itai, M. Otsuka, K. A. Asante, M. Muto, Y. Opoku-Ankomah, O. D. Ansa-Asare and S. Tanabe, Variation and distribution of metals and metalloids in soil/ash mixtures from Agbogbloshie e-waste recycling site in Accra, Ghana, *Science of the Total Environment*, 2014, **470**, 707-716.
10. E. Akortia, O. I. Olukunle, A. P. Daso and J. O. Okonkwo, Soil concentrations of polybrominated diphenyl ethers and trace metals from an electronic waste dump site in the Greater Accra Region, Ghana: Implications for human exposure, *Ecotox. Environ. Safe.*, 2017, **137**, 247-255.
11. T. Fujimori, T. Itai, A. Goto, K. A. Asante, M. Otsuka, S. Takahashi and S. Tanabe, Interplay of metals and bromine with dioxin-related compounds concentrated in e-waste open burning soil from Agbogbloshie in Accra, Ghana, *Environmental Pollution*, 2016, **209**, 155-163.
12. X. C. Lu, C. Q. Lin, W. K. Li, Y. Chen, Y. Q. Huang, J. C. H. Fung and A. K. H. Lau, Analysis of the adverse health effects of PM_{2.5} from 2001 to 2017 in China and the role of urbanization in aggravating the health burden, *Science of the Total Environment*, 2019, **652**, 683-695.
13. A. G. Allen, E. Nemitz, J. P. Shi, R. M. Harrison and J. C. Greenwood, Size distributions of trace metals in atmospheric aerosols in the United Kingdom, *Atmos. Environ.*, 2001, **35**, 4581-4591.
14. J. B. Milford and C. I. Davidson, THE SIZES OF PARTICULATE TRACE-ELEMENTS IN THE ATMOSPHERE - A REVIEW, *Journal of the Air Pollution Control Association*, 1985, **35**, 1249-1260.
15. S. M. Mudge, in *Introduction to Environmental Forensics*, eds. B. L. Murphy and R. D. Morrison, Academic Press, Third Edition edn., 2015, ch. 19, pp. 655-675.

16. WeatherOnline, www.weatheronline.co.uk).
17. G. B. Haxel, J. B. Hedrick and G. J. Orris, *Rare Earth Elements—Critical Resources for High Technology*, 2005.
18. R. Rudnick and S. Gao, *Composition of the Continental Crust. Treatise Geochem 3:1-64*, 2003.
19. S. M. Mudge, C. Bravo-Linares, L. Ovando-Fuentealba and J. P. Pinaud-Mendoza, A comparison between three unmixing models for source apportionment of PM_{2.5} using alkanes in air from Southern Chile, *Environmental Forensics*, 2017, **18**, 226-240.
20. S. Herat, Green Electronics through Legislation and Lead Free Soldering, *CLEAN – Soil, Air, Water*, 2008, **36**, 145-151.
21. F. Binz and B. Friedrich, Development of Secondary Antimony Oxides from Metallurgical Slags for the Application in Plastic Products, *J. Sust. Metall.*, 2017, **3**, 683-689.
22. P. Chancerel, M. Marwede, N. F. Nissen and K. D. Lang, Estimating the quantities of critical metals embedded in ICT and consumer equipment, *Resour. Conserv. Recycl.*, 2015, **98**, 9-18.
23. X. Liu, K. A. Salmeia, D. Rentsch, J. W. Hao and S. Gaan, Thermal decomposition and flammability of rigid PU foams containing some DOPO derivatives and other phosphorus compounds, *J. Anal. Appl. Pyrolysis*, 2017, **124**, 219-229.
24. M. Witt, M. Goniewicz, W. Pawlowski, K. Goniewicz and W. Biczysko, Analysis of the impact of harmful factors in the workplace on functioning of the respiratory system of firefighters, *Ann. Agr. Env. Med.*, 2017, **24**, 406-410.
25. L. R. Friedlander, N. Weisbrod and Y. J. Garb, Climatic and soil-mineralogical controls on the mobility of trace metal contamination released by informal electronic waste (e-waste) processing, *Chemosphere*, 2019, **232**, 130-139.
26. Y. Han, Z. W. Tang, J. Z. Sun, X. Y. Xing, M. N. Zhang and J. L. Cheng, Heavy metals in soil contaminated through e-waste processing activities in a recycling area: Implications for risk management, *Process Safety and Environmental Protection*, 2019, **125**, 189-196.
27. H. Lee, M. Bae, E. Lee and B. Mishra, Copper Extraction from Flue Dust of Electronic Waste by Electrowinning and Ion Exchange Process, *Jom*, 2019, **71**, 2360-2367.
28. T. Crommentuijn, D. Sijm, J. de Bruijn, M. van den Hoop, K. van Leeuwen and E. van de Plassche, Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations, *Journal of Environmental Management*, 2000, **60**, 121-143.
29. P. Bruce-Vanderpuije, D. Megson, E. J. Reiner, L. Bradley, S. Adu-Kumi and J. Gardella, J.A., The state of POPs in Ghana- A review on persistent organic pollutants: Environmental and human exposure, *Environmental Pollution*, 2019, **245**, 331-342.