

METALS IN AGBOGBLOSHIE E-WASTE RECYCLING SITE, ACCRA, GHANA: DISTRIBUTION, BIOACCESSIBILITY AND HEALTH RISK ASSESSMENT

Submitted by

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Declaration

I certify that the work in this thesis entitled “Metals in Agbogbloshie e-waste recycling site, Accra, Ghana: distribution, bioaccessibility and health risk assessment” has not previously been submitted for a degree nor has it been submitted as part of the requirement of a degree to any other university or institution other than Macquarie University.

I certify that the thesis is an original piece of research I authored. All assistance or help I have received in my research work and the preparation of this thesis have been duly acknowledged.

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Michael ACKAH

Date 30 September 2019

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Abstract

Due to the scarcity of information on the impacts of e-waste on terrestrial and aquatic systems, this study was designed to provide current and timely information on solid and aqueous phase contamination around two informal e-waste recycling sites in Agbogbloshie (Accra, Ghana) and Ashaiman (Tema, Ghana). Field procedures involved sampling 180 urban soil samples, 88 surface dust samples, 96 surface water samples, 21 sediment samples, 32 agricultural soils and 49 leafy vegetables in Agbogbloshie and control sites. Thirteen soil samples were collected in Ashaiman Fitter Line e-waste recycling site. Samples were analysed for total and bioaccessible metal concentrations and mineralogy. Elevated metal concentrations were found in soil and surface dust. Garden soil and leafy vegetables were not contaminated. Dissolved elements were found in small concentrations in the surface waters. Quartz was the dominant mineral in the dust, with albite, anglesite, calcite and tenorite. Bioavailability of metals in selected samples of floor dust, garden soils and leafy vegetables were determined using *in vitro* extraction employing simulated gastric solutions. Copper, zinc and lead were more bioaccessible in vegetables than in surface dust. Iron had the smallest bioaccessible fraction in both soil and vegetables. Lead in urban soils from burn area topsoils, burn area subsoils, dismantling area topsoils and dismantling area subsoils posed non-carcinogenic risks to children and adults in Agbogbloshie. Lead in soils from Ashaiman posed non-carcinogenic risks to children but not adults. Copper concentrations posed significant non-carcinogenic risks to children from burn area topsoils, burn area subsoils, dismantling area topsoils, and also in Ashaiman soil. Carcinogenic risks from arsenic ingestion of contaminated burn area subsoils and dismantling area topsoils was significant for children living in Agbogbloshie. Similarly, soils in Ashaiman posed carcinogenic risks to children living near the e-waste site.

List of abbreviations

Element symbols follow IUPAC periodic table of the elements

Be-Beryllium

Al-Aluminium

Na-Sodium

K-Potassium

Ca-Calcium

Ti-Titanium

V-Vanadium

Cr-Chromium

Fe-Iron

Co-Cobalt

Ni-Nickel

Cu-Copper

Zn-Zinc

Ga-Gallium

As-Arsenic

Se-Selenium

Br-Bromine

Rb-Rubidium

Sr-Strontium

Mo-Molybdenum

Ag-Silver

Cd-Cadmium

In-Indium

Sn-Tin

Sb-Antimony

Cs-Caesium

Ba-Barium

Ta-Tantalum

Au-Gold

Hg-Mercury

Pb-Lead

Bi-Bismuth

AAS- Atomic absorption spectrometry

ARMCANZ- Agriculture and Resource Management Council of Australia and New Zealand

ANZECC-Australian and New Zealand Environment and Conservation Council

BDL-Below detection limits

CCME- Canadian Council of the Ministers of the Environment

CRT- Cathode ray tube

EMPA- Swiss Federal Laboratories for Materials Science and Technology

FAO- Food and Agricultural Organisation

GSB- Ghana Standards Board

HDPE- High-density polyethylene

ICP-AES- Inductively coupled plasma atomic emission spectrometry

ICP-MS-Inductively coupled plasma mass spectrometry

MPX-Mega pixel

ND-Not detected

PAH- Polycyclic aromatic hydrocarbons

PXRF- Portable X-ray fluorescence

XRF-X-ray fluorescence spectrometry

USDOE- United States Department of Energy

USEPA- United States Environmental Protection Agency

WHO- World Health Organisation

Publications

The research publications arising from this thesis are;

Ackah M. 2017. Informal e-waste recycling in developing countries: review of metal(loid)s pollution, environmental impacts and transport pathways. *Environmental Science and Pollution Research* 24(31):24092-24101. doi:10.1007/s11356-017-0273-y.

Ackah M. 2019. Soil elemental concentrations, geoaccumulation index, non-carcinogenic and carcinogenic risks in functional areas of an informal e-waste recycling area in Accra, Ghana. *Chemosphere* 235:908-917. doi:10.1016/j.chemosphere.2019.07.014.

Conference presentation

A poster titled “Distribution, bioaccessibility and health risk assessment of trace metals in floor dust from an informal e-waste recycling site in Accra, Ghana” was presented at the 10th International Conference on the Analysis of Geological and Environmental Materials, Geoanalysis 2018, 8-13 July 2018. Macquarie University, Sydney, Australia.

CHAPTER 1: Introduction

1.1 Background to the study

E-waste is defined as discarded or end of life information and communication technologies (ICT) and other electrical/electronic equipment which is dependent on electric current or electromagnetic fields to function (UNEP 2007). Globally, e-waste generation now constitute about 8% of municipal solid waste streams and it is growing at an increasing rate annually (Widmer et al. 2005). In 2016, the global e-waste generation reached 44.7 Mt with Africa creating 2.2 Mt (Baldè et al. 2017). E-waste contains valuable recyclable materials such as ferrous and non-ferrous metals, precious metals, rare earth elements, plastics and glass. It also contains hazardous components such as toxic metals, organic substances and brominated flame retardants, which can be constituents of plastics (Sum 1991; Gramatyka et al. 2007). The chemical composition of e-waste varies depending on the age and type of discarded electronic product (Robinson 2009). Recent legislation in European Union (RoHS Directive 2002/95/EC) has minimised the use of toxic substances in electronic equipment including Cadmium, lead and mercury (Weiss et al. 2016). Consequently, hazardous materials content of e-waste are associated more with older electric and electronic items thus making e-waste temporarily and spatially heterogeneous (Robinson 2009). Chemical hazards are associated with metals (e.g., cadmium, lead) and flame retardants (e.g., polybrominated diphenyl ethers (PBDE), tetrabromobisphenol-A (TBBPA) (Tsydenova and Bengtsson 2011). Cathode ray tubes (CRT) screens, liquid crystal display (LCD) screens, batteries, circuit boards and plastics contain most of the hazardous substances found in consumer waste (Amankwaa et al. 2016; Tsydenova and Bengtsson 2011). End-of-life e-waste management practices include disposal in a landfill or through incineration or recycling which may include reprocessing for parts or refurbishment and reuse (Luther 2010). Mechanical recycling of e-waste in developing countries often results in significant metal pollutant emissions into air, water, soil and residual waste (Ackah 2017). Proper e-waste recycling requires regulated facilities such as integrated smelters. However, ICT is rarely recycled in proper facilities, especially in developing countries (Williams 2011). The growing quantities and complex composition of e-waste coupled with the lack of viable recycling systems and disposal and treatment costs of e-waste recycling is a challenge for many nations. Ghana's imports of used electrical and electronic equipment reached 215,000 t in 2009 (Amoyaw-Osei et al. 2011) while about 171,000 t making up 80% of the imports were informally recycled (Caravanos et al. 2013). Ghana is now seriously struggling with the lack of proper e-waste recycling facilities to recycle its own domestic e-waste and illegally imported e-waste from developed countries (Daum et al. 2017; Obiri et al. 2016; Srigboh et al. 2016). E-

waste is informally recycled with little to no emission controls in Agbogbloshie and Ashaiman in the Greater Accra Region of Ghana (Figure 1.1) (Grant and Oteng-Ababio 2013).



Figure 1.1 Location of sites mentioned in this chapter (Source: Google maps).

There are growing concerns about environmental impacts of informal e-waste recycling on human health and the environment worldwide (Heacock et al. 2016), because improper disposal and recycling of e-waste can release harmful materials such as Pb, Hg, Cd, Zn and Cr (VI), which can contaminate soil, water and air. Workers at and residents near informal e-waste recycling sites can suffer from long-term health problems such as an increased probability of developing cancers (Tetteh and Lengel 2017). There is a paucity of information on the health and associated environmental impacts from many of these informal e-waste sites. Potential health hazards from some hazardous e-waste components are described (Table 1.1).

Table 1.1 Environmental and health hazards associated with informal e-waste processes (Pinto 2008)

E-waste component	Process	Potential occupational hazard	Potential environmental hazard
Cathode ray tubes	Breaking, removal of Cu yoke and dumping	Silicosis, cuts from CRT glass, inhalation or contact with phosphor containing Cd or other metals	Pb, Ba and other heavy metals leaching into groundwater and release of toxic phosphor
Printed circuit boards	Desoldering and removing of computer chips	Sn and Pb inhalation, possible brominated dioxin, Be, Cd and Hg inhalation	Air emissions of the same substances
Dismantled printed circuit board processing	Open burning of waste boards	Toxicity to workers and nearby residents from Sn, Pb, brominated dioxin, Be, Cd and Hg inhalation	Sn and Pb contamination of the immediate environment, including surface and ground waters, brominated dioxins, Be, Cd and Hg inhalation
Chips and other Au-plated compounds	Chemical stripping using HNO ₃ and HCl along river banks	Acid contact with eyes, the skin may result in permanent injury, inhalation of mists and fumes of acids, chlorine and sulfur dioxide gases can cause respiratory irritation to severe effects including pulmonary edema, circulatory failure and death	Hydrocarbons, heavy metals, brominated substances etc. discharged directly into river and banks. Acidifies the river destroying fish and flora
Plastics from the computer and peripherals	Shredding and low-temperature melting	Probable hydrocarbon, brominated dioxin and PAH exposure to workers living in the burning works area	Emission of brominated dioxins and heavy metals and hydrocarbons
Secondary steel or Cu and precious metal smelting	Furnace recovers steel or Cu from waste	Exposure to dioxins and heavy metals	Emission of dioxins and heavy metals
Wires	Open burning to recover Cu	Brominated and chlorinated dioxin and PAH exposure to workers in the burning area	Hydrocarbon and ashes including PAH discharged into air, water and soil

1.2 Problem statement

People can be exposed to e-waste toxicants via food contamination and through occupational exposure of workers directly engaged in e-waste recycling (Kiddee et al. 2013). Exposure is greater for vulnerable groups including children, the elderly, and pregnant women (Carrizales

et al. 2006; Amankwaa 2014). There is a paucity of data on contamination around e-waste recycling sites however, an understanding of contamination of the ambient environment around e-waste recycling sites is of utmost importance to ensure the safety of the local ecosystems (Liu et al. 2008). Metal contaminants in agricultural soils can adversely affect food production where plants absorb and accumulate metals directly from soils. Rivers and lagoons in Agbogbloshie e-waste recycling area can serve as sinks and sources of metals. However, there are few data on concentrations of aqueous phase metal contaminants. Sediment contamination is of paramount interest (Chama et al. 2014). An assessment of aqueous phase contaminants and sediment contamination can help understand potential ecological risks and provide an understanding of relationships among contaminants.

1.3 Research sites

1.3.1 Agbogbloshie e-waste recycling site

Agbogbloshie e-waste recycling site (hereafter “Agbogbloshie”) covers 6.2 h of land in Accra, the capital city of Ghana (Caravanos et al. 2011) (Figure 1.1). Agbogbloshie is bounded by Abossey-Okai Road, Odaw River (in the upper reaches of Korle Lagoon) and the Agbogbloshie drain, <1 km from the central business district of Accra (Agyei-Mensah and Oteng-Ababio 2012). Agbogbloshie was once a thriving wetland, however, it is now littered with all kinds of remnant waste electrical and electronic equipment with the main electronic wastes processed including obsolete computers, monitors, refrigerators, scrap vehicles, television sets and used batteries (Figure 1.2). Used electronic equipment is manually dismantled at numerous small workshops scattered across the e-waste site to recover base and precious metals from older computers and other electronics for their economic value. Open-burning of printed circuit boards and capacitors is practiced on the bank of Odaw River and the boundaries of the site and this often results in thick dark smoke (Asante et al. 2016; Srigboh et al. 2016). E-waste recycling in Agbogbloshie started in 1993, when parts and components of spoilt second-hand fridges and computers, mostly imported from Europe were retrieved and used to fabricate household utensils for cooking and other metal tools (Amoako 2016). However, currently, Agbogbloshie has developed to become the largest and most prominent e-waste recycling site in Ghana (Caravanos et al. 2011; Asante et al. 2016; Amuzu 2018). A large residential slum housing both e-waste recyclers and their families are located 100 m across Odaw River. Agbogbloshie is also home to the biggest fresh food market in Accra.



Figure 1.2 Agbogbloshie informal e-waste recycling site in Accra. Here a worker is stripping Cu wires from refrigerator motors. Field assistant wearing nitrile gloves is sampling soil in the lower right foreground.

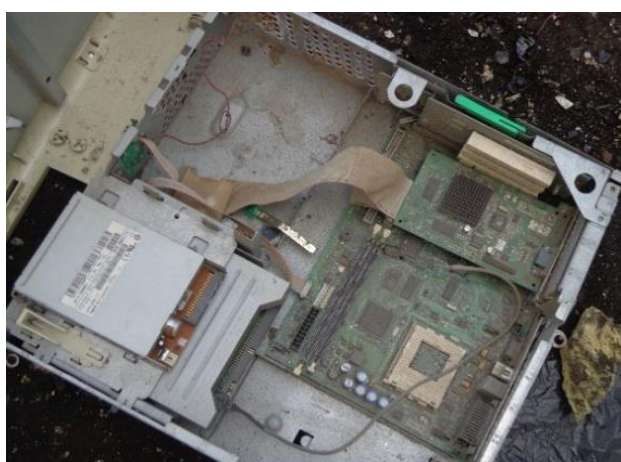


Figure 1.3 Computer central processing unit (CPU) with some components removed found in Ashaiman e-waste recycling site.



Figure 1.4 Printed circuit board dumped in Ashaiman e-waste recycling site.

1.3.2 Ashaiman e-waste recycling site

Activities at Ashaiman e-waste recycling site (hereafter “Ashaiman”) are mostly dismantling and open burning of e-waste (Figures 1.3 and 1.4). E-waste recycling activities have occurred at Ashaiman since 1999 (Okine 2014), however, it is much smaller than Agbogbloshie.

1.3.3 Odaw River and Korle Lagoon

Korle Lagoon is a major wetland in Accra. Korle Lagoon receives effluents from Odaw River, the principal drainage channel, with a catchment area covering 60% of Accra's population (Boadi and Kuitunen 2002), estimated to be around 2-3 million people (Ghana Statistical Service 2012). Tributaries of Odaw River includes the urban streams Onyasia, Dakobi and Ado.

1.4 Research hypotheses, aims and objectives

Environmental matrices in Agbogbloshie and Ashaiman can be significantly contaminated, and the extent of contamination is scarcely understood. Furthermore, an ecological assessment of critical water bodies such as the Odaw River and Korle Lagoon is essential due to possible leaching of e-waste pollutants from informal e-waste recycling activities in the overlying land areas. A study on metal pollution of several environmental matrices can provide comprehensive and current information to help establish the health risks to the population living in the area. Information on the most important metal pollutants in Agbogbloshie and Ashaiman can help our understanding of which metal pollutants are of concern when initiating pollution control and mitigation strategies to safeguard human and environmental health. The hypotheses for this study are;

- (1) Soil, surface dust, water and sediment in Agbogbloshie and soil in Ashaiman contain elevated concentrations of metals compared with control areas.
- (2) Metals in environmental matrices of concern are bioaccessible and pose human health risks, and
- (3) Land use activities can affect the metal distribution and health risks.

This research aims to assess dissolved and solid phase inorganic contaminants at Agbogbloshie and Ashaiman e-waste recycling sites in Ghana. Specific objectives were;

1. To assess the environmental impacts of informal e-waste recycling,
2. To collect soil, water, sediment, dust and plants within and around Agbogbloshie e-waste recycling site and Ashaiman e-waste recycling site,
3. To characterise elemental concentrations in collected samples and investigate their sources,
4. To measure bioavailable concentrations of inorganic contaminants in the surface dust, garden soils and vegetables using in-vitro techniques,
5. To assess the human health risks of metals in soils, floor dust and vegetables using a USEPA human health risk assessment model, and

6. To understand mineralogical phases of dust in Agbogbloshie e-waste recycling site.

1.5 Thesis outline

Chapter 1 gives a background to the research problem and presents the aims, objectives and hypotheses for the study. **Chapter 2** reviews the literature highlighting the main transport pathways of metal contaminants in informal e-waste recycling sites and presents a brief literature review of six studies on contamination in Agbogbloshie e-waste recycling sites. **Chapter 3** discusses the analytical techniques used in this study. **Chapter 4** characterises the total concentrations of 11 elements - Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in topsoils and subsoils around e-waste burn-areas and dismantling areas of Agbogbloshie e-waste recycling area. Characterisation of metal concentrations in both topsoils and subsoils will provide an understanding of the contamination in the e-waste recycling site. A further assessment of human health risks can address health impacts on vulnerable populations who may be exposed to these metals through inadvertent ingestion, inhalation and dermal contact. **Chapter 5** focusses on the spatial distribution of metals in e-waste impacted surface dust. Potential ecological risks of potentially toxic elements in surface dust were assessed. **Chapter 6** describes the concentrations and human health risk assessment of Mn, Fe, Ni, Cu, Zn, Ba and Pb collected from dismantling and other functional areas of Agbogbloshie e-waste recycling site. In this chapter, site-specific bioaccessibility factors derived from an invitro-extraction procedure were used to refine the human health risk assessment associated with metals in Agbogbloshie. Bioaccessibility factors are important in human health risk assessment studies to avoid under-estimation or over-estimation. An overestimation of health risks can lead to unnecessary expenditure on remediation. **Chapter 7** investigates bioaccumulation of five vegetables - African eggplant, hibiscus, amaranth, Egyptian spinach and lettuce from soils of two urban gardens situated on the banks of Korle Lagoon, which lies downstream of Agbogbloshie e-waste recycling site. Findings from this chapter can help understand the differences in contaminant concentrations among agricultural soils and that of urban soils in Agbogbloshie e-waste recycling area. **Chapter 8** investigates dissolved contaminants in Korle Lagoon. **Chapter 9** integrates the major findings of this study.

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CHAPTER 2: Literature Review

2.1 Introduction

E-waste comprises discarded electronic equipment, of which computers and mobile phones are disproportionately abundant because of their short life span (Robinson 2009). E-waste has become a subject of growing concern in developing countries due to the large volume of legal and illegal imports from developed nations into emerging economies in China, India, Brazil and some African nations including Ghana and Nigeria (Wu et al. 2015; Jun-Hui and Hang 2009; Otsuka et al. 2012). E-waste recycling in developing countries is fraught with both challenges and opportunities because there are no suitable recycling facilities to deal with the end-of-life management of growing quantities of e-waste. Proper e-waste recycling is important for environmental protection, resource recovery and to meet legislative requirements (Chancerel et al. 2009).

E-waste contains 60% of metals of which printed circuit boards contain the greatest concentration of metals (Cui and Forssberg 2003). Metals are used in electronics due to their unique properties. For example, platinum group metals are used mainly because of high conducting properties and chemical stability (Robinson 2009). Br has widespread use in brominated flame retardants in plastics of electronic equipment (McGrath et al. 2016). The presence of base metals such as Cu in e-waste makes it very attractive to recycle e-waste in developing countries (Robinson 2009).

E-waste is distinct from municipal solid waste and contains a heterogeneous mixture of hazardous substances including toxic metals and radioactive materials. E-waste is presently the fastest growing component of the municipal solid waste stream and contains precious metals such as Au and Ag. The valuable contents in e-waste provide an incentive for material recovery. In developing countries, e-waste recycling is practiced by the informal sector who derive employment through manually dismantling end of life electrical and electronic items and extracting base and precious metals using rudimentary techniques. The rudimentary techniques used by informal e-waste recyclers' cause emission of hazardous elements into sensitive ecological receptors such as waterbodies and agricultural soils. The ultimate destination for these pollutants is the food chain through bioaccumulation from soils.

Informal e-waste recycling presents human health and environmental hazards and risks including workplace contamination, occupational exposure and ecological exposure. Residents living near e-waste recycling facilities may be exposed via inhalation or ingestion of contaminated soil, dust, water and food supplies (Robinson 2009). E-waste recyclers can also

suffer from injuries and potential exposures resulting from original constituents of electronic equipment, substances added during the recovery process and substances formed from the recycling processes (Noel-Brune et al. 2013).

Agbogbloshie is the hub of e-waste recycling activity in Ghana (Prakash et al. 2010; Asante et al. 2012; Grant and Oteng-Ababio 2012). Agbogbloshie has attracted scientific and media attention in the last decade (Daum et al. 2017). In 2013, Blacksmith Institute ranked Agbogbloshie among the top ten toxic sites in the world (Blacksmith Institute 2013). A detailed study on workplace contamination in Ghana focused on Agbogbloshie (Brigden et al. 2008). Some studies were conducted to assess metal contamination of Agbogbloshie (Caravanos et al. 2011; Atiemo et al. 2012; Otsuka et al. 2012; Itai et al. 2014; Obiri et al. 2016).

2.2 Methods

A systematic search was conducted using terms such as “metal pollution, e-waste, impacts, pathways, Agbogbloshie e-waste site” in extensive databases such as Web of knowledge and PubMed. Some institutional reports on e-waste recycling were also assessed. Studies were retrieved for assessment based on their relevance to the objectives of this review. Six studies were selected for review on soil metal concentrations, covering nine years from 2008 to 2016. Similarly, studies on sediment, worker breathing zones and toxic emissions from the burning of e-waste containing brominated flame retardants and other organic pollutants were captured and the information briefly summarised.

2.3 Elemental concentrations in sampled matrices of selected studies

The six studies reviewed focused on the determination of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Sr, Cd, Sn, Sb, Ba, Hg, Pb and Br in soil, surface dust, bottom ash, sediments and water bodies. The location of study, sample sizes, analytical techniques and concentrations are shown (Table 2.1). Analytical techniques employed to assess metal contaminants were atomic absorption spectrometry, X-ray fluorescence spectrometry and inductively coupled plasma-mass spectrometry while the number of samples investigated ranged from 3 to 420 samples.

2.4 Metals in sediments and waterbodies near Agbogbloshie

Recycling of end-of-life electronics is environmentally beneficial, however, the processes and techniques used are often primitive and lack any pollution control measures (Wong et al. 2007). In developing countries, sites used for informal electronic waste recycling activities are located near water sources, where the water is used for cooling. In countries where environmental enforcement is not stringent such as Ghana, leachates containing toxic metals emanating from

informal e-waste recycling processes can enter these water resources. Sediments of Odaw River were found to contain appreciable concentrations of toxic Pb and Cd, ranging from 11 to 33 $\mu\text{g/g}$ and 0.07-0.62 $\mu\text{g/g}$ respectively (Chama et al. 2014). Sediments sampled from Korle Lagoon contained appreciable concentrations of Cu, Zn, Cd and Pb (Huang et al. 2014). Nickel, Cu, Cd, Hg and Pb were detected in water and sediments of a riverine system flowing close to Guiyu e-waste recycling site in China (Guo et al. 2009).

2.5 Metals in soils, soil-ash mixtures and surface dust

Soils are sinks for gaseous and atmospheric pollutants emitted from e-waste recycling (Liu et al. 2013). Open burning sites at Agbogbloshie contained elevated concentrations of many metals and organic substances present in electronics or those released from the combustion of materials contained in electronic devices (Brigden et al. 2008). More than 50% of contaminated soil samples had Pb concentrations greater than the USEPA residential soil Pb guideline of 400 mg/kg (Caravanos et al. 2011). Caravanos et al. (2011) measured Pb along the bank of Odaw River on the east side of the site, with a concentration exceeding the USEPA Pb guideline by 45-fold. The greatest Pb concentration in soil was measured at a weighing site at Agbogbloshie where Pb concentrations ranging from 351 to 5100 mg/kg were measured (Atiemo et al. 2012). A Pb concentration range of 100-14000 mg/kg in ash was measured (Otsuka et al. 2012). A recent study measured total and 1 M HCl extractable Pb concentration of 50-12000 and 100-14000 mg/kg respectively (Itai et al. 2014).

Table 2.1 Metal concentrations (mg/kg) and Br in dust, soil, soil/ash mixtures and bottom ash (concentrations reported to 3 significant figures)

Sampling period	Description of study sites	Sample Size	Analytical Technique	Concentrations (mg/kg)	References
Oct-March 2009	Weighing site, burning sites, dismantling site, worship centre, commercial area, road dust and school compound	10 surface dust samples per site	AAS (Varian AA240 FS)	Cr: 22-115, Mn: 91-294, Ni: 26-191, Zn:10600-30000, Cd: 4-72, Pb: 351-5100	Atiemo et al. 2012
2011	Burning area, 3 inland disposal and dismantling areas	100 soil samples	PXRF spectrometer (Innov-X Systems, model Alpha)	Pb: 913-5880	Caravanos et al. 2011
2008	2 burning sites with no disposal, 1 burning site within disposal, 1 lagoon adjacent to disposal and burning area, 1 below CRT glass within disposal area, Burning area adjacent to scrap dealer	4 soil/ash samples, 1 soil sample and 1 sediment sample	ICP-AES(Varian MPX Simultaneous Spectrometer)	Ni: 9-33, Cu:85-14300, Zn: 274-31300, As: <20, Sn: 7-1290, Hg: <0.5-0.6, Pb:110-5510	Brigden et al. 2008
August 2010	10 wire burning sites	10 soil samples	PXRF spectrometer (Innov-X Systems)	Cu:50-2200, Zn:200-160000, As:<50-1100, Br:20-1500, Sn:<50-1000, Hg:<20-50, Pb:100-14000	Otsuka et al. 2012
August 2010	2 burning locations	10 soil-ash mixtures	PXRF spectrometer (Omega Xpress PXRF; Innov-X Systems)	PXRF- Mn: Not Detected-212, Fe:10000-38000, Co: ND-65, Cu:53-22000, Zn:220-19000, As: ND-1100, Br:2-1500, Sr:31-150, Sn: ND -1000, Cd, Sb and Ba: ND, Hg: ND-150, Pb:100-14000 ICP-MS- Mn: 36-180, Fe: 13000-43000, Co: 2-467, Cu: 24-4330, Zn: 93-36700, As:37-253, Sr:1-4, Cd:1-28, In: ND-28, Sb:1-392; Cs:1-5, Ba:20-280, Pb:50-12000, Bi: ND -5	Itai et al. 2014
September 2012-June 2013	3 burning sites and 3 manual dismantling sites	210 bottom ash and 210 soil samples	AAS (Agilent)	Location 1- Cr:42±0, Co:123±0, Cu:7940±0, Zn: 276±0, As:20±0; Cd:2±0, Sn:225±0, Pb:5390±0 Location 2- Cr:37±0, Co:135±0; Cu:1430±0, Zn:783±0, As:1620±0, Cd:27±0, Sn:234±0, Pb:1690±0 Location 3- Cr:45±1, Co:96±2, Cu:2460±124, Zn:124±3, As:25±0, Cd:5±0, Sn:323±2, Pb:4650±238	Obiri et al. 2016

2.6 Metals in air and worker breathing zones

Toxic emissions containing metals and inorganic acids from crude e-waste recycling sites can leach into waterways and risk contaminating natural resources such as soil, crops, drinking water, fish and livestock (Sepúlveda et al. 2010). Heavy metals in air samples and within worker breathing zones were assessed in Agbogbloshie e-waste recycling site (Caravanos et al. 2011). Worker breathing zone's air concentrations of Al, Cu, Fe, and Pb, exceeded the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs) of 1.0, 1.0, 5.0 and 0.5 mg/m³ respectively. The exceedance was very much apparent for Al, whereby worker exposure concentrations were reported to be about seventeen times the ACGIH guideline value (Caravanos et al. 2011). Precious metal recovery from cathode ray tubes, printed wiring boards and cable sheaths using crude recycling practices may release metals and organic chemicals which may spread through the air via dust (Robinson 2009), and major pathways of exposure are ingestion, inhalation and absorption through the skin (Mielke and Reagan 1998). Open burning of e-waste can help recover base metals like Cu, Al and Fe, but there is the attendant problem of large releases of toxins such as dioxins, furans and PAH into the air. A summary of metals in air samples of the burning sites and worker breathing zones in Agbogbloshie e-waste recycling site is shown (Table 2.2).

2.7 Body burdens of metals in e-waste recycling workers

Chromium, Mn, Fe, Co, Cu, Zn, Se, Cd, Ba, Hg and Pb concentrations were assessed in urine and blood serum of 87 e-waste workers in Agbogbloshie and 87 persons from Makola Market, who acted as a control population (Caravanos et al. 2013). Metals were not elevated in blood serum concentrations and urine in the control population (Caravanos et al. 2013). In the exposed population, metals in blood serum concentrations were very small and this was attributed to a flaw in the analytical method because blood serum was analysed instead of whole blood (Caravanos et al. 2013). E-waste recycling workers in Agbogbloshie were exposed to toxic concentrations of Fe, Sb and Pb with greater concentrations in the urine of e-waste recycling workers than in urine of a control group (Asante et al. 2012). Asante et al. (2012) attributed the elevated metals concentrations in urine to consumption of contaminated fish and not from the local drinking water supply. A summary of the results is presented (Table 2.2).

Table 2.2 Metal concentrations in the urine (mg/L) of e-waste recycling workers and in air samples (mg/m³) of burning sites and worker breathing zones in Agbobloshie e-waste recycling site

Sampling period	Matrices	Sampling sites	Sample size	Concentrations	Reference
August 2008	urine	Recycling workers in Agbobloshie	20	Ti: < 0.01-0.18, V: 3-170, Cr: 0.18-29, Mn: 0.76-11, Fe: 19-540, Co: 0.041-9, Cu: 7-490, Zn: 178-2480, Ga: < 0.01-0.15, As: 15-222, Se: 6-64, Rb: 324-3980 Sr: 20-389, Mo: 6-463, Ag: <0.01, In: <0.01-0.08, Sn: 2-6, Sb: 0.12-3, Cs: 0.52-1, Ba: 1-20, Hg: < 0.05, Pb: 0.86-18.	Asante et al. 2012
2011	air	Burning sites for wires and plastics	3	Fe: BDL-7.8, Cu: BDL-1.5, Pb: BDL-0.72.	Caravanos et al. 2011
		Worker breathing zones	5	Al: BDL-6.5, Fe: 5.0-17, Cu: BDL-1.2, Pb: BDL-0.98.	

2.8 Other e-waste contaminants reported in Agbogbloshie e-waste area

Organic contaminants found in Agbogbloshie e-waste recycling site include endocrine disrupting substances such as brominated flame retardants (EMPA 2012). Brominated flame retardants are used in many products such as electronic circuitry to reduce material flammability and slow combustion to meet fire safety regulations (Alaee et al. 2003). Brominated flame retardants are mainly found as either component of the electrical and electronic equipment or are released during crude recycling. Persistent organic pollutants (POP), commonly found in electrical and electronic components include brominated flame retardants (polybrominated diphenyl ethers), polybrominated diphenyls, polychlorinated biphenyls (PCB), dibrominated diphenyl ethers, polychlorinated or polybrominated dioxins and dibenzofurans dioxins, hexabromocyclododecanes, and perfluoroalkyls (Grant et al. 2013). POP released during dismantling processes, specifically from incineration and smelting include polychlorinated dibenzodioxins, polychlorinated dibenzofurans, and dioxin-like polychlorinated biphenyls. Polycyclic aromatic hydrocarbons (PAH) are naturally occurring, hydrophobic and are formed as a result of incomplete combustion of coal, wood, gas, oil, meat, tobacco, and incense. PAH is also released during the burning of e-waste materials (Grant et al. 2013). Open burning of cables is a major source of dioxin emissions, a persistent organic pollutant that travels over long distances and has the tendency to bioaccumulate in organisms through the global food chain (EMPA 2012). Contamination levels of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/F) and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) have been found in the soils of Agbogbloshie in concentrations ranging from 83-3800 ng/g and 18-520 ng/g respectively (Tue et al. 2016). Dioxin-like PCB in open-burning sites ranged from 1.4 to 7.5 ng/g. The sources of these toxic contaminants were the on-site burning of brominated flame retardants in e-waste plastics (Tue et al. 2016). Similarly, concentrations of PCDD/F, as well as polychlorinated biphenyls in the blood of individuals working at e-waste recycling sites, were observed to be one and half times greater than a control group of similar ages (Wittsiepe et al. 2015).

2.9 Discussion

Elevated concentrations of metals occur in soils, surface dust and sediments in Agbogbloshie. A further assessment of metal pollutants and their potential health risks to the population is needed. Ghana can develop appropriate measures to curtail further contamination in Agbogbloshie by establishing mechanisms to reduce toxic exposures. For instance, the provision of appropriate facilities and policy framework could regulate the activities of informal

e-waste recyclers. Ghana recently passed e-waste legislation to provide a policy framework for the management of end-of-life electrical and electronic items. Ghana's e-waste legislation seeks to domesticate the Basel Convention into its national laws and establish an electrical and electronic waste management fund to support establishment treatment facilities, research and public education. Crude or rudimentary e-waste recycling techniques can be improved by providing support and education for informal e-waste recyclers who may not be fully aware of the health risks. Collaborations among the government and non-governmental organizations can help develop and pilot safe and environmental efficient e-waste recycling programmes aimed at reducing toxic impacts from e-waste recycling activities. Governments can also collaborate with scientists in developing countries by providing requisite funding to collect data, where lacking, especially data on actual domestic e-waste generation and imports of e-waste, legacy contamination in informal e-waste recycling sites and human health risks.

2.10 Conclusion

Crude e-waste recycling contaminates soil, water, air and human tissues with toxic metals. Crude e-waste recycling activities such as the open burning of e-waste can contribute to regional pollution levels. There is an urgent need to remediate areas which have been contaminated by metals and organic pollutants to safeguard human health. People living near informal e-waste recycling activities risk are being exposed to toxic contaminants, without effective and adequate measures being put in place to address the contamination. There is a critical need for further research on contamination in environmental media such as soils, sediments, waters and local produce growing near contaminated e-waste recycling sites. These data on environmental contamination can help policy makers and environmental managers with information on the priority contaminants of concern to help design effective pollution-mitigation strategies.

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CHAPTER 3: Analytical techniques

3.1 Introduction

In this chapter, analytical methods used in this research are discussed. Energy dispersive X-ray fluorescence spectrometry was used for elemental analysis of waters, soils, dust and vegetables while X-ray diffractometry was used for mineralogical determinations of dust.

3.2 Energy dispersive X-ray fluorescence spectrometry (EDXRF)

EDXRF is a simple, cost-effective, rapid and non-destructive multi-elemental analytical technique suitable for chemical elemental analysis of liquid and solid samples (Ene et al. 2010; Gupta 2014). X-ray fluorescence spectrometry is based on the principle of interaction of X-rays with matter. When a beam of X-rays originating e.g. from X-ray tubes) impinges on a sample; it will interact with the atoms in the sample by three processes, namely, the photoelectric effect and coherent (Rayleigh) and incoherent (Compton) scattering (Wobrauschek et al. 2010). For the photoelectric effect to occur, the energy of the impinging photons must be large enough to create a vacancy in one of the shells of the studied elements causing elements to emit (fluoresce) secondary X-rays with discrete energies that are characteristic for these elements (Towett 2013; Brouwer 2006; Wobrauschek et al. 2010). A detection system measures energy of the emission lines and their counts for qualitative and quantitative analysis. Qualitative analysis can be done using spectral line energies while photon counts are related to the concentrations of elements for quantitative analysis.

Total reflection X-ray fluorescence (TXRF) spectrometry is a variant of EDXRF using a special excitation geometry (Wobrauschek and Streli 2010). In TXRF, the narrow-collimated beam impinges at grazing incidence on a special sample carrier at an angle less than the critical angle and thus the beam is totally reflected (Misra 2011). Concentrations of different elements from sodium to uranium are measured after evaluating the X-ray intensities of their characteristic lines and comparing these intensities with that of the internal standard characteristic X-ray line with corrections for the sensitivities (Misra 2011). TXRF is useful for multi-elemental analysis of different types of samples-liquids, solutions, powder, suspensions, solid, thin films and aerosols (Salomone et al. 2017). TXRF is useful for elemental analyses of wastewater, rainwater and groundwater (Stosnach 2005; Eksperiandova et al. 2002; Espinoza-Quiñones et al. 2015), soils and sediments (Towett et al. 2013; Bilo et al. 2014), and plants, including vegetables (Günther and von Bohlen 1990; Alvarez et al. 2003). The most significant advantages of TXRF are improved detection limits, which can be in the picogram range, some three orders of

magnitude lower than traditional geometry XRF (Wobrauscheck and Streli 2010). Other advantages are that TXRF analysis require small sample volumes, are insensitive to matrix effects due to the low glancing angle of the primary X-ray beam, multi-elemental capability and ease of operation (Borgese et al. 2018). TXRF does not require large volumes of reagents. TXRF does not need frequent calibration, due to the use of an internal standard addition method for elemental quantification (Borgese et al. 2018) and the intrinsic stability of the X-ray tube and electronics.

3.3 X-ray diffractometry (XRD)

XRD is a technique widely used for identification of crystalline materials such as minerals and inorganic compounds (Bunaciu et al. 2015), semi-crystalline phases, nanomaterials and even amorphous phases (Hansford 2016). An X-ray diffraction pattern obtained from an unknown sample is compared with patterns from a reference database such as that maintained by the International Centre for Diffraction Data (ICDD) (Ernrich and Oppen 2011). X-ray diffractometry is based on the uniqueness of the diffraction pattern of each distinct crystalline phase, based on the set of d spacings that are specific to each crystal structure (Hansford 2016). In XRD, a sample is irradiated with X-rays, which interacts with the sample causing diffraction of the X-rays (Harris and White 2008). Diffractometry is based on a thin beam of radiation (typically electromagnetic, though X-rays, γ -rays, electrons and neutrons can all be observed to scatter), of an appropriately small wavelength, incident to a crystal lattice, being scattered or “diffracted” in specific directions and angles depending on the distances of atoms in the crystal lattice, thus forming a “diffraction pattern” (Heimann 2016). Interaction of the incident rays with the crystal lattice of the sample must produce constructive interference (and a diffracted ray) when conditions satisfy Bragg’s Law, represented by the equation;

$$n \cdot \lambda = 2d \cdot \sin \theta,$$

where n is the order of interference, λ is the wavelength of the X-rays in Å, d is the lattice plane spacing and θ is the glancing angle. Bragg’s equation provides the condition for constructive interference of X-rays scattering from atomic planes of a crystal. Bragg’s equation also provides the important link between the measured angle θ and a characteristic lattice dimension d , i.e., the spacing of lattice planes parallel to a crystal face with the Miller index (Heimann 2016). By scanning the powdered sample through a range of 2θ angles, all possible diffraction directions of the crystal lattice should be attained due to the random orientation of powdered materials. Diffraction peaks are detected, processed and counted and conversion of diffraction peaks to d -spacings allow identification of the mineral because each mineral has a set of unique d -spacings.

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CHAPTER 4: Soil elemental concentrations, geo-accumulation index, non-carcinogenic and carcinogenic risks in functional areas of an informal e-waste recycling area in Accra, Ghana.

Abstract

This study assesses the contamination and human health risks of major, minor and trace elements in the topsoil and subsoil of two informal e-waste recycling sites in Accra, Ghana. Lead contributed the greatest ingestion risks in functional areas of Agbogbloshie and Ashaiman e-waste recycling sites in Ghana. Arsenic presents carcinogenic risks occur to children from the dismantling area topsoils. Among the non-carcinogenic risks, ingestion was more significant in the e-waste recycling sites than risks due to dermal exposure. Non-carcinogenic risks due to dermal contact of soils were insignificant in Agbogbloshie and Ashaiman. Children were more susceptible to non-carcinogenic ingestion risks than adults. Burn area and dismantling area topsoils contributed greatly to the non-carcinogenic ingestion risks in Agbogbloshie. Lead and Cu are the most important elements posing the greatest non-carcinogenic risks to children and adults. Lead hazard quotients for children in burn area topsoils and dismantling area topsoils were 7.4 to 7.6 times greater than Pb hazard quotients for adults. Mean geoaccumulation index values of Pb and Cu indicated extreme contamination of topsoils with these metals. A “novel environmental assessment tool” based on the ASTDR total impact points confirmed that Pb and Cu were the dominant metals in topsoils and subsoils of two functional areas (burn-areas and dismantling areas) in Agbogbloshie.

Keywords: risk assessment, soil toxicity, priority metals, geo-accumulation index.

4.1 Introduction

Electric and electronic items (EEE) use many metal(loid)s (hereafter “metals”) due to their unique properties. The presence of base metals such as Cu in e-waste makes it very attractive to recycle e-waste in developing countries (Robinson 2009). E-waste comprises discarded electronic appliances, of which computers and mobile phones are disproportionately abundant because of their short lifespan (Robinson 2009). E-waste chemical composition varies with the type and age of discarded appliance (Borthakur 2016).

Urban soils serve as a sink for metals emitted into the environment from anthropogenic and geogenic sources (Eze et al. 2010). Urban areas are affected by anthropogenic activities more than in rural areas (Iwegbue and Martincigh 2018).

Ghana has conducted e-waste recycling since 1990 (Daum et al. 2017). E-waste recycling has expanded from the main processing site into other secondary sites in Ghana’s capital city,

Accra, as well as other cities in Ghana (Grant and Oteng Ababio 2016). Agbogbloshie e-waste recycling site is located near a residential slum community, known as Old Fadama, where residents lack access to basic health care and nutrition (Owusu-Ansah et al. 2016). Informal practices of e-waste recycling can expose indigenous communities to highly toxic e-waste related mixtures, through inhalation, contact with contaminated or toxic dust and soil, and through the oral intake of contaminated locally produced foods (Frazzoli et al. 2010).

E-waste can contain over 1000 chemicals (Robinson 2009). Many metals in electronics are useful for their unique properties, such as Cu used as conductors, Pb and Sn in solders, Ba in dielectrics, and Ni and Cd in batteries (Teller 2006). Chromium, Co, Cu, Fe, Mn, Mo, Ni, Zn, Ca, Mg, K and Na are macro- or micro-nutrients needed for normal growth and development in living organisms (Chapman and Wang 2000). Some elements including Cd, Pb and Hg do not have any nutritional or biochemical functions (Chapman and Wang 2000) and are toxic. Other elements, considered as essential micronutrients such as Fe, Cu and Zn can become toxic and exhibit adverse physiological effects during excessive intake above permissible limits (Petruzzelli et al. 2010; Mahmood et al. 2012). Heavy metals are generally persistent, bioaccumulate, and have the potential to cause adverse health effects (Adriano 2003). Chromium (VI), Cd and Pb are known carcinogens and Pb is a neurotoxicant and teratogen (Duruibe et al. 2007).

Children are more susceptible to the neurotoxic effects of Pb than adults because children tend to absorb more Pb and excrete proportionally less Pb from their bodies, thus retaining relatively more Pb in their bodies (Hassanien and Elshahawy 2001). Lead can be retained particularly in the bones from where it can desorb, leading to chronic effects over years to decades. Furthermore, pica and hand-to-mouth activities of children make them more vulnerable to lead toxicity than adults (Papanikolaou et al. 2005). The poor legislation, low socio-economic conditions and poorly enforced environmental regulations in low-income countries may cause children and other vulnerable groups in society to be exposed to environmental contamination (Goldman and Tran 2002; Massey 2004).

Ashaiman is an emerging e-waste recycling site (Quayson 2016) while Agbogbloshie is the e-waste recycling hub (Obiri et al. 2016). In Agbogbloshie, recyclers manually dismantle computer components including motherboards in the open or under shade. Cable sheaths are burnt on the banks of a lagoon generating smoke and other toxic emissions into the open air. Metal-laden dust from informal e-waste sites is dispersed by wind and water during rainfall or flooding and windstorms (Kushi et al. 2013). Metal-laden dust can settle and contaminate edible plants especially leafy vegetables growing near the e-waste sites. Humans who consume metal

contaminated vegetables may suffer potential health effects (Luo et al. 2011). In a metal-contaminated environment, inadvertent soil and dust ingestion and the soil-plant-food pathway can be very important ways in which humans are exposed (Ljung et al. 2007; Laidlaw and Filippelli 2008). Children are the most sensitive to environmental contaminants among exposed population (Perkins et al. 2014). Metal contamination in surface dust (Atiemo et al. 2012), vegetables (Fosu-Mensah et al. 2017) and soils and sediments (Akortia et al. 2017; Chama et al. 2014, Kyere et al. 2016; Obiri et al. 2016) have been studied in Ghana. However, the potential health risks of the population living near e-waste recycling sites have been scarcely studied. Other studies assessed the health risks of the population living near fuel stations in Accra, Ghana (Afrifa et al. 2015) and Kumasi, Ghana (Nkansah et al. 2017). Health risk studies in Agbogbloshie informal e-waste recycling site were conducted with a limited number of samples and only topsoils and bottom ash samples were assessed (Obiri et al. 2016), with no comprehensive information on health risks associated with subsoils.

Urban soils are highly dispersed due to intense human activities and may be brought in from elsewhere and may not reflect local contamination (Wong et al. 2006). This study contributes to health risk assessment in informal e-waste recycling sites by studying both topsoils and subsoils of Agbogbloshie in southern Ghana. Studies assessing the health risks associated with e-waste impacted soils in Ashaiman, an emerging e-waste recycling site was rare. It is hypothesised that e-waste recycling activities in these two informal e-waste recycling sites - Agbogbloshie and Ashaiman - will contaminate soils and result in elevated concentrations of metals leading to carcinogenic and non-carcinogenic risks to the residents living in those areas. Non-carcinogenic risks are associated with a wide range of chronic toxicity including neurotoxicity, development toxicity, mutagenicity and reproductive toxicity (Man et al. 2010). A USEPA health risk assessment model has been widely applied to assess the health risks of metal contaminants associated with anthropogenic activities to gain a comprehensive assessment of health risks in the environment to safeguard human health (Albering et al. 1999; Wcislo et al. 2002). This study;

- (1) determines the concentrations of nine metals (Cr, Fe, Cu, Zn, , Ag, Cd, Sn, Ba and Pb) and two metalloids (As and Se) in topsoils and subsoils at Agbogbloshie and Ashaiman, (2) assesses non-carcinogenic and carcinogenic risks using the USEPA health risk assessment model, (3) determines the priority metals contributing to the pollution using an environmental assessment model, and
- (4) explores relationships among the metals using principal components analysis (PCA).

4.2 Materials and methods

4.2.1 Study areas

Agbogbloshie and Ashaiman (Figures 4.1, 4.2) are in the Greater Accra Region of Ghana. Agbogbloshie is the main hub of e-waste processing, recycling and disposal in Ghana. The e-waste hub is adjacent to the largest yam and onion market in Ghana. The e-waste site has some amenities including a mosque and a police station. Residential shanty dwellings border the site and serve as homes for e-waste recyclers and their families. Agbogbloshie e-waste recycling site is 2 km from the centre of the central business district of Accra, Ghana. Informal recycling of e-waste in Agbogbloshie e-waste recycling site comprises 40 to 60% of all e-waste processing in Ghana (Ramezan 2013). Ashaiman, located close to the Ashaiman-Tema highway is 4 km north of Tema city and about 30 km from Accra. The main e-waste recycling activities are open-burning and dismantling and dumping of residual materials.

4.2.2 Geology

Agbogbloshie area is underlain by sandstones with coarse materials such as grits, breccias and pebble beds as well as finer grained shales (Obiri et al. 2016). The soil is clayey, giving rise to lateritic soil groups which are easily erodible (Kesse 1985).

4.2.3 Collection of soil samples, sample pre-treatment and elemental analysis

Sample collection was carried out in December 2016 to January 2017 in Agbogbloshie and Ashaiman (Figure 4.1). Agbogbloshie e-waste area was stratified into two e-waste recycling hotspots (i.e., open burn and dismantling areas). Sampling points were located to ± 5 m using a Garmin global positioning system receiver using the WGS84 geoid, 30 N projection zone. Soils (n=180) were collected from the burn area and dismantling sites using a soil auger. For this study purposes, these soils were categorized into topsoils (i.e., those samples collected from 0 cm up to 30 cm depth) and subsoils (i.e., those samples collected from 30 cm up to 100 cm depth). In all 39 topsoils were collected from the burn area, 41 topsoils from the dismantling areas, while 63 subsoils and 37 subsoils were collected from the burn area and dismantling areas respectively. Two control samples were collected at spots where there were no e-waste recycling activities evident. Topsoils (n=13) were collected from Ashaiman “Fitter-line” e-waste site. Fewer topsoils were collected in Ashaiman because the e-waste recycling was conducted on a smaller scale, compared to Agbogbloshie. The soil samples were oven-dried at 40 °C for 72 h, crushed using a mortar and pestle and sieved through a 2 mm stainless steel sieve with a nylon mesh to remove gravels. The sieved soil samples were milled using a Retch

MM301 mill with tungsten carbide vials and balls for 10 min at 25 Hz. X-ray fluorescence spectrometry was used to determine the elemental concentrations in the soil samples. Approximately 10 g of the powdered soil sample was placed in a 10 ml polyethylene cup and sealed using a 3.6 µm thick polyester X-ray film. The polyethylene cup containing the soil sample was placed in a test stand and analysed for elemental concentrations using an Olympus Delta Pro X-ray fluorescence spectrometer with a 50 kV Ta anode tube, with three measurement conditions of 60 s each in soil calibration mode. Measurement conditions were 50 kV, 4 W, 60 s with aluminium filter; 15 kV, 4 W, 60 s with no filter; and 5 kV, 4 W, 60 s with no filter. The analytical area was a 6 × 4 mm ellipse. Measurements were made in air. Repeated measurements of an acid-washed quartz (SiO₂) showed analytes (Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb) to be below detection limits for all measurements. Accuracy was constrained using repeated analysis of two United States National Institute of Standards and Technology standard reference materials (NIST 2710a, 2711a) which showed inaccuracies better than 10% for elements more abundant than 0.1 wt.% and better than 20% for trace elements more than double the limit of quantification. The detection limits, laboratory accuracy errors and precision as relative percentage difference for the elements are shown (Table 4.1).

Table 4.1 Detection limit, inaccuracy and precision of XRF analysis of soils based on repeated measurements of certified reference materials (NIST 2710a, 2711a).

Metal(loid)s	Detection limit (mg/kg)	% Inaccuracy	Relative Standard Deviation (%)
Cr	55	0.0	0.9
Fe	<1	13.9	12
Cu	11	3.8	0.9
Zn	<1	4.7	1.1
As	12	5.2	1.1
Se	2	^b	^b
Ag	3	2.8	2.4
Cd	4	2.4	7.5
Sn	7	^a	12
Ba	161	1.5	2.0
Pb	10	1.2	0.8

^a No certified value reported for Sn in NIST 2710a, 2711a. ^b Se was below limit of detection (LOD) in NIST 2710a, 2711a.



Figure 4.1 Location of sampling sites in Agbogbloshie.

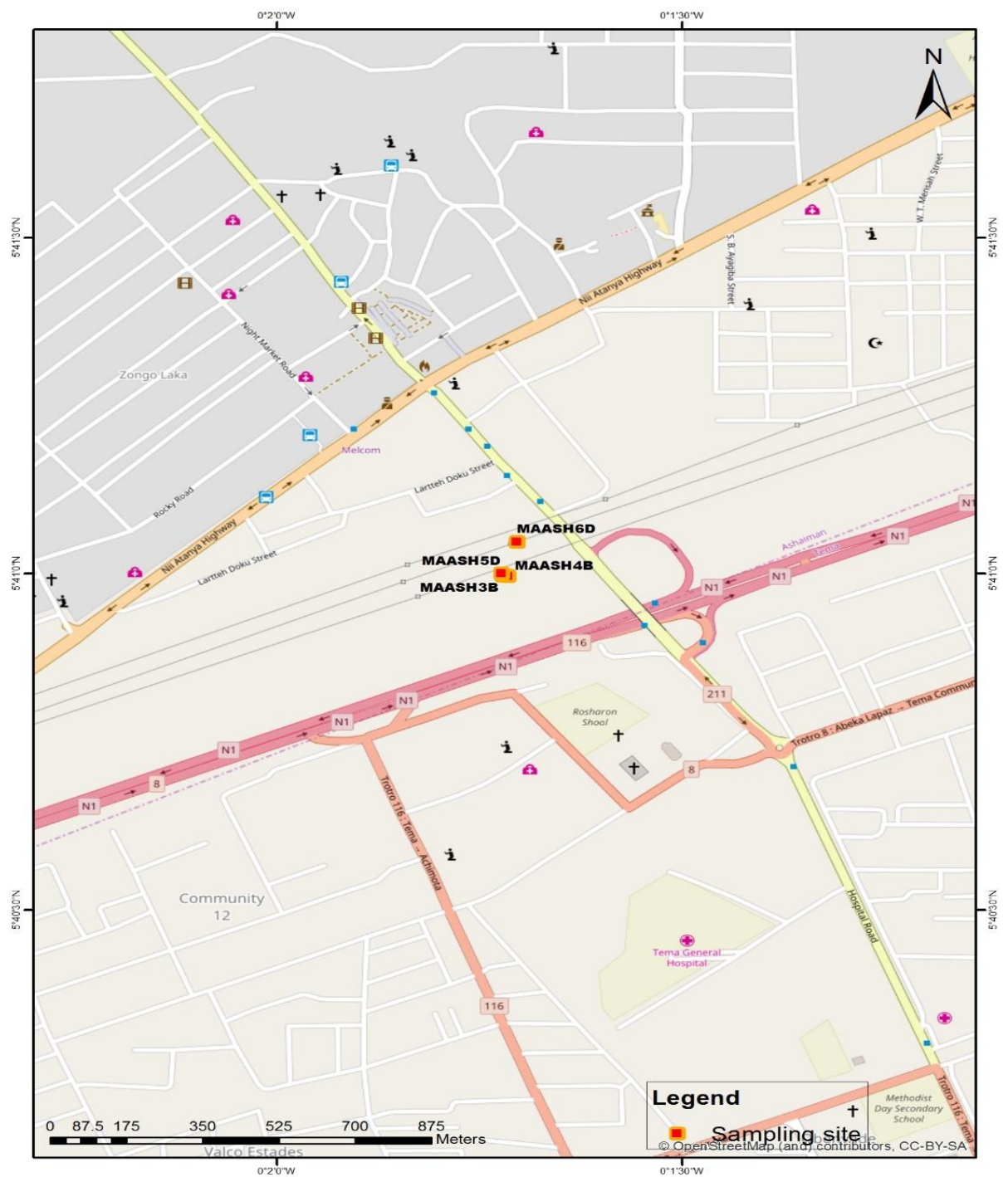


Figure 4.2 Location of sampling sites in Ashaiman.

4.2.4 Data analysis

Geoaccumulation index (Igeo) was used to assess contamination by comparing current and pre-industrial concentrations (Müller 1969). Igeo was calculated using equation 4.1;

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5B_n} \right) \quad (4.1)$$

Where C_n = total concentration of element 'n' in the surface layer of the soil tested, and B_n = concentration of element 'n' in the earth crust. A factor of 1.5 is used because of possible variations of the background data due to lithological variations. The quantity Igeo is calculated using global average shale data (Turekian and Wedepohl 1961). Geoaccumulation index is distinguished into seven classes (Müller 1981) (Table 4.2).

Table 4.2 Geoaccumulation index (Igeo) of contamination levels in sediments.

Igeo class	Igeo value	Contamination level
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

4.2.5 Human Health Risk Assessment (HHRA)

Human health risk assessment involves estimating probable adverse health impacts in human populations exposed to chemicals or environmental hazards in a contaminated environment (Li et al. 2014, USEPA 1997). Exposure to toxic metals from e-waste can occur through three main pathways, namely (1) direct ingestion of soil particles, (2) inhalation through the mouth and nose of re-suspended particles, and (3) dermal absorption of particles adhered to the exposed skin. Human health risks were assessed separately for children and adults, due to differences in physiological and behavior (Li et al. 2014). Non-carcinogenic health risks were estimated using total concentrations of toxic elements in soil samples. Average daily intake (ADI) for children and adults were derived using equations described in United States Environmental Protection Agency (USEPA) health risk handbook (USEPA 1996; 1997; 2011). ADI was used to calculate levels of human exposure to heavy metals through different exposure pathways; ingestion and dermal exposure routes, previously described as the main routes of exposure to contaminated soil in e-waste recycling sites (Obiri et al. 2016). The ADI via ingestion and dermal absorption was evaluated using equation 4.2 (USEPA 1997);

$$ADI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (4.2)$$

where C= concentration of the chemical (mg/L, mg/kg, mg/m³), IR= ingestion rate (L/day, kg/day, m³/day), EF= exposure frequency (day/year). ED= exposure duration (year), BW= body weight of the individual exposed (kg) and AT= period, over which the dose is averaged (day).

Exposure dose from ingestion and dermal contact was calculated from Equations 4.3 and 4.4 respectively;

$$ADI_{\text{ingestion}} = \frac{C_s(C_v) \times SIR \times EF \times ED}{BW \times AT} \quad (4.3)$$

where $ADI_{\text{ingestion}}$ = average daily intake of metals from soil ingestion (mg/kg/day), C_s = concentration of metal in soil (mg/kg) and SIR= soil ingestion rate (mg/day);

$$ADI_{\text{dermal}} = \frac{C_s \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (4.4)$$

where ADI_{dermal} is the average daily intake of metals from dermal absorption (mg/kg/day), SA is the exposed skin surface area (cm²), AF is the skin adherence factor (mg/cm²/day) and ABS is the dermal absorption factor (dimensionless).

Non-carcinogenic risks were evaluated using hazard quotient (HQ) (equation 4.5). HQ was evaluated as a ratio of the average daily intake of contaminants from each exposure route or the dose (ADI) to the toxicity threshold value or the reference dose (RfD) (USEPA 1989);

$$HQ = \frac{ADI}{RfD} \quad (4.5)$$

If $HQ > 1$, the exposed population is likely to experience adverse health effects; however, if $HQ < 1$, the exposed population is unlikely to experience any adverse health effects (USEPA 1986). The Hazard Index (HI), which is the sum of the hazard quotients (HQs) from all applicable pathways, is calculated using equation 4.6;

$$HI = \sum HQ_i = \sum \frac{ADI_i}{RfD_i} \quad (4.6)$$

Hazard index (HI) value > 1 means there is potential for adverse health effects on human health, however, if the $HI < 1$, the exposed population is unlikely to experience any adverse health effects (Li et al. 2014).

Reference dose for dermal absorption (RfD_{dermal}) is extrapolated from oral reference dose values (USEPA 2002). RfD_{dermal} is calculated using equation 4.7;

$$RfD_{\text{dermal}} = RfD_o \times ABS_{\text{GI}} \quad (4.7)$$

where RfD_{abs} is the adjusted reference dose for dermal exposure (mg/kg/day) and ABS_{GI} is the gastrointestinal absorption factor, which is dimensionless.

Carcinogenic risks were evaluated by calculating the incremental probability of individual developing cancer over a lifetime due to carcinogenic exposure using equation 4.8;

$$\text{Cancer Risk (CR)} = \text{ADI} \times \text{CSF} \quad (4.8)$$

where CSF is the cancer slope factor (mg/kg/day).

The USEPA acceptable or tolerable range of carcinogenic risk is 1×10^{-6} to 1×10^{-4} . Generally, USEPA recommends that carcinogenic risk $\leq 1 \times 10^{-6}$ is negligible, whereas carcinogenic risk $\geq 1 \times 10^{-4}$ is likely to be harmful to humans (Wei et al. 2015).

The dermal cancer slope factor (SF_{dermal}) is calculated using equation 4.9;

$$SF_{\text{dermal}} = \frac{SF_o}{ABS_{\text{GI}}} \quad (4.9)$$

where SF_{dermal} = dermally adjusted slope factor (mg/kg/day) and SF_o = oral slope factor (mg/kg/day).

4.2.6 Principal Component Analysis (PCA)

PCA is a data reduction technique which reduces the dimensionality of the original data, by providing information on the most significant factors or parameters (Joliffe and Morgan 1992). PCA with Varimax rotation method ensured that variables were mean-centered and PCs with Eigen values > 1 were retained while simultaneously reducing the variables with lesser contributions (Helena et al. 2000). Kaiser-Meyer-Olkin (KMO) and Bartlett's tests were conducted on the dataset to determine suitability for PCA. High KMO values (close to 1), indicates that a PCA may be useful (Pejman et al. 2015).

4.3 Results and Discussion

The percentage and number of positively detected elements in soil samples from Agbogbloshie and Ashaiman are shown (Table 4.3). Soil elemental data in the two e-waste sites are shown (Tables 4.4 and 4.5). Chromium, Fe, Zn, Ba and Pb had the greatest concentrations in soils, followed by Cu, Sn, Ag, Cd, Se and As in Agbogbloshie (Table 4.3). Chromium, Cd, Ba, and Pb had the greatest concentrations in burn-area subsoil samples while Fe, Se, and Sn had the greatest concentrations in the burn area topsoil samples (Table 4.4). Copper, Zn, As and Ag had the greatest mean concentrations in dismantling area topsoil samples in Agbogbloshie (Table 4.4). Mean concentrations of Fe, Cu, Zn, Se, Cd, Sn, Ba, Pb except for Cr, As and Ag in all the soil samples was greater than their respective concentrations in the average continental shale (Table 4.4) (Turekian and Wedepohl 1961). Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in burn area topsoil samples were 998, 258000, 51000, 55900, 8, 22, 39, 44, 6100, 7670, 15900 mg/kg respectively (Table 4.4). Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in burn area subsoil samples were 616, 204000, 38000, 13200, 310, 22, 44, 38, 5240, 9980 and 35300 mg/kg respectively (Table 4.4). Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in dismantling area topsoil samples were 241, 311000, 306,000, 9690, 531, 9, 83, 42, 3830, 3910 and 33800 mg/kg respectively (Table 4.4). Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in dismantling area subsoil samples were 182, 163000, 29400, 4410, 7, 6, 37, 13, 1810, 3920 and 2970 mg/kg respectively (Table 4.4). Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in soil samples of all functional areas were greater than their concentrations in control (Table 4.4).

Relatively small elemental concentrations in the control samples show that there were elevated metal concentrations in soils of Agbogbloshie, compared with the control area which has no e-waste recycling activities. Maximum concentrations of Cr, Cu, Zn, Se, Ag, Cd, Sn, Ba and Pb in all soils in burn area topsoils and dismantling area topsoils, exceeded their respective Canadian Soil Quality Guideline values (CCME 1995), except for As (Table 4.4). Soil samples with concentrations exceeding Dutch Soil intervention values were greatest for Cu (72%), followed by Zn (57%), Pb (57%), Ba (38%), Cd (16%) Cr (6%) and As (2%) (Table 4.4). In Ashaiman, the greatest % exceedances of Dutch Soil intervention values were 62%, 57% and 46% for Cu, Zn and Pb respectively. Soils with metal concentrations greater than Dutch intervention value pose ecological risks and require immediate attention. Mean concentrations of all metals were greater than their respective background concentrations in the control, except for Cr, whose mean concentration in the dismantling subsoils was smaller than the control soil.

Mean concentrations obtained for topsoils from burn areas were similar to values in Atiemo et al. (2012). The percentage detection of metals in Ashaiman soils was in this order: Cr = Fe = Cu = Zn = Ba > Sn > Ag > Cd = Se > As (Table 4.3). Arsenic was detected in only one sample in Ashaiman, suggesting As has not accumulated in the soil compared with other elements such as Cr, Fe, Cu, Zn, Ba and Pb. Iron recorded the greatest mean concentrations, followed by Cu, Zn, Pb, Sn and Ba while the smallest metal concentrations in Ashaiman was recorded by Cd < Ag < As < Se (Table 4.5).

Table 4.3 Number and percentage of contaminated soils in the functional areas of Agboglobshie and the topsoils of Ashaiman.

Element	Agboglobshie		Ashaiman	
	Number of contaminated samples in functional areas (n)	% element detection	Number of contaminated samples (n)	% element detection
Cr	39 ^a ,63 ^b ,41 ^c ,37 ^d	100	13	100
Fe	39 ^a ,63 ^b ,41 ^c ,37 ^d	100	13	100
Cu	39 ^a ,62 ^b ,41 ^c ,37 ^d	99	13	100
Zn	39 ^a ,63 ^b ,41 ^c ,37 ^d	100	13	100
As	2 ^a ,9 ^b ,2 ^c ,3 ^d	18	1	8
Se	14 ^a ,26 ^b ,12 ^c ,12 ^d	36	3	23
Ag	32 ^a ,21 ^b ,36 ^c ,20 ^d	61	4	31
Cd	28 ^a ,17 ^b ,20 ^c ,7 ^d	40	3	23
Sn	39 ^a ,60 ^b ,41 ^c ,34 ^d	97	9	69
Ba	39 ^a ,63 ^b ,41 ^c ,37 ^d	100	13	100
Pb	39 ^a ,63 ^b ,41 ^c ,37 ^d	100	13	100

^a - burn area topsoils, ^b -burn area subsoils, ^c -dismantling area topsoils, ^d -dismantling area subsoils.

Table 4.4 Elemental data (mg/kg) of topsoils, subsoils and soils from a control area in Agbogbloshie.

Functional area	Statistics	Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
Burn area topsoils (n=39)	Maximum	998	258000	51000	55900	8	22	39	44	6100	7670	15900
	Mean	139	39900	10400	7010	8	11	16	14	1130	1220	5080
	Standard deviation	212	63100	13600	9780	1	6	11	9	1330	1450	4880
	Median	68	22200	2670	4390	8	10	15	11	648	797	2630
Burn area subsoils (n=63)	Maximum	616	204000	38000	13200	310	22	44	38	5240	9980	35300
	Mean	26900	5320	2170	68	7	18	16	490	851	2700	26900
	Standard deviation	31900	11400	3300	127	5	12	10	1080	1770	6260	31900
	Median	21700	216	591	5	5	19	15	57	263	253	21700
Dismantling area topsoils (n=41)	Maximum	241	311000	306000	9690	531	9	83	42	3830	3910	33800
	Mean	103	56800	11200	1820	271	5	16	11	585	965	2380
	Standard deviation	60	63000	48200	1870	368	2	18	9	852	985	5240
	Median	85	29000	1470	1140	271	4	10	7	274	566	1390
Dismantling area subsoils (n=37)	Maximum	182	163000	29400	4410	7	6	37	13	1810	3920	2970
	Mean	60	33400	1800	866	5	3	12	8	338	689	846
	Standard deviation	36	30700	4810	954	2	1	8	3	440	762	901
	Median	50	24800	650	621	5	3	10	7	138	368	446
Control area soil concentrations		61	36500	14	40	6	2	3	<4	<161	253	31
Average continental shale (Turekian and Wedepohl 1961)		90	47200	45	95	13	0.6	13	0.3	6	580	20
Canadian soil Quality Guidelines (CCME 1995)		87	-	91	360	12	2.9	40	22	300	2000	600
% of soils > Canadian soil quality guidelines		26%	-	82%	79%	2%	29%	1%	4%	41%	9%	57%
Dutch soil guidelines (target value) (VROM 2000)		100	-	36	140	29	-	-	0.8	-	160	85
% of soils > Dutch soil target values		19%	-	92%	84%	2%	-	-	40 %	-	96%	87%
Dutch soil guidelines (intervention values) (VROM 2000)		380	-	190	720	55	-	-	12	-	625	530
% of soils > Dutch soil intervention values		6 %	-	72%	57%	2%	-	-	16%	-	38%	57%

Table 4.5 Elemental data of topsoils (mg/kg) in Ashaiman.

Sampling site	Statistic	Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
Ashaiman e-waste recycling site (n=13)	Maximum	87	34600	27500	7900	6	7	10	14	2300	594	7050
	Mean	59	15600	6060	2010	6	5	7	11	599	457	1690
	Standard deviation	17	9410	8930	2690	0	2	2	4	836	76	2490
	Median	57	15900	235	272	6	6	6	12	166	441	138
Canadian soil quality guidelines		87	-	91	360	12	2.9	40	22	300	2000	600
% of soils > Canadian soil quality guidelines		0%	-	69%	46%	0%	23%	0%	0%	31%	0%	46%
Dutch soil guidelines (target value)		100	-	36	140	29	-	-	0.8	-	160	85
% of soils > Dutch soil target values		0%	-	77%	69%	0%	-	-	23%	-	100%	54%
Dutch soil guidelines (intervention values)		380	-	190	720	55	-	-	12	-	625	530
% of soils > Dutch soil intervention values		0%	-	62%	57%	46%	-	-	8%	-	0%	46%

4.3.1 Pollution assessment

Geoaccumulation index (Igeo) is useful to evaluate anthropogenic contamination from soils by comparing soil concentration with background concentration. Background concentrations from the average shale following Turekian and Wedepohl (1961) were used in the calculation of mean Igeo values for the burn area topsoil and subsoil and dismantling area topsoil and subsoil. Burn area topsoils were uncontaminated with Cr, Fe, As and Ba, moderately contaminated with Cd, moderately to strongly contaminated with Cu, Zn, and Ag and strongly contaminated with Sn and Pb (Figure 4.3a). Burn area subsoils showed strong contamination with Pb and Sn and moderate to strong contamination with Cu, Zn and Ag (Figure 4.3b). Open burning to recover metals such as Cu result in significant toxic air emissions and toxic ash deposition (Asante et al. 2012, Itai et al. 2014). In the dismantling area topsoils, Cr, Fe, Ba, As and Se showed no contamination (Figure 4.4a). Copper and Sn, Ag and Pb showed strong to extreme contamination and extreme contamination respectively. In dismantling area subsoil, Pb and Sn showed strong contamination, while Cu, Zn and Ag showed moderate to strong contamination (Figure 4.4b). In Agbogloboshie, both topsoil and subsoil were contaminated with Pb. Silver showed extreme contamination in the dismantling area topsoils. Silver is abundant as precious metals in printed circuit boards (Cayumil et al. 2016). In Ashaiman, soils were uncontaminated with Cr, Fe, As, Ag and Ba and moderately to strongly contaminated with Zn and Se. Copper and Pb showed strong contamination while Cd and Sn showed strong to extreme contamination (Figure 4.5). In Ashaiman, soils were contaminated with Cd, Sn, Pb and Cu because of extensive e-waste recycling activities mainly burning of copper sheaths and dismantling of printed circuit boards, which releases metal-laden dust into urban soils. Previous studies had reported similar Igeo classifications for Cu, Ag, Sn and Pb in informal e-waste recycling sites (Atiemo et al. 2012; Pradhan and Kumar 2014).

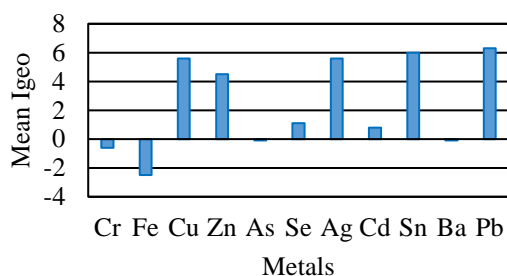


Figure 4.3 (a) Mean Igeo of elements in burn area topsoils of Agboglobshie.

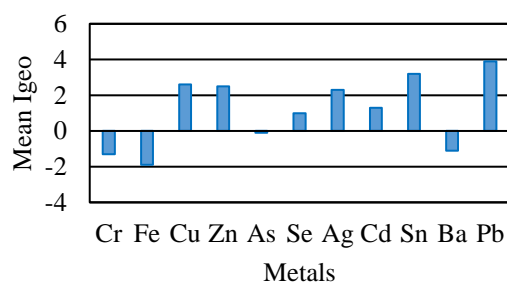


Figure 4.3 (b) Mean Igeo of elements in burn area subsoils of Agboglobshie.

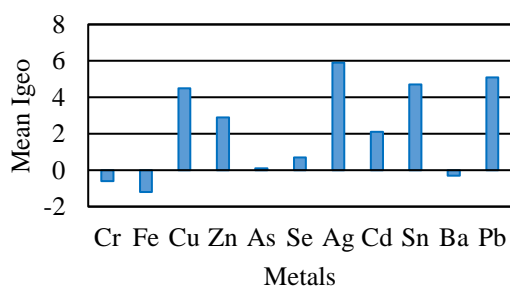


Figure 4.4 (a) Mean Igeo of elements in dismantling area topsoils of Agboglobshie.

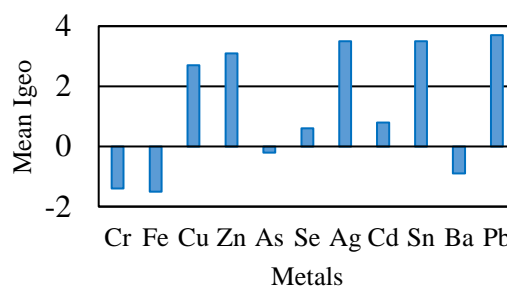


Figure 4.4 (b) Mean Igeo of elements in dismantling area subsoils of Agboglobshie.

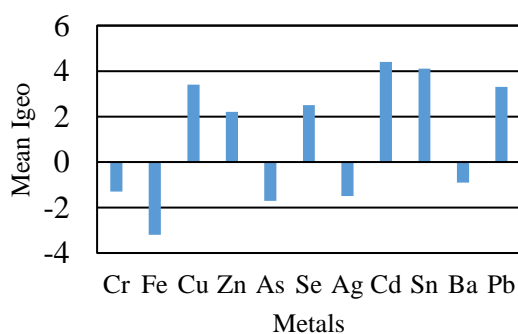


Figure 4.5 Mean Igeo of elements in soils of Ashaiman.

4.3.2 Hazard quotients for ingestion and dermal routes of exposure

E-waste recyclers and residents living near Agboglobshie and Ashaiman can be exposed to contaminated urban soils through ingestion and dermal contact. Mean, maximum and minimum hazard quotients of ingestion and dermal exposures for Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb from different functional areas of Agboglobshie and topsoils of Ashaiman are shown

(Tables 4.7, 4.8). Hazards quotients for Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb and cancer risk for As using exposure factors derived from literature (Table 4.6).

Table 4.6 Parameters used to calculate average daily intake.

Parameters	Unit	Children	Adult	Reference
Soil ingestion rate (SIR)	mg/day	200	100	USEPA 2011
Exposure frequency (EF)	days	350	350	USDOE 2011
Conversion factor (CF)	dimensionless	1×10^{-6}	1×10^{-6}	USEPA 2011
Exposure duration (ED)	years	6	24	USEPA 2011
Body weight (BW)	kg	15	55.9	Lee-Steere 2009
Averaging time (AT)	days	$365 \times ED$	$365 \times ED$	USEPA 2011
Exposed skin surface area (SA)	cm^2	1600	4350	Lee-Steere 2009
Skin adherence factor (AF)	$\text{mg}/\text{cm}^2/\text{day}$	0.2	0.7	USEPA 1993
Dermal absorption factor (ABS)	dimensionless	0.001	0.001	Chabukdhara and Nema 2013

4.3.3 Carcinogenic risks

Carcinogenic risks for As was evaluated in this study since chronic slope factor for ingestion is only available for As (USEPA 1992). As carcinogenic risks for children and adults in burn area topsoil were 7.64×10^{-6} and 1.03×10^{-6} respectively. Carcinogenic risks in the burn area topsoil were $< 1 \times 10^{-4}$, and therefore the burn area topsoil does not pose carcinogenic risks to children and adults. The carcinogenic risks for children and adults in burn area subsoil were 1.95×10^{-4} and 2.62×10^{-5} respectively. Carcinogenic risks for children from burn area subsoils were greater than the target value of 1×10^{-4} , indicating that children may suffer carcinogenic risks during their lifetime. The carcinogenic risks for adults from burn area subsoils were smaller than the target value of 1×10^{-4} and did not present carcinogenic risks to adults over a lifetime. Carcinogenic risks for children and adults from dismantling area topsoil were 2.64×10^{-4} and 3.55×10^{-5} respectively. Dismantling area topsoil does not present carcinogenic risks to adults. Topsoil from the dismantling area present carcinogenic risk to children since the carcinogenic risk for children is greater than the target value of 1×10^{-4} . Carcinogenic risks resulting from ingestion of As in dismantling area subsoils for children and adults were 8.0×10^{-6} and 1.07×10^{-6} respectively. Arsenic concentrations in dismantling area subsoil did not present carcinogenic risks to children and adults because the carcinogenic risk values were smaller than the target value of 1×10^{-4} . Arsenic carcinogenic risks to children and adults respectively in soils from Ashaiman was 1.18×10^{-4} and 1.58×10^{-5} . Carcinogenic risks for children were greater than the target value of 1×10^{-4} and children could develop cancer from ingesting As-contaminated soils from Ashaiman. On the other hand, the carcinogenic risks for

adults from Ashaiman soils were smaller than the target value of 1×10^{-4} , hence do not present carcinogenic risks to adults.

4.3.4 Non-carcinogenic ingestion risks

Mean HQs of Cr, Fe, Zn, As, Se, Ag, Cd, Sn, Ba in burn area topsoil do not present any non-carcinogenic ingestion risks to children and adults since HQs for these metals were less than 1. Maximum Cr HQ for children in burn area topsoil was 4.44 (Table 4.7). The maximum HQ of Cr, therefore, presents non-carcinogenic ingestion risks to children since maximum HQ for Cr was greater than 1. Maximum and Mean HQ of Cu for children in burn area topsoil were 17×10^0 and 3.48×10^0 respectively (Table 4.7). Maximum and mean HQ of Cu for adults in burn area topsoil were 4.67×10^{-1} and 2.28×10^0 respectively (Table 4.7). Copper, therefore, presents non-carcinogenic ingestion risks to children, but not adults. HQ of Cu was greater than 1 in 45% of burn area topsoil. Maximum and mean HQ of Pb for children and adults were 60.7×10^0 and 19.4×10^0 respectively while maximum and mean HQ of Pb for adults were 8.14×10^0 and 2.60×10^0 respectively (Table 4.7). Lead presents non-carcinogenic ingestion risks to both children and adults with Pb HQ > 1 in 90% of burn area topsoil and 60% of burn area topsoil respectively. Lead contributed 77.5% of non-carcinogenic ingestion risks to children in burn area topsoil.

Mean HQs in decreasing order for children and adults exposed to metals from burn area topsoil were Pb > Cu > Fe > Cr > Zn > Cd > Ba > Sn > Ag > As > Se and Pb > Cu > Cr > Zn > Cd > Ba > Sn > Ag > As > Se > Fe respectively. Lead and Cu were the priority metals in the topsoil of the burn area that posed the greatest non-carcinogenic ingestion risks to children and adults. Mean HQs of Cr, Fe, Zn, As, Se, Ag, Cd, Sn and Ba do not present non-carcinogenic ingestion risks to children for the burn area subsoils, since the mean HQs were less than 1. Maximum HQs of Cr, Fe, Cu, As, Ag, Cd, and Pb do present non-carcinogenic ingestion risks to children for the burn area topsoil children as the HQ for these elements were greater than 1.

Mean HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn and Ba do not pose non-carcinogenic ingestion risks to adults for the burn area subsoils. Mean HQ of Pb of 1.38×10^0 pose non-carcinogenic ingestion risks to adults for the burn area subsoils. Maximum HQs of Cr, Fe, Zn, Se, Ag, Cd, Sn and Ba do not present non-carcinogenic ingestion risks for burn area topsoil. Maximum HQs of Cu, As and Pb of 1.75×10^0 , 1.85×10^0 and 1.80×10^1 pose non-carcinogenic ingestion risks to adults for the burn area subsoils. The percentage of burn area subsoils which posed Pb non-carcinogenic ingestion risks to children and adults were 49% and 27% respectively.

Mean HQs in decreasing order for children and adults exposed to metals from burn area subsoils were Pb > Cu > Fe > As > Cr > Ag > Cd > Zn > Ba > Sn > Se and Pb > Cu > As > Ag > Cd > Ba > Fe > Cr > Sn > Zn > Se respectively. Lead and Cu were the priority metals in burn area subsoils which posed non-carcinogenic risks to children. Lead is the most important metal for non-carcinogenic ingestion risks to adults. Mean HQs of Cr, Zn, As, Se, Ag, Cd, Sn and Ba in the dismantling area topsoil do not present any non-carcinogenic ingestion risks to both children and adults since HQs for these metals were less than 1. Iron, Cu and Pb mean HQs of 1.08×10^0 , 3.63×10^0 and 8.83×10^0 respectively in dismantling area topsoil presented non-carcinogenic ingestion risks to children since HQs for these metals were greater than 1. Chromium, Fe, Cu, As, Cd, Pb maximum HQs of 1.07×10^0 , 5.92×10^0 , 1.02×10^2 , 2.36×10^1 , 1.12×10^0 and 1.29×10^2 respectively in dismantling area topsoil presented non-carcinogenic ingestion risks to children. Iron and Cu presented non-carcinogenic risks to only children but not adults. Iron and Cu HQs were > 1 in 33% and 38% of dismantling area topsoil respectively. Mean HQs in decreasing order for children and adults exposed to metals from dismantling area topsoil were Pb > Cu > Fe > As > Cd > Zn > Ba > Cr > Ag > Sn > Se and Pb > Cu > As > Cr > Sn > Fe > Zn > Ba > Ag > Sn > Se respectively. Mean HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba in dismantling area subsoils do not present any non-carcinogenic risks to children since HQs for these metals were less than 1.

Mean HQs of Pb presents non-carcinogenic ingestion risks to children and adults respectively in 58% and 16% of subsoils. Mean HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb do not present non-carcinogenic ingestion hazards to adults. Maximum HQs of Fe, Cu and Pb of 3.11×10^0 , 9.79×10^0 and 11.3×10^0 respectively in dismantling area subsoils do present non-carcinogenic ingestion risks to children while maximum HQs of Cu and Pb of 1.31×10^0 and 1.52×10^0 respectively presents non-carcinogenic ingestion risks to adults. Maximum HQs of Cr, Fe, Zn, As, Se, Ag, Cd, Sn, Ba do not present non-carcinogenic ingestion risks to adults since HQs for these metals were less than 1. Mean HQs in decreasing order for children and adults respectively were Pb > Fe > Cu > Cr > Ba > Cd > Zn > As > Ag > Sn > Se and Pb > Fe > Cu > Cr > Ba > Cd > Zn > Ag > Sn > Se. In Ashaiman e-waste recycling site, Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb mean HQs do not present non-carcinogenic ingestion risks to adults since mean HQs for these metals were less than 1. Lead mean HQ of 6.45×10^0 presents non-carcinogenic ingestion risks to children. Chromium, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba do not present non-carcinogenic risks to children in Ashaiman e-waste recycling site. HQ of Pb non-carcinogenic risks were seven times that of adults and this finding agrees with studies on urban soils in Bangladesh (Ali et al. 2017).

Table 4.7 Ingestion hazard quotients of metals from soils in burn and dismantling areas in Agboglobhie and Ashaiman.

Area	Age	Statistics	Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
Burn-area topsoils (n=39)	Child	Mean	6.16×10^{-1}	7.61×10^{-1}	3.48×10^0	3.11×10^{-1}	1.70×10^{-2}	1.03×10^{-2}	3.52×10^{-2}	2.61×10^{-1}	5.03×10^{-2}	8.11×10^{-2}	19.4×10^0
		Min	9.33×10^{-2}	1.24×10^{-3}	2.7×10^{-2}	6.44×10^{-3}	3.07×10^{-1}	6.67×10^{-3}	0.8×10^{-2}	1.28×10^{-1}	7.56×10^{-4}	1.54×10^{-2}	3.24×10^{-1}
		Max	4.44×10^0	4.92×10^0	17×10^0	2.49×10^0	3.56×10^{-1}	5.87×10^{-2}	1.03×10^{-1}	1.17×10^0	2.71×10^{-1}	5.11×10^{-1}	60.7×10^0
		HQ>1	4	5	17	1	none	none	none	1	none	none	38
	Adult	Mean	8.26×10^{-2}	1.36×10^{-6}	4.67×10^{-1}	4.18×10^{-2}	2.28×10^{-3}	1.38×10^{-3}	4.72×10^{-3}	3.50×10^{-2}	6.75×10^{-3}	1.09×10^{-2}	2.60×10^0
		Min	1.25×10^{-2}	2.21×10^{-9}	3.62×10^{-3}	8.65×10^{-4}	4.11×10^{-2}	8.94×10^{-4}	1.07×10^{-3}	1.72×10^{-2}	1.01×10^{-4}	2.07×10^{-3}	4.35×10^{-2}
		Max	5.95×10^{-1}	8.81×10^{-6}	2.28×10^0	3.33×10^{-1}	4.77×10^{-2}	7.87×10^{-3}	1.38×10^{-2}	1.57×10^{-1}	3.64×10^{-2}	6.86×10^{-2}	8.14×10^0
		HQ>1	none	none	8	none	none	none	none	none	none	none	24
Burn-area subsoils (n=63)	Child	Mean	4.20×10^{-1}	5.13×10^{-1}	1.74×10^0	9.63×10^{-2}	4.34×10^{-1}	7.30×10^{-3}	3.89×10^{-1}	1.13×10^{-1}	2.07×10^{-2}	5.68×10^{-2}	10.3×10^0
		Min	2.8×10^{-2}	5.55×10^{-2}	6.67×10^{-3}	1.5×10^{-3}	1.33×10^{-1}	4×10^{-3}	2.07×10^{-1}	7.73×10^{-2}	2.49×10^{-4}	4.8×10^{-3}	1.35×10^{-1}
		Max	2.74×10^0	3.88×10^0	12.7×10^0	5.85×10^{-1}	13.8×10^0	5.87×10^{-2}	2.92×10^0	1.01×10^0	2.33×10^{-1}	6.66×10^{-1}	1.35×10^2
		HQ>1	6	4	11	none	2	none	11	1	none	none	31
	Adult	Mean	5.64×10^{-2}	6.89×10^{-2}	2.34×10^{-1}	1.29×10^{-2}	5.82×10^{-2}	9.8×10^{-4}	5.22×10^{-2}	1.52×10^{-2}	2.78×10^{-3}	7.62×10^{-3}	1.38×10^0
		Min	3.76×10^{-3}	7.45×10^{-3}	8.94×10^{-4}	2.01×10^{-4}	1.79×10^{-2}	5.37×10^{-4}	2.77×10^{-2}	1.04×10^{-2}	3.34×10^{-5}	6.44×10^{-4}	1.81×10^{-2}
		Max	3.67×10^{-1}	5.21×10^{-1}	1.70×10^0	7.85×10^{-2}	1.85×10^0	7.87×10^{-3}	3.92×10^{-1}	1.36×10^{-1}	3.12×10^{-2}	8.93×10^{-2}	1.80×10^1
		HQ>1	none	none	8	none	2	none	none	none	none	none	17
Dismantling area topsoils (n=41)	Child	Mean	4.48×10^{-1}	1.08×10^0	3.63×10^0	8.09×10^{-2}	5.88×10^{-1}	3.77×10^{-3}	3.82×10^{-2}	1.43×10^{-1}	2.54×10^{-2}	6.28×10^{-2}	8.83×10^0
		Min	1.2×10^{-1}	3.75×10^{-3}	2.3×10^{-2}	8.89×10^{-4}	4.89×10^{-1}	6.13×10^{-3}	7.73×10^{-3}	8.8×10^{-2}	4.44×10^{-4}	1.01×10^{-2}	2.07×10^{-1}
		Max	1.07×10^0	5.92×10^0	1.02×10^2	4.31×10^{-1}	2.36×10^1	2.37×10^{-2}	2.21×10^{-1}	1.12×10^0	1.70×10^{-1}	2.61×10^{-1}	1.29×10^2
		HQ>1	1	13	16	none	1	none	none	1	none	none	35
	Adult	Mean	6.01×10^{-2}	1.45×10^{-2}	4.87×10^{-1}	1.08×10^{-2}	7.88×10^{-2}	5.05×10^{-4}	5.12×10^{-3}	1.92×10^{-2}	3.4×10^{-3}	8.43×10^{-3}	1.19×10^0
		Min	1.61×10^{-2}	5.03×10^{-4}	3.09×10^{-3}	1.19×10^{-4}	6.56×10^{-2}	8.23×10^{-4}	1.04×10^{-3}	1.18×10^{-2}	5.96×10^{-5}	1.36×10^{-3}	2.78×10^{-2}
		Max	1.44×10^{-1}	7.94×10^{-1}	13.7×10^0	5.78×10^{-2}	3.17×10^0	3.18×10^{-3}	2.97×10^{-2}	1.5×10^{-1}	2.28×10^{-2}	3.5×10^{-2}	17.3×10^0
		HQ>1	none	none	3	none	1	none	none	none	none	none	15
Dismantling area subsoils (n=37)	Child	Mean	2.65×10^{-1}	6.35×10^{-1}	6.01×10^{-1}	3.85×10^{-2}	1.78×10^{-2}	2.85×10^{-3}	1.75×10^{-2}	4.19×10^{-2}	1.38×10^{-2}	4.6×10^{-2}	3.22×10^0
		Min	1.02×10^{-1}	1.25×10^{-1}	3×10^{-3}	2.17×10^{-3}	1.47×10^{-1}	6.13×10^{-3}	6.4×10^{-3}	1.57×10^{-1}	4.44×10^{-4}	1.16×10^{-2}	1.07×10^{-1}
		Max	8.09×10^{-1}	3.11×10^0	9.79×10^0	1.96×10^{-1}	3.11×10^{-1}	1.49×10^{-2}	9.87×10^{-2}	3.47×10^{-1}	8.03×10^{-2}	2.61×10^{-1}	11.3×10^0
		HQ>1	none	5	4	none	none	none	none	none	none	none	23
	Adult	Mean	3.56×10^{-2}	8.52×10^{-2}	8.07×10^{-2}	5.17×10^{-3}	2.39×10^{-3}	3.82×10^{-4}	2.35×10^{-3}	5.62×10^{-3}	1.85×10^{-3}	6.17×10^{-3}	4.32×10^{-1}
		Min	1.37×10^{-2}	1.68×10^{-2}	4.03×10^{-4}	2.92×10^{-4}	1.97×10^{-2}	8.23×10^{-4}	8.59×10^{-4}	2.11×10^{-2}	5.96×10^{-5}	1.56×10^{-3}	1.56×10^{-3}
		Max	1.09×10^{-1}	4.17×10^{-1}	1.3×10^0	2.63×10^{-2}	4.17×10^{-2}	2×10^{-3}	1.32×10^{-2}	4.65×10^{-2}	1.08×10^{-2}	3.5×10^{-2}	1.52×10^0
		HQ>1	none	none	1	none	none	none	none	none	none	none	6
Ashaiman E-waste recycling site (n=13)	Child	Mean	2.52×10^{-1}	2.98×10^{-1}	2.02×10^0	8.95×10^{-2}	2.62×10^{-1}	1.43×10^{-2}	1.86×10^{-2}	2.81×10^{-1}	2.66×10^{-2}	3.05×10^{-2}	8.76×10^{-2}
		Min	1.24×10^{-1}	1.56×10^{-3}	8.33×10^{-3}	3.56×10^{-3}	-	9.07×10^{-3}	1.36×10^{-2}	1.49×10^{-1}	3.91×10^{-4}	2.39×10^{-2}	26.9×10^0
		Max	3.87×10^{-1}	6.58×10^{-1}	9.18×10^0	3.51×10^{-1}	-	1.79×10^{-2}	2.67×10^{-2}	3.73×10^{-1}	1.02×10^{-1}	3.96×10^{-2}	6.45×10^0
		HQ>1	none	none	7	none	none	none	none	none	none	none	6
	Adult	Mean	3.39×10^{-2}	4.00×10^{-2}	2.71×10^{-1}	1.20×10^{-2}	3.52×10^{-2}	1.92×10^{-3}	2.50×10^{-3}	3.77×10^{-2}	3.57×10^{-3}	4.09×10^{-3}	8.65×10^{-1}
		Min	1.67×10^{-2}	2.10×10^{-4}	1.12×10^{-3}	4.77×10^{-4}	-	1.22×10^{-3}	1.82×10^{-3}	2.00×10^{-2}	5.25×10^{-5}	3.21×10^{-3}	1.18×10^{-2}
		Max	5.19×10^{-2}	8.83×10^{-2}	1.23×10^0	4.72×10^{-2}	-	2.40×10^{-3}	3.58×10^{-3}	5.01×10^{-2}	1.37×10^{-2}	5.31×10^{-3}	3.60×10^0
		HQ>1	none	none	2	none	none	none	none	none	none	none	4

4.3.5 Non-carcinogenic dermal risks

Metal concentrations in the soils (i.e., burn area topsoil, burn area subsoil, dismantling area topsoil, dismantling area subsoil) and Ashaiman do not present non-carcinogenic risks from dermal absorption. Mean dermal HQ of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb for children in burn area topsoil were 1.52×10^{-4} , 1.22×10^{-3} , 5.57×10^{-3} , 4.98×10^{-4} , 2.72×10^{-5} , 1.65×10^{-3} , 1.41×10^{-3} , 8.35×10^{-3} , 4.02×10^{-5} , 1.85×10^{-3} and 3.10×10^{-2} respectively (Table 4.8). Mean dermal HQ of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb for adults in burn area topsoil were 3.87×10^{-4} , 3.11×10^{-3} , 1.42×10^{-2} , 1.27×10^{-3} , 6.94×10^{-5} , 4.22×10^{-5} , 3.60×10^{-3} , 2.13×10^{-2} , 1.03×10^{-4} , 4.74×10^{-3} and 7.91×10^{-2} respectively.

Mean dermal HQs of the elements do not present non-carcinogenic dermal risks to children since dermal HQ for these metals were less than 1. Maximum dermal HQ of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in burn area topsoil do not pose non-carcinogenic dermal risks to children and adults since the maximum HQ for these elements were less than 1 (Table 4.8). Mean HQ of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in burn area subsoils were < 1 and do not pose non-carcinogenic dermal risks to children.

Maximum HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in burn area subsoils do not pose non-carcinogenic dermal risks to children and adults since HQ for these metals were less than 1 (Table 4.8). Mean HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in dismantling area topsoil does not pose non-carcinogenic dermal risks to children and adults since HQ for these metals were less than 1. Maximum HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in dismantling area topsoil does not pose non-carcinogenic dermal risks to children and adults.

Mean and maximum HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb do not pose non-carcinogenic dermal hazards to children and adults. Maximum HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn and Ba do not pose non-carcinogenic dermal risks to adults except Pb. Chromium, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb mean dermal HQ do not pose non-carcinogenic dermal risks to children and adults since mean HQs for these metals were less than 1.

Mean dermal HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb for children in soils from Ashaiman were 6.21×10^{-5} , 4.77×10^{-4} , 3.23×10^{-3} , 1.43×10^{-4} , 4.20×10^{-4} , 2.29×10^{-5} , 7.44×10^{-4} , 8.99×10^{-3} , 2.13×10^{-5} , 6.97×10^{-4} and 1.03×10^{-2} respectively. Mean dermal HQs of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb for adults in soil from Ashaiman were 1.59×10^{-4} , 1.22×10^{-3} , 8.26×10^{-3} , 3.66×10^{-4} , 1.07×10^{-3} , 5.85×10^{-5} , 1.90×10^{-3} , 2.30×10^{-2} , 5.44×10^{-5} , 1.78×10^{-3} , 2.63×10^{-2} respectively.

Table 4.8 Dermal hazard quotients of metals from soils in burn and dismantling areas in Agboglobhie and Ashaiman.

Area	Age	Statistics	Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
Burn-area topsoils (n=39)	Child	Mean	1.52×10 ⁻⁴	1.22×10 ⁻³	5.57×10 ⁻³	4.98×10 ⁻⁴	2.72×10 ⁻⁵	1.65×10 ⁻⁵	1.41×10 ⁻³	8.35×10 ⁻³	4.02×10 ⁻⁵	1.85×10 ⁻³	3.10×10 ⁻²
		Min	2.30×10 ⁻⁵	1.98×10 ⁻⁶	4.32×10 ⁻⁵	1.03×10 ⁻⁵	4.91×10 ⁻⁴	1.07×10 ⁻⁵	3.2×10 ⁻⁴	4.10×10 ⁻³	6.04×10 ⁻⁷	3.52×10 ⁻⁴	5.19×10 ⁻⁴
		Max	1.09×10 ⁻³	7.88×10 ⁻³	2.72×10 ⁻²	3.98×10 ⁻³	5.69×10 ⁻⁴	9.39×10 ⁻⁵	4.11×10 ⁻³	3.75×10 ⁻²	2.17×10 ⁻⁴	1.17×10 ⁻²	9.70×10 ⁻²
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
	Adult	Mean	3.87×10 ⁻⁴	3.11×10 ⁻³	1.42×10 ⁻²	1.27×10 ⁻³	6.94×10 ⁻⁵	4.22×10 ⁻⁵	3.60×10 ⁻³	2.13×10 ⁻²	1.03×10 ⁻⁴	4.74×10 ⁻³	7.91×10 ⁻²
		Min	5.87×10 ⁻⁵	5.06×10 ⁻⁶	1.10×10 ⁻⁴	2.63×10 ⁻⁵	1.25×10 ⁻³	2.72×10 ⁻⁵	8.17×10 ⁻⁴	1.05×10 ⁻²	1.54×10 ⁻⁶	8.99×10 ⁻⁴	1.32×10 ⁻³
		Max	2.79×10 ⁻³	2.01×10 ⁻²	6.95×10 ⁻²	1.02×10 ⁻²	1.45×10 ⁻³	2.40×10 ⁻⁴	1.05×10 ⁻²	9.59×10 ⁻²	5.54×10 ⁻⁴	2.99×10 ⁻²	2.48×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
Burn-area subsoils (n=63)	Child	Mean	1.03×10 ⁻⁴	8.21×10 ⁻⁴	2.79×10 ⁻³	1.54×10 ⁻⁴	6.90×10 ⁻⁴	1.17×10 ⁻⁵	6.20×10 ⁻⁴	3.63×10 ⁻³	1.66×10 ⁻⁵	1.30×10 ⁻³	1.64×10 ⁻²
		Min	6.89×10 ⁻⁶	8.89×10 ⁻⁵	1.07×10 ⁻⁵	2.40×10 ⁻⁶	2.10×10 ⁻⁴	6.40×10 ⁻⁶	3.30×10 ⁻⁴	2.47×10 ⁻³	1.99×10 ⁻⁷	1.10×10 ⁻⁴	2.20×10 ⁻⁴
		Max	6.74×10 ⁻⁴	6.21×10 ⁻³	2.03×10 ⁻²	9.36×10 ⁻⁴	2.20×10 ⁻²	9.39×10 ⁻⁵	4.67×10 ⁻³	3.24×10 ⁻²	1.86×10 ⁻⁴	1.52×10 ⁻²	2.15×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
	Adult	Mean	2.60×10 ⁻⁴	2.10×10 ⁻³	7.13×10 ⁻³	3.93×10 ⁻⁴	1.77×10 ⁻³	2.98×10 ⁻⁵	1.59×10 ⁻³	9.27×10 ⁻³	4.23×10 ⁻⁵	3.31×10 ⁻³	4.20×10 ⁻²
		Min	1.85×10 ⁻⁵	2.30×10 ⁻⁴	2.70×10 ⁻⁵	6.12×10 ⁻⁶	5.40×10 ⁻⁴	1.63×10 ⁻⁵	8.40×10 ⁻⁴	6.32×10 ⁻³	5.08×10 ⁻⁷	2.80×10 ⁻⁴	5.50×10 ⁻⁴
		Max	1.72×10 ⁻³	1.59×10 ⁻²	5.17×10 ⁻²	2.39×10 ⁻³	5.63×10 ⁻²	2.40×10 ⁻⁴	1.19×10 ⁻²	8.28×10 ⁻²	4.76×10 ⁻⁴	3.88×10 ⁻²	5.49×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
Dismantling area topsoils (n=41)	Child	Mean	1.10×10 ⁻⁴	1.73×10 ⁻³	5.81×10 ⁻³	1.29×10 ⁻⁴	9.40×10 ⁻⁴	6.03×10 ⁻⁶	1.53×10 ⁻³	4.57×10 ⁻³	2.03×10 ⁻⁵	1.44×10 ⁻³	1.41×10 ⁻²
		Min	2.95×10 ⁻⁵	6.00×10 ⁻⁶	3.68×10 ⁻⁵	1.42×10 ⁻⁶	7.82×10 ⁻⁴	9.81×10 ⁻⁶	3.09×10 ⁻⁴	2.82×10 ⁻³	3.56×10 ⁻⁷	2.30×10 ⁻⁴	3.31×10 ⁻⁴
		Max	2.64×10 ⁻⁴	9.47×10 ⁻³	1.63×10 ⁻¹	6.89×10 ⁻⁴	3.78×10 ⁻²	3.80×10 ⁻⁵	8.85×10 ⁻³	3.58×10 ⁻²	1.36×10 ⁻⁴	5.96×10 ⁻³	2.06×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
	Adult	Mean	2.81×10 ⁻⁴	4.42×10 ⁻³	1.48×10 ⁻²	3.30×10 ⁻⁴	2.40×10 ⁻³	1.54×10 ⁻⁵	3.90×10 ⁻³	1.17×10 ⁻²	5.18×10 ⁻⁵	3.66×10 ⁻³	3.61×10 ⁻²
		Min	7.54×10 ⁻⁵	1.53×10 ⁻⁵	9.40×10 ⁻⁵	3.63×10 ⁻⁶	2.00×10 ⁻³	2.51×10 ⁻⁵	7.90×10 ⁻⁴	7.19×10 ⁻³	9.08×10 ⁻⁷	5.90×10 ⁻⁴	8.45×10 ⁻⁴
		Max	6.73×10 ⁻⁴	2.42×10 ⁻²	4.17×10 ⁻¹	1.76×10 ⁻³	9.64×10 ⁻²	9.70×10 ⁻⁵	2.26×10 ⁻²	9.15×10 ⁻²	3.47×10 ⁻⁴	1.52×10 ⁻²	5.26×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
Dismantling area subsoils (n=37)	Child	Mean	6.53×10 ⁻⁵	1.02×10 ⁻³	9.62×10 ⁻⁴	6.16×10 ⁻⁵	2.84×10 ⁻⁵	4.55×10 ⁻⁶	7.00×10 ⁻⁴	1.34×10 ⁻³	1.10×10 ⁻⁵	1.05×10 ⁻³	5.16×10 ⁻³
		Min	2.52×10 ⁻⁵	2.00×10 ⁻⁴	4.80×10 ⁻⁶	3.48×10 ⁻⁶	2.35×10 ⁻⁴	9.81×10 ⁻⁶	2.56×10 ⁻⁴	5.04×10 ⁻³	3.56×10 ⁻⁷	2.65×10 ⁻⁴	1.71×10 ⁻⁴
		Max	1.99×10 ⁻⁴	4.98×10 ⁻³	1.57×10 ⁻²	3.14×10 ⁻⁴	4.98×10 ⁻⁴	2.39×10 ⁻⁵	3.95×10 ⁻³	1.11×10 ⁻²	6.42×10 ⁻⁵	5.97×10 ⁻³	1.81×10 ⁻²
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
	Adult	Mean	1.67×10 ⁻⁴	2.60×10 ⁻³	2.46×10 ⁻³	1.57×10 ⁻⁴	7.26×10 ⁻⁵	1.16×10 ⁻⁵	1.79×10 ⁻³	3.42×10 ⁻³	2.82×10 ⁻⁵	2.68×10 ⁻³	1.32×10 ⁻²
		Min	6.42×10 ⁻⁵	5.10×10 ⁻⁴	1.23×10 ⁻⁵	8.88×10 ⁻⁶	5.99×10 ⁻⁴	2.51×10 ⁻⁵	6.54×10 ⁻⁴	1.29×10 ⁻²	9.08×10 ⁻⁷	6.77×10 ⁻⁴	4.36×10 ⁻⁴
		Max	5.08×10 ⁻⁴	1.27×10 ⁻²	4.00×10 ⁻²	8.01×10 ⁻⁴	1.27×10 ⁻³	6.10×10 ⁻⁵	1.01×10 ⁻²	2.83×10 ⁻²	1.64×10 ⁻⁴	1.52×10 ⁻²	4.62×10 ⁻²
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
Ashaiman E-waste recycling site (n=13)	Child	Mean	6.21×10 ⁻⁵	4.77×10 ⁻⁴	3.23×10 ⁻³	1.43×10 ⁻⁴	4.20×10 ⁻⁴	2.29×10 ⁻⁵	7.44×10 ⁻⁴	8.99×10 ⁻³	2.13×10 ⁻⁵	6.97×10 ⁻⁴	1.03×10 ⁻²
		Min	3.06×10 ⁻⁵	2.5×10 ⁻⁶	1.33×10 ⁻⁵	5.69×10 ⁻⁶	-	1.45×10 ⁻⁵	5.44×10 ⁻⁴	4.78×10 ⁻³	3.13×10 ⁻⁷	5.47×10 ⁻⁴	1.4×10 ⁻⁴
		Max	9.52×10 ⁻⁵	1.05×10 ⁻³	1.47×10 ⁻²	5.62×10 ⁻⁴	-	2.86×10 ⁻⁵	1.07×10 ⁻³	1.19×10 ⁻²	8.17×10 ⁻⁵	9.05×10 ⁻⁴	4.30×10 ⁻²
		HQ>1	none	none	none	none	none	none	none	none	none	none	none
	Adult	Mean	1.59×10 ⁻⁴	1.22×10 ⁻³	8.26×10 ⁻³	3.66×10 ⁻⁴	1.07×10 ⁻³	5.85×10 ⁻⁵	1.90×10 ⁻³	2.30×10 ⁻²	5.44×10 ⁻⁵	1.78×10 ⁻³	2.63×10 ⁻²
		Min	7.82×10 ⁻⁵	6.38×10 ⁻⁶	3.4×10 ⁻⁵	1.45×10 ⁻⁵	-	3.70×10 ⁻⁵	1.39×10 ⁻³	1.22×10 ⁻²	7.99×10 ⁻⁷	1.40×10 ⁻³	3.58×10 ⁻⁴
		Max	2.43×10 ⁻⁴	2.69×10 ⁻³	3.75×10 ⁻²	1.44×10 ⁻³	-	7.30×10 ⁻⁵	2.72×10 ⁻³	3.05×10 ⁻²	2.09×10 ⁻⁴	2.31×10 ⁻³	1.10×10 ⁻¹
		HQ>1	none	none	none	none	none	none	none	none	none	none	none

4.3.6 Human health impacts from exposure to E-waste impacted urban soils

Chromium, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb were present in varying concentrations in topsoils and subsoils of Agbogbloshe and Ashaiman e-waste recycling sites. These elements are present in varying concentrations in older computers. For example, in computers, Cr is associated with data tapes and floppy disks (Robinson 2009; Gaidajis et al. 2010). In computer waste, Fe constitutes 20 % by weight with other elements including Cu, Zn, Hg, Cd and Pb constituting 17 % (Needhidasan et al. 2014). Copper is found in printed wiring boards as well as in refrigerator motors and circuit wires (Nnorom and Osibanjo 2008). Zinc is used as galvanising on steel frames and as component of phosphor used as coatings in older CRT and paint pigments (Wu et al. 2008). Arsenic is used in small quantities in e-waste as gallium arsenide in light emitting diodes (Pant et al. 2012), with As (III) compounds more toxic than As (V) compounds. Selenium is used in older photocopying machines as a photoconductive coating applied to the photocopying drum (Gaidajis et al. 2010). Silver is used in printed circuit boards as a conducting material (Khaliq et al. 2014). Cadmium is present in e-waste as Ni-Cd rechargeable computer batteries, contact switches and older cathode ray tubes (Pant et al. 2012). Tin is used as Pb-free Sn alloys in soldering of microelectronics during manufacturing of printed circuit boards (Jha et al. 2012) and as components of Sn-Pb solders in microelectronics assemblies (Abtew and Selvaduray 2000). Barium is used as getters in CRT (Teller 2006; Leclerc et al. 2015) and as components of CRT panel glasses (M  ar et al. 2007). Lead is a constituent of solders in older electrical and electronic items and as shielding in CRT funnel glass (Herat 2008).

The health effects from exposure to Cr (VI) can cause skin rashes, liver and kidney damage (Adaramodu et al. 2012) while high tissue Fe concentrations cause the progression and development of pathological conditions including certain cancers, liver, heart conditions and immune system dysfunction (Fraga and Oteiza 2002). Exposure to Cu can damage the liver, brain and other organs (Gaetke and Chow 2003) while exposure to Zn can cause ischemia, cytotoxicity and trauma (Pant et al. 2012). Exposure to As can cause skin irritation, brain damage and miscarriage (Kumar and Singh 2014) while exposure to Cd can result in Itai Itai disease, which is a disease of the bone structure (Inaba et al. 2005) and significant ingestion to Cd can cause immediate poisoning and damage to the liver and kidney (Kimani 2009).

Health effects associated with excessive intake of Pb include deleterious effects on the central nervous system, kidney and reduction in the ability to produce red blood cells (Papanikolaou et al. 2005). Lead causes retarded intellectual development in children (Needleman and Bellinger

1991). Lead can cause congenital disabilities such as low birth weight, stillbirth and miscarriage (Caserta et al. 2013). A human health risks assessment of urban soils from burn areas and dismantling areas of Agbogbloshe and Ashaiman posed non-carcinogenic ingestion risks from Cr with the maximum HQ in topsoil of the burn area. Iron posed non-carcinogenic ingestion risks to children with the maximum HQ from topsoil from the dismantling area. Copper posed non-carcinogenic ingestion risks to children with the most significant maximum HQ from burn area topsoils. Zinc posed non-carcinogenic ingestion risks to children with the most significant maximum HQ from topsoil of the burn area. Arsenic posed non-carcinogenic ingestion risks to children with the most significant maximum HQ from subsoil of the burn area. Silver posed non-carcinogenic risks to children with the most significant maximum HQ from subsoil of the burn area. Cadmium posed non-carcinogenic ingestion risks to children with the most significant maximum HQ from topsoil of the burn area. Lead posed non-carcinogenic risks to children with the most significant maximum HQ from topsoil of the burn area. Arsenic and Ag in subsoils were found to exhibit significant non-carcinogenic risks to children. Metals concentrate in topsoils in contaminated sites. However, some elements had leached into subsoils of Agbogbloshe. Leached metals could be important exposure sources during soil excavations. Metals could leach into subsoils, facilitated by soil acidity (Ohajinwa et al. 2018), and unvegetated landscape in Agbogbloshe e-waste site (Obiri et al. 2016). In e-waste impacted areas, health risks from subsoils can be significant. Children were more susceptible to ingestion risks than adults due to the hand-to-mouth behavior of children (Ali et al. 2017). Adults, on the other hand, were more susceptible to dermal risks than children. This finding agrees with the findings of toxic metal exposure from street dust of a Zn smelting area in China (Zheng et al. 2010). Soils of the two e-waste recycling sites studied do not present non-carcinogenic risks due to dermal absorption for the following metals; Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn and Ba. This finding agrees with a recent study of metals in indoor dust from electronic workshops, cybercafes and offices in southern Nigeria (Iwegbue et al. 2018). The most significant contributions to chronic risks in this study were from Pb and Cu and this agrees with findings of health risks assessment in an urban area in Bangladesh (Ali et al. 2017), Agbogbloshe e-waste recycling site, Ghana (Obiri et al. 2016) and a municipal solid waste dump in Enugu, Nigeria (Ajah et al. 2015). Ingestion risks were the most important regarding metal exposure to both children and adults and this agrees with the findings on the health risk assessment of surface soil and road dust in Guiyu, China (Yekeen et al. 2016).

4.3.7 Soil toxicity

A novel environmental assessment model based on the environmental and health impacts of each element and median concentrations of elements (Strezov and Chaudhary 2017) were applied to prioritise the most important elements causing toxicity in Agbogbloshie. The total impact points for Cr, Cu, Zn, As, Se, Ag, Cd, Sn, Ba, and Pb were obtained from the Agency for Toxic Substances and Disease Registry database (ATSDR 2015). The assessment showed that Pb, Zn and Cu were more toxic in burn area topsoils, with decreasing toxicity order: Pb > Zn > Cu > Ba > Sn > Cr > Cd > As > Ag > Se > Fe. Metals in burn area subsoils was in this descending toxicity order: Zn > Pb > Ba > Cu > Cr > Sn > Cd > Ag > As > Se > Fe. In dismantling topsoils, the decreasing toxicity order was: Pb > Cu > Zn > Ba > As > Sn > Cr > Cd > Ag > Se > Fe while in dismantling area subsoils, decreasing toxicity order was: Pb > Zn > Cu > Ba > Sn > Cr > Cd > As > Ag > Se > Fe. Lead is a main component of solders in printed circuit boards of computers and cathode ray tube (CRT) glass. Lead is the most important metal pollutant across all functional areas since it is abundant in solders of printed circuit boards of older electronic components (Jang and Townsend 2003).

4.3.8 Source apportionment using PCA

Principal component analysis was applied to the combined dataset to explore relationships among metals. PCA was conducted using principal component extraction with an Eigen value >1 after varimax rotation with Kaiser Normalisation (Tepanosyan et al. 2016). The principal component matrix (Table 4.9) showed that the first three principal components with Eigen values >1 accounted for 74.8% of the total variance. PCA 1 accounted for 47.2% of the total variance and contained strong loadings (> 0.6) of Cd, Sn and Pb and moderate loadings (> 0.5) of Zn. Industrial activities such as incineration or open burning of e-waste and breakage or dismantling of metal concentrated printed circuit boards could result in emissions of elements into soils. Tin and Pb are used as solders in printed circuit boards of older computers while Cd and Pb are components of CRT funnel glasses (Duan et al. 2011). PCA 2 accounted for 17.2% of the total variance and contained strong loadings (> 0.6) of Fe, As, Ba and moderate loading (> 0.5) of Pb. Iron and Ba are abundant and their association with As may have shown that these elements originated from a common source in the soils. Iron, As and Ba are components of light emitting diodes (LED) of electronics and they are also used as dopants in semiconductors. PCA 3 accounted for 10.5% of the total variance and contained strong loadings (> 0.6) of Cr, Cu and Se and moderate loading (> 0.5) of Zn and Ag. Chromium, Cu, Se, Zn and Ag are abundant in e-waste (Chen et al. 2010). Rotated component matrix showing the component scores and communalities is shown (Table 4.10).

Table 4.9 Total variance explained for variables in soils.

Component	Initial Eigen values			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	5.19	47.2	47.2	5.19	47.2	47.2	2.78	25.3	25.3
2	1.89	17.2	64.4	1.89	17.2	64.4	2.77	25.2	50.4
3	1.15	10.5	74.8	1.15	10.5	74.8	2.68	24.4	74.8
4	0.87	7.88	82.7						
5	0.64	5.82	88.5						
6	0.39	3.55	92.1						
7	0.34	3.10	95.2						
8	0.21	1.87	97.0						
9	0.18	1.61	98.7						
10	0.09	0.84	99.5						
11	0.06	0.50	100						

Table 4.10 Rotated component matrices for variables in soils.

Element	Component			Communality
	1	2	3	
Cr	-0.032	0.382	0.841	0.854
Fe	-0.089	0.890	0.160	0.826
Cu	0.457	-0.012	0.686	0.679
Zn	0.566	0.217	0.542	0.661
As	0.373	0.652	-0.110	0.576
Se	0.190	-0.192	0.746	0.629
Ag	0.411	0.470	0.557	0.699
Cd	0.687	0.249	0.491	0.776
Sn	0.891	0.012	0.221	0.842
Ba	0.242	0.857	0.113	0.805
Pb	0.757	0.552	0.071	0.883

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. Bold values represent strong loadings > 0.6.

4.4 Conclusion

Geoaccumulation indices were used to assess pollution from Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in soils of two informal e-waste recycling sites in Ghana. Maximum concentrations of Cr, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb in soils from the informal e-waste recycling sites were greater than the concentrations in soils from the control site. Copper, Sn and Pb had contaminated urban topsoils and subsoils of Agbogbloshie. Contamination by the metal pollutants was greater for topsoils than subsoils in Agbogbloshie. Burn area topsoils were the most contaminated, followed by dismantling area topsoils, dismantling area subsoils, and burn area subsoils. Chromium, Fe, Cu, Zn, As, Se, Ag, Cd, Sn, Ba and Pb hazard quotients showed that ingestion is the main route for exposure to non-carcinogenic risks in Agbogbloshie and Ashaiman. Among the elements studied, Pb contributed to the highest non-carcinogenic ingestion risks in Agbogbloshie and Ashaiman e-waste recycling areas. Exposure through ingestion pathway to As from the dismantling topsoils and burn areas subsoils of Agbogbloshie e-waste recycling area pose carcinogenic risks to children. Principal component analysis showed that Cd, Sn and Pb originated from similar sources. Areas affected by long-term e-waste recycling should be assessed for their potential impacts on the health of the population living in those areas.

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CHAPTER 5: Spatial distribution and potential ecological risks of vanadium, chromium, manganese, nickel, copper, zinc, molybdenum, cadmium, barium and lead in the surface dust of Agbogbloshie e-waste recycling site, Accra-Ghana

Abstract

Vanadium, chromium, manganese, nickel, copper, zinc, molybdenum, cadmium, barium and lead concentrations in surface dust collected from Agbogbloshie e-waste recycling site was mapped using geostatistics and geographical information system (GIS). Furthermore, the potential ecological risk index was calculated to differentiate the risks associated with individual elements and the collective risks associated with metal concentrations. Potential ecological risk index showed that the greatest ecological risks were from Cd, Cu and Pb.

Keywords: spatial prediction, ordinary kriging, geostatistics.

5.1 Introduction

The desire to satisfy many needs through electronic revolution coupled with the desire to continuously replace damaged or outdated electronic products have resulted in the massive generation of e-waste (Heacock et al. 2015; Lundgren 2012). Developed countries generate massive amounts of e-waste, collecting only small amounts. For example, in Europe, 35% (3.3 million tonnes) of e-waste were collected domestically, while the rest was speculated to be exported abroad (Banacu et al. 2014). About 50-80% of e-waste is exported to developing countries in Africa and Asia (Pant et al. 2012). In developing countries, e-waste are handled largely by the informal sector who are involved in the reuse of discarded electronic devices and sub-standard recycling (Banacu et al. 2014).

Potentially hazardous elements which are components of e-waste include iron, hexavalent chromium, copper, aluminum, tin, lead, nickel, silver, gold, vanadium, arsenic and selenium (Grant et al. 2013). Lead is a known neurotoxicant which can affect the brain, liver, kidney and bones (Chen et al. 2011; Herat 2007). Arsenic and Cr (VI) are known carcinogens while Hg, Cd and Ni are suspected carcinogens (Schmidt 2002). Nickel is present in electronics as Ni-Cd batteries and as a component of the electron gun of cathode ray tubes (Pant et al. 2012). Exposure to Ni can cause allergies and skin cancer (Pant et al. 2012). Metals are persistent, bioaccumulative and are mobile in the environment due to changing environmental and climatic conditions (Ha et al. 2014). Previous studies on metal concentrations of soils in Agbogbloshie e-waste site established elevated concentrations of metals in the e-waste recycling site (Itai et al. 2014; Kyere et al. 2016). However, information on the spatial distribution of metals is lacking.

Geostatistical methods were applied extensively in urban and agricultural environment to predict the concentrations and spatial distribution of metals (Martín et al. 2006; Guagliardi et al. 2012; Solgi and Oshvandi 2018). Ordinary kriging is useful in the interpolation of point samples using spatial autocorrelation and is preferred because it gives the best linear prediction of minimal errors from the deleterious effects of clustering in samples on the quality of interpolated estimates (Ha et al. 2014; Li et al. 2017). Trace metals can pose direct and indirect effects on plants, animals and humans, with the direct effects being its negative effects on crop yield and the indirect effect by entering the food chain with potential negative impacts on human health (Wuana and Okieimen 2011). Excessive amounts of particularly toxic metals can increase morbidity from life-threatening diseases such as cancer, liver damage, kidney damage and leukemia (Guan et al. 2014). Long-term inputs of metals from anthropogenic sources can also result in imbalances to the environment (Jiang et al. 2014). In this study, I hypothesise that the concentrations and distribution of metal contaminants in informal e-waste recycling sites may pose ecological risks to biota in Agbogbloshie e-waste recycling area.

This study;

- (1) determines the concentrations of 10 elements-V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb in surface dust in Agbogbloshie e-waste recycling site,
- (2) identifies patterns of spatial distribution among the elements,
- (3) assesses mineralogical characteristics of surface dust in Agbogbloshie e-waste recycling site and
- (4) determines the potential ecological risk of metals in the surface dust of Agbogbloshie E-waste recycling site based on this elements-V, Cr, Mn, Ni, Cu, Zn, Mo, Cd and Pb.

5.2 Materials and methods

5.2.1 Study area

Agbogbloshie e-waste recycling site in Accra, Ghana is a site where used electrical and electronic equipment ranging from older computers, mobile phones, refrigerators, microwave oven, printers, blenders, etc., are dismantled to recover base metals such as Al, Cu, Fe in informal workshops using rudimentary tools such as chisels and hammers. Agbogbloshie also serve as residence for those engaged in the recycling, as well as their families.

5.2.2 Sampling, sample preparation and elemental analysis

Surface dust samples (n=88) were collected from dismantling workshops and near residential areas within Agbogbloshie e-waste recycling site in December 2017. Sampling points were located to ± 5 m using a Garmin global positioning system receiver using the WGS84 geoid, 30 N projection zone. Surface dust samples were air-dried at 40 °C, sieved through a 250 μ m nylon mesh size and analysed for elemental concentrations using an Olympus Delta Pro X-ray fluorescence (XRF) spectrometer with 50 kV Ta anode tube. Analyses of the dust were undertaken under three measurement conditions of 60 s each in soil calibration mode. Matrix-matched certified reference materials manufactured by the National Institute of Standards and Technology (NIST 2710a, 2711a) were used to constrain the accuracy of XRF measurements. Percentage difference between the measured and certified values were within 10 % of the certified values for V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb. Dust were milled for mineralogical analysis.

5.2.3 Mineralogical analysis

Mineralogy was determined on selected dust sub-samples (n=17) using a PANalytical X'Pert Pro MPD X-ray diffractometer with Cu K α radiation and the tube operated at 45 kV and 40 mA. Diffraction patterns were collected over a range of 5 to 95 °2 θ with a measurement time of 15 mins. Mineral phases were identified by comparing diffractograms with standard reference patterns in the ICDD PDF2 inorganic database and PAN-ICSD structural database, interrogated through the PANalytical software High Score + v 2.2. 1.

5.2.4 Data analysis

SPSS software v.20.0 (IBM, USA) was used for data analysis. Summary statistics of the data included the mean, median, minimum, maximum, standard deviation, the coefficient of variation and skewness. Contamination assessment was derived using background values from the average shale (Turekian and Wedepohl 1961). Analysis of variance (ANOVA) was performed on elemental data and means were compared using Tukey's post hoc test with SPSS version 20 software. The significance level was set at $p \leq 0.05$.

5.2.5 Geostatistical analysis

Geographical information system (GIS) (ArcGIS v10.6, ESRI, Redlands, CA, USA) with spatial analysis tools was used to map the spatial variability among elemental concentrations in dust samples. Kriging was used to produce spatial prediction maps. To implement kriging, the semivariance model which produced the minimum prediction errors was selected (Ha et al. 2014). The following steps were used to arrive at the interpolation maps (Mashal et al. 2015). The first step assessed the data to determine its distribution. The second step characterised the spatial distribution by computing the semivariance and testing for isotropy (Selker et al. 1999). Semivariance is expressed in equation 5.1;

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (5.1)$$

where $\gamma(h)$ is the semivariance, h is the lag distance, $Z(x)$ is the regionalized variable, $N(h)$ the number of pairs of sample data taken at a distance h . The third step involves the selection of the model which presents the best empirical fit. The sill/nugget ratio was explored for the spatial dependency of the values while the root means square error (RMSE) of the models was used to evaluate the accuracy of interpolation. In general, a sill/nugget ratio $\leq 25\%$ indicates strong spatial dependency and $\geq 75\%$ indicates weak spatial dependency (Bhunias et al. 2018). The final step involves using ordinary kriging to generate prediction maps for the variables at unknown locations by assuming a constant unknown mean, where the value at the unsampled point can be predicted by a linear weighting of the variation between the surrounding points derived from the variogram analysis (equations 5.2 a and b) (Mashal et al. 2015);

$$Z(X_0) = \mu + \varepsilon(X_0) \quad (5.2a)$$

$$Z(X_0) = \sum \lambda_i Z(X_i), \sum \lambda_i = 1 \quad (5.2b)$$

where μ is an unknown constant and $\varepsilon(X_0)$ is the error associated with the unknown location X_0 . $Z(X_0)$ is the estimated value of Z at X_0 and λ_i is the weight that gives the best possible estimation from the surrounding points.

5.2.6 Potential ecological risk index and contamination factor

Potential ecological risk index (RI) measures the sensitivity of the biological community to the overall contamination of a site (Hakanson 1980). RI is the sum of the potential ecological risk

of an individual element. It is evaluated based on the contamination factor of element i (Cf_i), potential ecological risk factor (ER_i), and the sediment biological toxic response factor (Tr_i). RI is evaluated using the equation from Hakanson (1980) (equation 5.3);

$$RI = \sum_{i=1}^n Er^i = \sum_{i=1}^n Tr^i \times Cf^i \quad (5.3)$$

where Tr^i is the biological toxic response coefficient of an individual element, and Cf^i is the contamination factor for every element. RI is categorised into four classes (Hakanson 1980). Potential ecological risk index (RI) is a comprehensive index that assesses the overall ecological risks of an area. RI is classified into four categories. RI of a site presents low ecological risks if RI is less than 150. RI presents moderate ecological risks if RI is greater or equal to 150 but less than 300. RI presents considerable ecological risks if RI is greater than 300 but less than 600. RI presents very high ecological risks if RI is greater than or equal to 600 (Hakanson 1980). Potential ecological risk factor (ER_i) is classified into five categories. ER_i of a site presents low ecological risks if ER_i is less than 40. ER_i presents moderate ecological risks if ER_i is greater or equal to 40 but less than 80. ER_i presents considerable risks if ER_i is greater or equal to 80 but less than 160. ER_i presents high risks if ER_i is greater or equal to 160 but less than 300. ER_i presents very high ecological risks if ER_i is greater or equal to 320 (Hakanson 1980).

Contamination factor (CF) is useful for assessing soil contamination of a single element relative to its pre-industrial levels (average shale) (Hakanson 1980). Contamination factor is applicable to soils and CF classification is such that CF less than 1 show low contamination factor; CF greater than 1 but less or equal to 3 is classified as moderate contamination factor; CF greater than 3 but less or equal to 6 is classified as considerable contamination factor; CF greater than 6 is regarded as a very high contamination factor (Kyere et al. 2016).

5.3 Results

5.3.1 Metal concentrations in floor dust

Summary statistics of elemental data (mean, median, minimum, maximum, standard deviation, the coefficient of variation and skewness) and mean of contamination factors (CF) are shown (Table 5.1). Concentrations of 10 elements (V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb) varied between 33 and 86, 22 and 127, 145 and 956, 6 and 186, 30 and 8100, 127 and 3970, 2 and 17, 2 and 9, 330 and 931, 50 and 1900 mg/kg respectively (Table 5.1). Mean concentrations of V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb were 86, 127, 956, 186, 8100, 3970, 17, 9, 931 and

1900 respectively (Table 5.1). Median concentrations of V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb were 84, 120, 546, 92, 4450, 3370, 14, 8, 814 and 1420 mg/kg respectively. Standard deviation for many elements were great due to the heterogeneous nature of the dust samples. Mean concentrations in this study were generally greater because dust samples were taken from dismantling workshops with intensive dismantling of circuit boards to recover Cu and other base metals. Mean and maximum concentrations of Cr, Ni, Cu, Zn, Mo, Cd, Ba and Pb were greater than their respective Dutch soil target values (Table 5.1). Mean and maximum concentrations of Cu, Zn, Ba and Pb were greater than their respective Dutch soil intervention values (Table 5.1). Mean concentrations of V were smaller than Dutch soil target and intervention values, however, the maximum concentration of V was greater than the Dutch soil target value but within the Dutch soil intervention value. Coefficients of variation (CV) decreased in this order: Ni (196%), Mn (171%), Cu (152%), Cd (100%), Pb (99%), Mo (94%), Zn (78%), Ba (58%), Cr (48%) and V (40%). The large CV for Ni, Mn, Cu, Cd, Pb, Mo and Zn indicated the wide variations in metal distribution in surface dust. Moderate CV of V and Cr indicates the non-homogenous distribution of these elements at the study sites. Mean CF for V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb were 0.66, 1.41, 1.12, 2.74, 180, 41.7, 6.72, 31.4, 1.61 and 94.9 respectively. Vanadium showed low contamination; Cr, Mn, Ni and Ba showed moderate contamination; Cu, Zn, Mo, Cd and Pb showed very high contamination factor (Table 5.1).

Table 5.1. Summary statistics of metal concentrations (mg/kg) in surface dust, the mean contamination factor and % of samples exceeding Dutch Soil Guideline values.

Statistics	V	Cr	Mn	Ni	Cu	Zn	Mo	Cd	Ba	Pb
Mean	86	127	956	186	8100	3970	17	9	931	1900
Median	84	120	546	92	4450	3370	14	8	814	1420
Minimum	33	22	145	6	30	127	2	2	330	50
Maximum	248	286	13700	2490	91600	17200	93	71	3830	9790
Standard deviation	34	61	1630	365	12300	3100	16	9	538	1890
CV (%)	40	48	171	196	152	78	94	100	58	99
Skewness	1.85	0.56	6.17	5.27	4.36	2.18	2.49	4.25	3.06	2.17
Mean CF	0.66	1.41	1.12	2.74	180	41.7	6.72	31.4	1.61	94.9
Dutch Soil Target value	100	100	-	35	36	140	3	0.8	160	85
Dutch Soil Intervention value	380	380	-	210	190	720	200	12	625	530
% of samples > Dutch soil target values	29.5%	61.4%	-	83%	99%	100%	92%	100%	100%	99%
% of samples > Dutch soil intervention values	0%	0%	-	22.7%	94.3%	93.2%	0%	23.9%	77.3%	81.8%

Table 5.2 Potential ecological risk factors for 9 metals in the surface dust of Agbogbloshe e-waste recycling site.

ER ⁱ	V	Cr	Mn	Ni	Cu	Zn	Mo	Cd	Pb
Minimum	0.51	0.49	0.17	0.40	3.33	1.34	8.65	200	12.4
Maximum	1.33	6.36	16.2	183	10178	181	534	7100	2448
Average	3.82	2.82	1.12	13.7	901	41.7	101	942	475

ERⁱ for individual metals showed that the greatest contribution to the ecological risk factor from nine metals was from Cd, followed by Cu, Pb, Mo, Zn, Ni, V, Cr and Mn in decreasing order (Table 5.2). RI calculated based on these seven metals-Cr, Ni, Cu, Zn, Mo, Cd and Pb was 2477 indicating very high ecological risk. Ecological management measures need to consider the impacts of metals such as Cd, Cu, Pb and Mo since these are the metals which contributed most to the risk index of the surface dust in Agbogbloshe e-waste recycling site.

5.3.2 Correlation analysis

Metals originating from similar sources can exhibit correlations. Correlation analysis of metal concentrations of V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb in surface dust samples showed there were significant positive correlations ($p=0.01$) among V-Cr, V-Ni, V-Cu, V-Zn, V-Mo, V-Cd, V-Ba and V-Pb (Table 5.3), indicating that these elements came from similar sources. Stronger correlations ($p=0.05$) were found among V-Ba, Cr-Zn, Ni-Pb, Cu-Pb and Cd-Pb. Vanadium has widespread uses in electronics and metallurgy (Krishna and Govil 2007). Vanadium, Mn, Cr and Ni are components of steel and superalloys in electronics (Larbi et al. 2015). However, Mn showed weak correlations with other elements, except Cr and Zn with correlations of 0.411 and 0.560, that were both significant at the 0.01 probability level.

Table 5.3 Correlation matrix of metals in surface dust.

	V	Cr	Mn	Ni	Cu	Zn	Mo	Cd	Ba	Pb
V	1									
Cr	0.625 ^a	1								
Mn	0.112	0.411 ^a	1							
Ni	0.361 ^a	0.396 ^a	0.155	1						
Cu	0.414 ^a	0.484 ^a	0.012	0.612 ^a	1					
Zn	0.441 ^a	0.646 ^a	0.560 ^a	0.382 ^a	0.450 ^a	1				
Mo	0.345 ^a	0.332 ^a	0.054	0.503 ^a	0.276 ^a	0.406 ^a	1			
Cd	0.228 ^a	0.327 ^a	0.005	0.165	0.471 ^a	0.256 ^b	0.199	1		
Ba	0.874 ^a	0.385 ^a	0.056	0.239 ^b	0.292 ^a	0.286 ^a	0.222 ^b	0.160	1	
Pb	0.390 ^a	0.425 ^a	0.193	0.598 ^a	0.654 ^a	0.454 ^a	0.420 ^a	0.571 ^a	0.269 ^b	1

^a-Correlation is significant at the 0.01 level (two-tailed) ^b- Correlation is significant at the 0.05 level (two-tailed).

5.3.3 Spatial distribution

The spatial distribution of metal concentrations are shown (Figures 5.1a, b). Red and brown colours indicate contamination “hotspots”. The spatial distribution maps show elevated metal concentrations with the “hotspots” near e-waste workshops than the residential areas (Figures 5.1a-c). Contamination was more pronounced for Cu, Zn, Mo, Cd and Pb than for V and Cr. Copper, Zn, Mo, Cd and Pb showed similar spatial distribution patterns. Similar spatial distribution patterns among the metal elements may indicate similar sources for those elements. Spatial distribution of metals indicated the influence of informal e-waste recycling activities (Fu et al. 2013; Quan et al. 2015; Kyere et al. 2016).

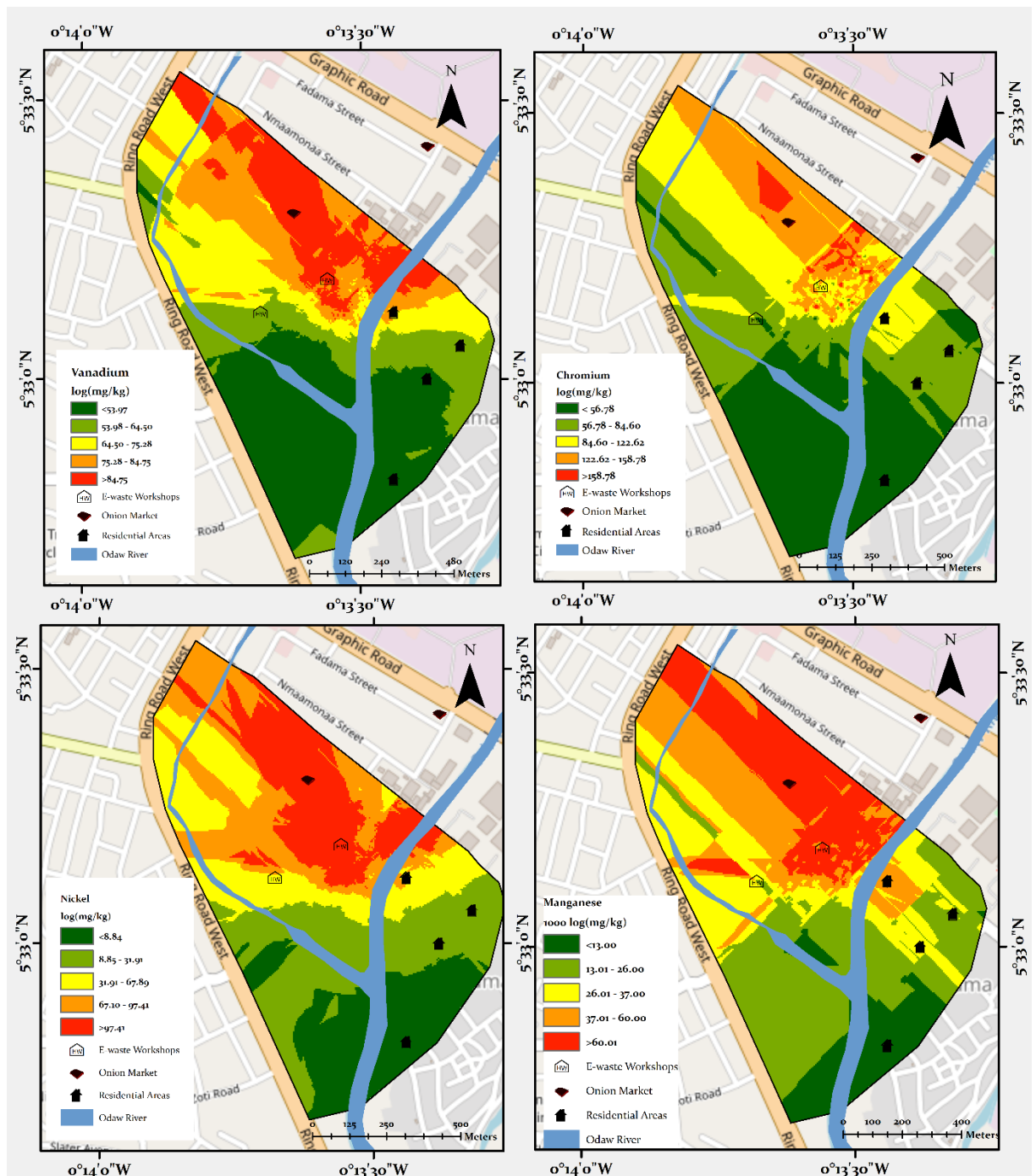


Figure 5.1 a Spatial distribution maps of V, Cr, Mn and Ni in surface dust of Agbogbloshie.

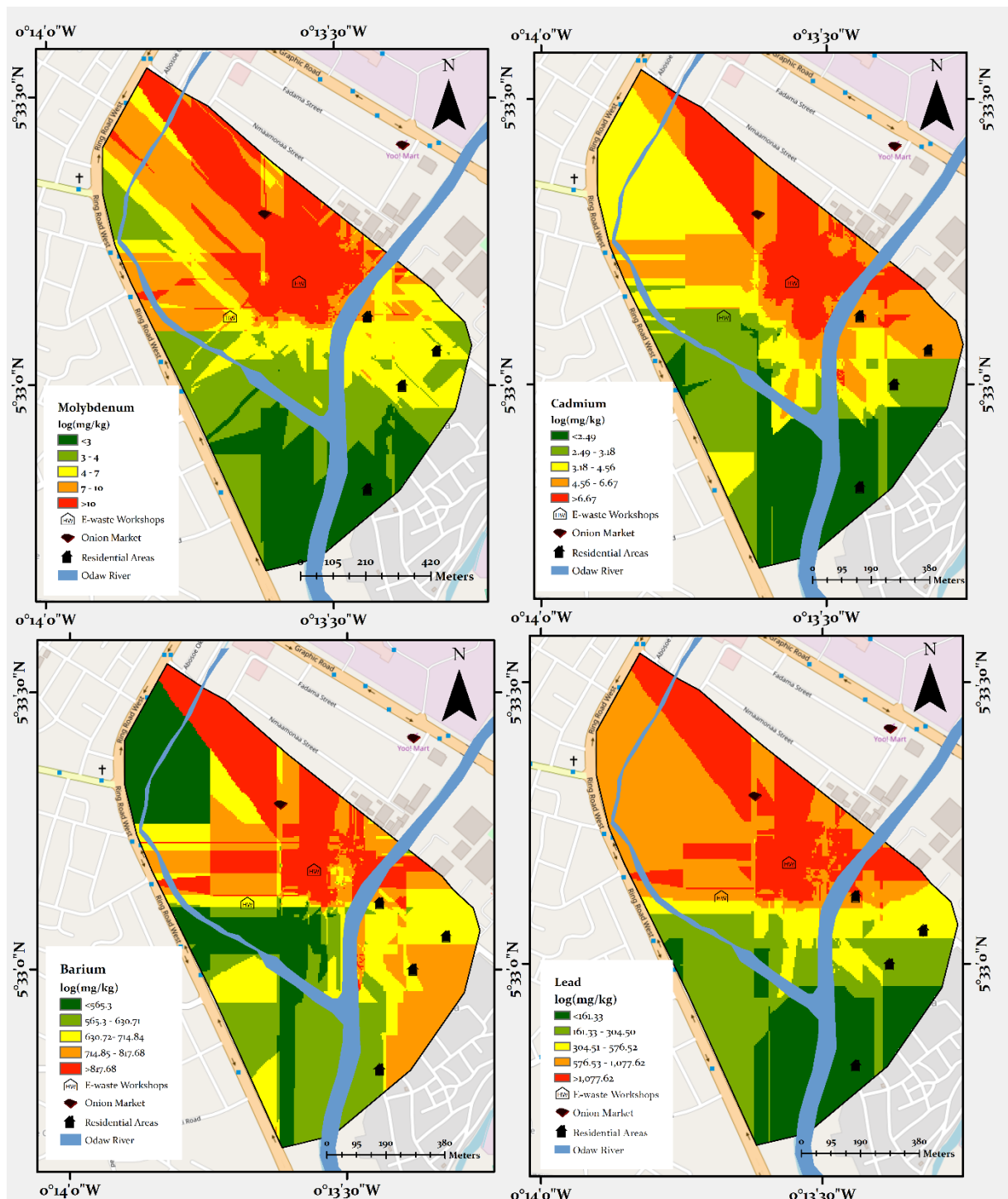


Figure 1b Spatial distribution maps of Mo, Cd, Ba and Pb in surface dust of Agbogbloshie.

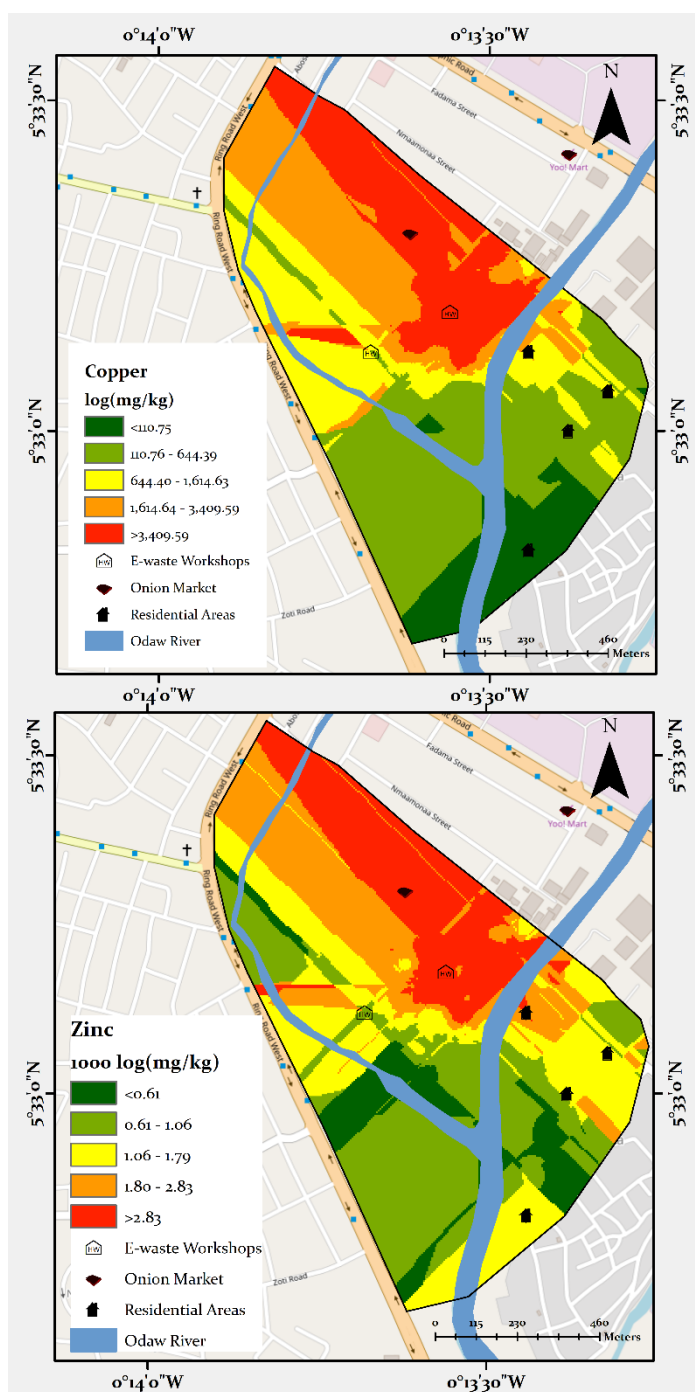


Figure 1c Spatial distribution maps of Cu and Zn in surface dust of Agbogbloshie.

Parameters (nugget, sill and range) used for semi-variogram fitting are shown in Table B1 (Appendix B). Gaussian models provided the best fit for the spatial autocorrelation (Table B1). The sill to nugget ratio of the elements was less than 25% indicating strong spatial variability.

5.3.4 Agglomerative cluster analysis

Agglomerative cluster analysis grouped dust samples into 3 groups (Figure 5.3). Group I constituted 72% of samples and were characterised by small concentrations of all elements- V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb. Group II constituted 41% of samples and were characterised by greatest concentrations of Mn, Zn, Mo and Ba and moderate concentrations of Cr, Ni, Cu, Cd and Pb. Samples in this group were collected from dismantling workshops and included DS100, D42, D162, DS94, D55, DS138, RC, DS6, DS125, D58, DS19, DS115, DS97, DS118, DF15, D66, D44, DS129 and D49 (Figure 5.3). Group III constituted 6% of samples and were characterised by greatest concentrations of Cu and Pb and moderate concentrations of V, Zn, Ba and Mn. Samples in this group were collected from the dismantling areas and included D76, DS119, DS139, ST2 and D55 (Figure 5.3). Mean concentrations and significance differences at $p \leq 0.05$ probability level of the three groups are shown in Table 5.6. Tukey post hoc tests showed there were significant differences for Cu, Cd and Pb among the three clusters, while there were significant differences between only two clusters for V, Cr, Mn, Ni, Zn, Mo and Ba at the 0.05 probability level. Copper, Cd and Pb concentrations in surface dust were significantly different while the concentrations of V, Cr, Mn, Ni, Zn, Mo and Ba were not significantly different at the 0.05 probability level.

Mean concentrations of metals in surface dust varied among the clusters or groups: for group III, metal concentrations were in the decreasing order: $Cu > Zn > Pb > Ba > Mn > Ni > Cr > Mo > V > Cd$. For group II, metal concentrations were in the decreasing order: $Cu > Zn > Pb > Ba > Mn > Ni > Cr > V > Mo > Cd$. For group I, metal concentrations were in the decreasing order: $Zn > Cu > Pb > Ba > Mn > Cr > Ni > Mo > Cd$. Most samples were collected in outdoor areas of Agbogboshie e-waste recycling site and metal concentrations reflected contamination in urban soils. There were significant differences among the mean concentrations of Cu, Pb and Cd among the three groups or clusters (Table 5.5).

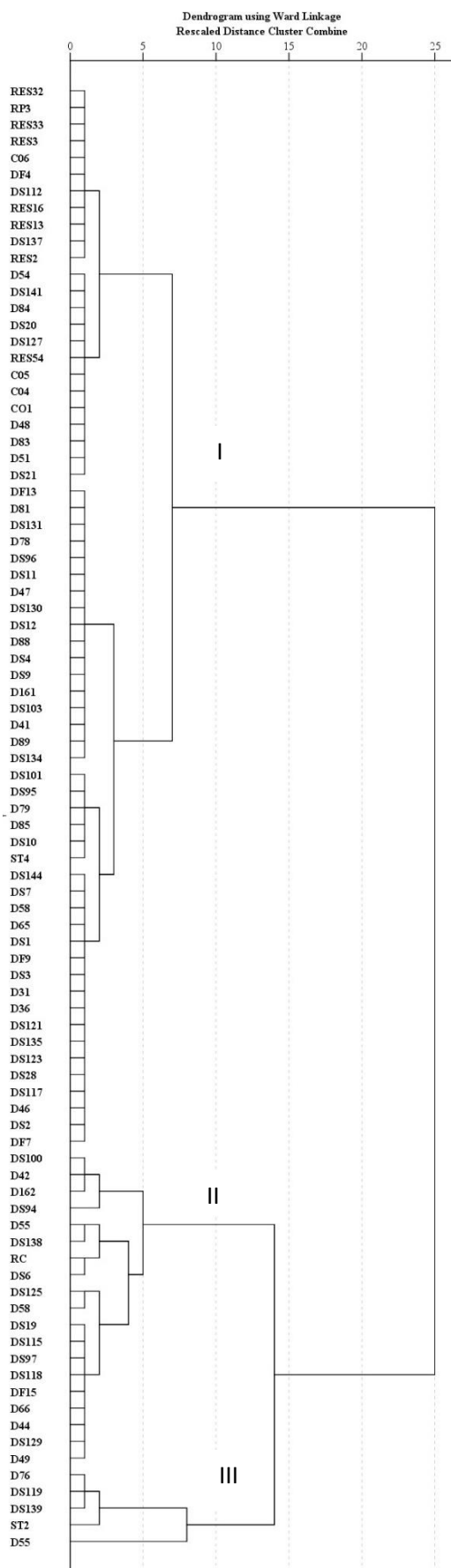


Figure 5.3 Dendrogram showing clustering among the surface dust samples.

Table 5.5 Comparison of means of metal concentrations (mg/kg) among clusters.

Metal	Cluster I	Cluster II	Cluster III
V	78 ^a	109 ^b	104 ^{ab}
Cr	110 ^a	166 ^b	189 ^{bc}
Mn	667 ^a	2000 ^b	690 ^{ab}
Ni	107 ^a	329 ^b	664 ^{bc}
Cu	3470 ^a	13400 ^b	47300 ^c
Zn	2940 ^a	6640 ^b	3970 ^{bc}
Mo	13 ^a	29 ^b	26 ^{bc}
Cd	7 ^a	12 ^b	27 ^c
Ba	822 ^a	1270 ^b	1035 ^{bc}
Pb	1160 ^a	3300 ^b	6070 ^c

Values with different letters indicate the means are significantly different at $p \leq 0.05$ probability level (Tukey post hoc test) within each row.

5.3.5 Potential ecological risks

Potential ecological risk index (Hakanson 1980) is useful to differentiate the risks associated with individual elements as well as the overall risks from all elements (Islam et al. 2015). The potential ecological risk index (RI) was calculated based on six metals-Cr, Ni, Cu, Zn, Cd and Pb for all samples and samples within the three groups. The toxic coefficients factors for Cr, Ni, Cu, Zn, Cd and Pb were 2, 5, 5, 1, 30 and 5 respectively (Hakanson 1980). The toxic coefficient factor for Mn and Mo were 1 and 15 respectively (ur Rehman et al. 2018). The objectives were to assess which metals pose the greatest risk individually and collectively in Agbogloboshie. Cadmium, Cu and Pb were the dominant elements posing the greatest potential ecological risks in the study area.

5.3.6 Mineral phases in selected surface dust samples

The mineralogy of the dust samples was dominated by quartz (SiO_2) with smaller contributions from other minerals including albite ($(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$), anglesite (PbSO_4), anorthite ($\text{Al}_2\text{Ca}_{0.71}\text{Na}_{0.25}\text{O}_8\text{Si}_2$), bromargyrite (AgBr), calcite (CaCO_3), covellite (CuS), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), microcline (KAlSi_3O_8), paratacamite ($\text{Cu}_2\text{Cl}(\text{OH})_3$), rutile (TiO_2), spinel ($\text{Fe}(\text{CuFe})\text{O}_4$), stolzite (PbWO_4) and tenorite (CuO). The qualitative mineralogy of the dust is shown (Table A2, Appendix A). The presence of carbonate minerals such as calcite and oxide minerals such as litharge, tenorite, rutile, spinel in the surface dust, rather than sulphide minerals

such as covellite may account for enhanced mobility of metals in mineral reservoirs and this may in turn affect metal solubility in gastric or intestinal fluids during soil or sediment ingestion.

5.4 Discussion

Informal recycling of e-waste in Agbogbloshie has dispersed metals into surface dust in Agbogbloshie e-waste recycling and surrounding areas, with the main pollutants of anthropogenic origin. In this study, mean concentrations of Cu, Zn, Ba and Pb were greater than Dutch soil intervention values. Elevated concentrations of Cr, Mn, Ni, Zn and Pb were found in this study, compared with the maximum concentrations of these elements reported by Atiemo et al. (2012). Long-term impacts of toxic emissions from informal e-waste recycling activities at the e-waste site over the years has led to elevated metal concentrations in dust. Smaller particle size ($< 250 \mu\text{m}$) adheres to the fingers of children, and are responsible for causing health risks from ingesting contaminated dust due to the hand-to-mouth behaviour of children. Smaller particle size fraction also means a larger specific surface area and consequently more metal adsorption sites. The maximum concentration of Cd in this study was comparable with Cd in surface dust from Agbogbloshie (Atiemo et al. 2012). Mean concentrations of Ni, Cu, Zn, Ba, Cd and Pb in this study were greater than mean concentrations for these elements in soils from Agbogbloshie (Kyere et al. 2016). Metals were found in the greatest concentrations in areas where informal dismantling of older electronics occurs. European Union has moved to restrict certain hazardous substances including Cd, Cr (VI), and Hg in electrical and electronic products in the RoHS directive 2002/95/EC. The consequence of this directive is that older electrical and electronic items are more problematic than the newer electrical and electronic items. During dismantling activities, metal-laden dust from metallic contaminated e-waste components including printed circuit boards can disperse contaminating surrounding soils and air. Metal-laden dust may contain inhalable particles which may be toxic to dismantling workers who are engaged in dismantling without personal protective equipment.

Quartz (SiO_2) is an important raw material in panel and funnel glasses of cathode ray tubes (CRT) (Andreola et al. 2005). CRT recycling is a major challenge for electronic recyclers as it constitutes approximately 47 wt. % of commercial electronics such as televisions and 30% of data processing equipment and it also contains other elements including Ba, Sr and Pb (Herat 2008). Due to lack of recycling facilities for CRT glass in Agbogbloshie, dumping of broken CRT glass is a common occurrence especially along the banks of Korle Lagoon. Metals and compounds released from CRT glass may leach into surface water and end up trapped in

sediments. Metals can also leach into deeper soil profiles, thus reducing the viability of the soil for productive uses such as for food production.

Significant concentrations of Cu, Zn and Pb were found in surface dust in Agbogbloshie and these concentrations were comparable with concentrations detected in dust in Nigeria (Ohajinwa et al. 2018), and Guiyu in China (Leung et al. 2008). Dust can concentrate metals and serve as a secondary source of pollution in Agbogbloshie. Particulates containing toxic metals may travel over long distances contaminating local food grown around Agbogbloshie, bioaccumulating in humans who consume these foods, especially leafy vegetables.

Children, because of their mouthing behavior can ingest contaminated surface dust and can suffer greater effects of metal absorption due to their higher absorption in their bloodstream compared to adults. Exposure to chemical mixtures could be a significant health concern. In Agbogbloshie e-waste recycling site, potential risks will be enhanced from older electronics containing toxic substances including Cd, Pb and Cu. Cadmium and Pb are minimised in new electronics under the European RoHS directive. Cadmium has a long biological half-life in kidney and bones (Chen et al. 2011) and Pb can cross the blood-brain barrier of children under five years of age and cause toxic effects including low intellectual development of children, especially those under five years. Chromium present little ecological risk from dust due to its smaller concentrations in electronics. Metals are persistent, remaining in the environment for long periods and are bioaccumulative in humans. To reduce toxic emissions from end-of-life electronics in Agbogbloshie, an integrated e-waste recycling system incorporating formal and semi-formal recycling can be developed and piloted to reduce toxic emissions. Environmental Protection Agency and other stakeholders including Non-Governmental Organisations can develop and implement education campaigns on safe e-waste recycling for informal e-waste recyclers who may not be fully aware of the impacts of e-waste recycling on their health, that of their families and the environment.

5.5 Conclusion

Spatial distribution of V, Cr, Mn, Ni, Cu, Zn, Mo, Cd, Ba and Pb in the largest informal e-waste recycling site in Ghana was assessed using geostatistical tools and geographical information systems. Concentrations of 8 elements- Cr, Ni, Cu, Zn, Mo, Cd, Ba and Pb exceeded Dutch Soil Guidelines target values, while concentrations of 4 elements - Cu, Zn, Ba and Pb - exceeded Dutch Soil Guidelines intervention values. Copper, Zn, Mo, Cd and Pb showed very high contamination factors among the elements. The most significant contributions to the risk index

were from Cd, Cu and Pb. The mineralogical phases for selected dust samples were dominated by quartz with smaller contributions from other minerals.

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CHAPTER 6: Metal distribution, bioaccessibility and health risk assessment of floor dust from informal e-waste recycling in Accra, Ghana.

Abstract

An analysis of floor dust from five functional areas (i.e., dismantling, wire stripping, roadside, commercial and storage) in Agbogbloshie (Accra, Ghana) for total and bioaccessible concentrations showed mean concentration ranges of 1070 to 11400 mg/kg of Cu, 1350 to 5590 mg/kg of Zn, and 809 to 9150 mg/kg of Pb. Mean metal concentrations of Cu, Zn and Pb respectively exceeded the Canadian soil quality guidelines of 91 mg/kg, 410 mg/kg and 600 mg/kg for these elements (CCME 1999). Mean bioaccessible concentration in floor dust samples from the functional areas ranged from 13 to 3210 mg/kg for Cu, 78 to 2580 mg/kg for Zn and 6 to 372 mg/kg for Pb. Estimation of non-carcinogenic human health risks indicated that ingestion was more important than dermal and inhalation pathways. Lead contributed the greatest non-carcinogenic risks in the study area. Lead carcinogenic risks were greater than the USEPA threshold of 1×10^{-4} , indicating cancer risks to children and adults engaged in informal e-waste recycling activities.

Keywords: bioaccessibility factor, exposure pathways, functional areas.

6.1 Introduction

Informal e-waste recycling involves dismantling of end-of-life electronics using rudimentary tools, to retrieve valuable elements. There is little to no reduction of environmental emissions, and few safeguards for human health. Mechanical and metallurgical recycling can generate dust and effluents containing toxic metals and other chemicals (Cui and Forssberg 2003). In the Agbogbloshie (Ghana) e-waste recycling area, recyclers engage in manual stripping and disassembling of obsolete electrical and electronic equipment to isolate metals and open burning to remove metals from plastic sheaths and casings (Azuka 2009). Open incineration of insulation foams containing polyurethane (PUR) from obsolete refrigerators and open incineration of e-waste plastics containing halogenated flame retardants such as polybrominated diphenyl ethers and plasticizers such as phthalates can contribute to health risks and environmental contamination in Agbogbloshie (Prakash et al. 2010).

Widespread contamination of surface dust by metals (Cu, Zn, and Pb) in Agbogbloshie has been reported (Atiemo et al. 2012). Elevated concentrations of Pb were reported in urine and blood of e-waste recycling workers (Asante et al. 2012). Exposure to e-waste materials and associated pollutants can occur through exposure to contaminated soil, dust, air, water and food (Grant et al. 2013). The most important pathway for exposure to toxic metals for children is through inadvertent ingestion of soils through hand-to-mouth behavior (Mielke and Reagan

1998; Mielke et al. 1999; Laidlaw et al. 2014; Lu et al. 2011; Imram et al. 2017). Measurements of bioavailability of soil-borne contaminants are important to determine associated human health risks in an environmental matrix (Darko et al. 2017) accurately. Assessment of potential carcinogenic and non-carcinogenic risks from soil metals allows informed decisions which may reduce human and environmental exposure to toxic metals (Chen et al. 2015). Bioaccessible metals are more readily available for absorption by humans. For example, lead in the minerals cotunnite (PbCl_2) or litharge (PbO) are more bioavailable than lead in galena (PbS) (Dieter et al. 1993). Similarly, barite (BaSO_4) is an insoluble mineral (Abbasi et al. 2016). As a consequence of mineral solubility, the total concentrations of a contaminant are not a reliable predictor of the actual exposure (Gourlay-Francé and Tusseau-Vuillemin 2013) and instead, estimation of the bioaccessible fraction (BAF) of solid phase contaminants can help provide more accurate assessments of human health risks.

Site-specific data on bioaccessible concentrations of chemical elements is useful for accurate human health risk assessments (Lee et al. 2006; Li et al. 2014b). Bioaccessibility tests can be used as a surrogate for measuring metal bioavailability since they are simpler and less costly to perform (Stopford et al. 2003). Bioaccessibility is defined as the proportion of a chemical present in ingested soil and sediment particles, which can be mobilised in the gut, after ingestion, and available for intestinal absorption (Peijnenburg and Jager 2003). Human health risk assessment (HHRA) involves estimating probable adverse health impacts in human populations exposed to chemicals or environmental hazards in a contaminated environment (Li et al. 2014a, USEPA 1997). A previous assessment of human health risks in Agbogbloshe e-waste site focused on only the ingestion and inhalation exposure pathways for 11 elements- V, Cr, Mn, Co, Cu, Zn, As, Se, Cd, Sb and Pb (Itai et al. 2014). Ingestion and inhalation are not the only exposure pathways for humans; therefore, it is imperative to assess other pathways including dermal contact to gain comprehensive information about the exposures. Contributions of ingestion, dermal absorption and inhalation exposures to the overall risks may be different for different age groups. Moreover, including site-specific bioaccessibility in this study can provide an assessment and prevent under or over-estimations of the health risks. This study;

(1) assesses total and bioaccessible concentrations of Mn, Fe, Ni, Cu, Zn, Ba and Pb in floor dust of five functional areas (i.e., wire stripping, dismantling, storage area, roadside and food vending) of Agbogbloshe e-waste recycling site, and (2) estimates non-carcinogenic risks and carcinogenic risks on human health through ingestion, dermal and inhalation pathways for dismantling workers.

6.2 Materials and methods

6.2.1 Measurements of bioaccessibility

Bioavailability studies can generate site-specific data for the estimation of health risks. Bioavailability can be determined only through expensive and complex laboratory studies using experimental animals which also require ethical considerations, so relatively simple solubility tests have been developed as surrogates to determine the bioavailability fraction (Hansen et al. 2007). The simple solubility tests referred to are in-vitro extraction tests which can be used to predict the bioavailability of inorganic substances from solid matrices by simulating the human gastrointestinal environment (Bruce et al. 2007). Bioaccessibility is the percentage of an administered dose that is soluble in the gastrointestinal environment and available for absorption. Bioavailability, on the other hand, refers to the fraction (%) of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract (Ruby et al. 1999). Bioaccessibility and bioavailability are interrelated (Morrison and Gulson 2007), however, bioaccessibility can be distinguished from bioavailability based on processes that determine exposure to contamination from the soil or sediment matrix (Semple et al. 2004). Bioavailability of soil contaminants includes all the processes of contaminant uptake from ingestion to internal exposure concentrations in the target organs (e.g., blood for Pb and kidney for Cd (Hansen et al. 2007). The processes that determine exposure to contaminated soil and sediment includes the release of a solid-bound contaminant (A) and subsequent transport (B), transport of bound contaminants (C), uptake across a physiological membrane (D) and incorporation into a living system (E) (Figure 6.1). These processes - A, B, C and D constitute bioaccessibility processes while process D relates to bioavailability, where the contaminant can pass through a physiological barrier into a living system (NRC 2003; Semple et al. 2004).

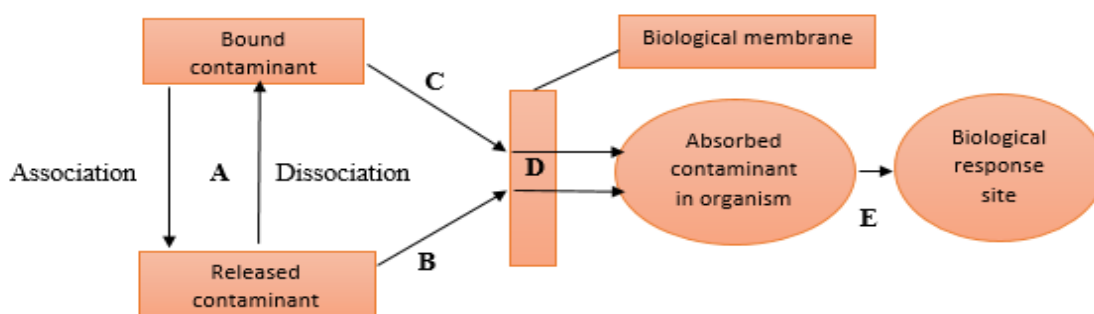


Figure 6.1 Bioavailability processes that determine exposure to contaminated soil or sediment matrix (Sources: NRC 2003; Ehlers and Luthy 2003; Semple et al. 2004).

The physiologically based extraction test (PBET) is a popular in-vitro extraction method which has been validated using in-vivo models (Ruby et al. 1996; Rodriguez et al. 1999; Kelly et al. 2002; Oomen et al. 2003; Shroeder et al. 2004). PBET has two phases - stomach or gastric and gastrointestinal phases, with the gastric phase providing a conservative and cost-effective approach for estimating oral bioaccessibility due to its smaller pH range of 1.2 to 2.5 (Boros et al. 2017).

6.2.2 Sampling and sample preparation

Floor dust samples (n=16) including replicate samples (n=3) were collected in December 2016, from five functional areas of Agbogbloshie e-waste recycling site by gently sweeping back and forth with a plastic brush and dustpan. The samples were then placed in ziplock[®] plastic bags. Sampling sites were located to ± 5 m using a Garmin global positioning system receiver using the WGS84 geoid, 30 N projection zone. Locations of the five functional areas were e-waste dismantling workshops (n = 7), a wire stripping area (n = 4), a storage site (n = 1), roadside (n=3) and commercial area (n = 1) (Table 6.1).

Table 6.1 Description of sampling locations.

Site description	Latitude (°N)	Longitude (°W)
Dismantling areas	5°33'08.21"	0°13'31.69"
	5°33'10.01"	0°13'29.42"
	5°33'06.95"	0°13'32.23"
	5°33'08.64"	0°13'33.78"
	5°33'12.46"	0°13'29.57"
	5°33'09.14"	0°13'30.36"
	5°33'08.68"	0°13'30.29"
Wire stripping area	5°33'15.91"	0°13'29.46"
	5°33'14.18"	0°13'28.60"
Roadside	5°33'14.44"	0°13'29.17"
Storage area	5°33'12.71"	0°13'34.72"
Commercial area	5°33'11.09"	0°13'33.96"

Dust samples were oven-dried at 40 °C for 48 hours and the < 250 µm fraction separated for analysis using a nylon mesh sieve. The < 250 µm fraction was powdered using a Retsch MM-301 mixer mill with tungsten carbide vials and balls, operated at 25 Hz for 10 min. The tungsten carbide vials and balls were cleaned by milling acid-washed quartz sand (UNILAB Ajax Finechem B/No 1510204652), in between samples to prevent inter-sample cross-contamination.

6.2.3 Quality Assurance / Quality Control

Replicate dust samples were collected during field sampling. All plasticware and glassware used were soaked overnight in 10 % HNO₃ and thoroughly washed with 18 MΩ.cm (Type I) deionised water (Millipore Synergy, Merck Australia). Reagent blanks and duplicate samples were included in the sampling and analysis to detect contamination and assess method precision.

6.2.4 Elemental analyses

Approximately 10 g of < 250 µm powdered sediment was placed in a 10 mL polyethylene cup and sealed using a 3.6 µm thick polyester X-ray film. The sample was placed in a test stand and analysed for bulk elements using an Olympus Delta Pro X-ray fluorescence spectrometer with 50 kV Ta anode tube, with three measurement conditions of 60 s each in soil calibration mode. Measurement conditions were 50 kV, 4 W, 60 s with aluminium filter; 15 kV, 4 W, 60 s with no filter; and 5 kV, 4 W, 60 s with no filter. The analytical area was a 6 x 4 mm ellipse. Measurements were made in air. Repeated measurement of an acid-washed quartz blank (SiO₂) showed analytes (Mn, Fe, Ni, Cu, Zn, Ba, and Pb) to be below detection limits for all

measurements. Accuracy was constrained using repeated analysis of two United States National Institute of Standards and Technology standard reference materials (NIST 2710a, 2711a), which showed inaccuracies better than 10% for elements more abundant than 0.1 weight (wt)% and better than 20% for trace elements more than double the limit of quantification.

6.2.5 pH determination

pH (CaCl₂) was determined on an extracted dust solution ratio of 1:10 (v/v) using 0.01 M CaCl₂ solution with a calibrated pH meter (Denver Instrument Model 250), after shaking for 1 h.

6.2.6 Bioaccessibility determination

Bioaccessibility was determined on selected dust samples (n=16) using surrogate (gastric) fluids (Intawongse and Dean 2008). The gastric solution was prepared by adding 1.25 g pepsin (Sigma Aldrich, Australia), 0.5 g sodium citrate (Sigma Aldrich, Australia), 0.5 g malic acid (Sigma Aldrich, Australia), 420 µL lactic acid (Sigma Aldrich, Australia), 500 µL acetic acid (Sigma Aldrich, Australia) to 1 L 18 MΩ.cm (Type I) deionised water (Millipore Synergy, Merck Australia). pH of the gastric solution was adjusted to 1.5 by adding 12 M trace metal grade HCl (Sigma Aldrich, Australia). Gastric solution (30 mL) was added to 0.3 g of the dust sample in a clean 50 mL HDPE bottle. The sample solution mixture was placed in a shaking water bath at 37 °C and rotated horizontally at 30 rpm for 1 h. Once the extraction process was completed, the supernatant was filtered through a 0.45 µm cellulose acetate Sartorius MiniSart syringe filter and acidified with concentrated HNO₃. The supernatant was analysed for trace metals using total reflection X-ray fluorescence (TXRF) spectrometry using Ga as internal standard. For TXRF spectrometry, 50 µL of 20 mg.L⁻¹ Ga spike was added to 450 µL of sample and mixed on a vortex mixer for 15 s. 10 µL of spiked acidified sample was placed on a siliconised quartz disc and dried on a hot plate at 60 °C for 15 min. Elemental compositions of the evaporites on the discs were measured using a Bruker S2 Picofox TXRF with Mo anode tube, and measurement conditions of 30 kV, no filter and a measurement time of 600 s. Limits of quantification depend on the matrix but are typically ~5 µg.L⁻¹ for elements in this study. Inaccuracy, constrained using a Merck XVI multi-element standard, was better than 10 % where concentrations exceeded 0.1 mg.L⁻¹.

The oral bioaccessibility (%) was calculated from the measured concentrations using equation 6.1;

$$\text{Oral bioaccessibility (\%)} = \frac{\text{Bioaccessible concentration (mg/kg)}}{\text{Total concentration (mg/kg)}} \times 100 \quad (6.1)$$

6.2.7 Human Health Risk Assessment

E-waste recyclers are exposed to health risks through three exposure pathways; inadvertent ingestion, dermal exposure and inhalation of dust particles. Human health risk assessment involves estimating probable adverse health impacts in human populations exposed to chemicals or environmental hazards in a contaminated environment (Li et al. 2014a, USEPA 1997). Human health risks were assessed separately for children and adults, due to differences in physiology and behavior (Li et al. 2014a). Exposure factors were derived using equations described in the United States Environmental Protection Agency (USEPA) health risk handbook (USEPA 1996, 1997, 2011). Average daily intake (ADI) was used to calculate levels of human exposure to heavy metals through oral ingestion. Oral ingestion risk is a very important pathway for exposure in e-waste recycling environments (Obiri et al. 2016). ADI via ingestion, dermal and inhalation was evaluated using equations 6.2, 6.3 and 6.4 respectively (USEPA 1997);

$$ADI_{\text{ingestion}} = \frac{C_d \times DIR \times BAF \times EF \times ED}{BW \times AT} \quad (6.2)$$

where $ADI_{\text{ingestion}}$ = average daily intake of metals from dust ingestion (mg/kg/day), C_d = metal concentration in the dust (mg/kg), DIR = dust ingestion rate (mg/day), EF = exposure frequency (day/year). BAF = bioaccessible fraction (Lu et al. 2011), determined in this study, ED = exposure duration (year). BW = body weight of the individual exposed (kg) and AT = time over which the dose is averaged (day);

$$ADI_{\text{dermal}} = \frac{C_d \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \quad (6.3)$$

where ADI_{dermal} = average daily intake of metals from dermal absorption (mg/kg/day), SA = exposed skin surface area (cm²), AF = adherence factor (mg/cm²/day) and ABS = dermal absorption factor (unitless);

$$ADI_{\text{inhalation}} = \frac{C_d \times InhR \times EF \times ED}{PEF \times BW \times AT} \quad (6.4)$$

where $ADI_{\text{inhalation}}$ = average daily intake of metals from dust inhalation (mg/kg/day), PEF = particle emission factor (m³/kg), $InhR$ = dust inhalation rate (m³/day). Non-carcinogenic risks were evaluated using the hazard quotient (HQ). Hazard quotient was evaluated as a ratio of the average daily intake of contaminants from each exposure route or the dose (ADI) to the toxicity threshold value or the reference dose (RfD) (USEPA 1989) (equation 6.5);

$$HQ = \frac{ADI}{RfD} \quad (6.5)$$

If $HQ > 1$, the exposed population is likely to experience adverse health effects; however, if $HQ < 1$, the exposed population is unlikely to experience adverse health effects (USEPA 1986). The Hazard Index (HI) is the sum of the hazard quotients (HQs) from all applicable pathways and is calculated using equation 6.6;

$$HI = \sum HQ_i = \sum \frac{ADI_i}{RfD_i} \quad (6.6)$$

Hazard index (HI) value > 1 means there is potential for adverse effects on human health, however, if $HI < 1$, the exposed population is unlikely to experience any adverse health effects (Li et al. 2014b).

Reference dose for dermal absorption (RfD_{dermal}) is extrapolated from the oral reference dose values by multiplying the oral reference dose by the gastrointestinal absorption factor (ABS_{GI}). RfD_{dermal} is calculated using equation 6.7;

$$RfD_{\text{dermal}} = RfD_o \times ABS_{GI} \quad (6.7)$$

RfD_{abs} = adjusted reference dose for dermal exposure (mg/kg/day) and ABS_{GI} = gastrointestinal absorption factor, which is unitless.

6.2.8 Geo-accumulation index

The Geo-accumulation index (I_{geo}) was used to assess contamination by comparing current and pre-industrial concentrations (Müller 1969). I_{geo} was computed using equation 6.10;

$$I_{\text{geo}} = \frac{\log_2 C_n}{1.5B_n} \quad (6.10)$$

where C_n = total concentration of element 'n' in the surface layer of the soil tested and B_n = concentration of element 'n' in the earth crust. A factor of 1.5 was used to account for variations of the background data due to lithological variations (Müller 1969). The Geo-accumulation index (I_{geo}) was calculated using background concentrations from global average shale data (Turekian and Wedepohl 1961). I_{geo} is distinguished into seven classes of contamination (Table 6.2).

Table 6.2 Geo-accumulation index (Igeo) for contamination levels in sediments (Müller 1981).

Igeo class	Igeo value	Contamination level
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

6.3 Results and Discussion

6.3.1 Total and bioaccessible concentrations in floor dust

The concentrations of metals in floor dust are shown (Table 6.3). For comparison, the metal concentrations in dust were compared to the Canadian environmental quality guidelines for soil. Floor dust from the functional areas was contaminated with Ni, Cu, Zn and Pb. Floor dust concentrations were highly heterogenous, as shown by their large standard deviations.

Table 6.3 pH and elemental data of floor dust from the five functional areas (mean \pm 1 standard deviation).

pH and Elemental concentrations	Dismantling	Wire stripping	Roadside	Storage	Commercial area	Canadian Environmental Quality Guidelines for soil ^a
pH	6.27	7.01	6.68	6.67	9.57	
Mn (mg/kg)	615 \pm 459	551 \pm 158	416 \pm 95	766 \pm 0	540 \pm 0	
Fe (wt %)	6 \pm 4	5 \pm 2	4 \pm 1	8 \pm 0	4 \pm 0	
Ni (mg/kg)	151 \pm 179	79 \pm 28	49 \pm 18	610 \pm 0	98 \pm 0	89
Cu (mg/kg)	7600 \pm 7490	11400 \pm 9850	1070 \pm 709	4120 \pm 0	3770 \pm 0	91
Zn (mg/kg)	5590 \pm 5830	3600 \pm 2800	1350 \pm 646	4740 \pm 0	2440 \pm 0	410
Ba (mg/kg)	953 \pm 487	812 \pm 116	719 \pm 122	1480 \pm 0	1750 \pm 0	2000
Pb (mg/kg)	3210 \pm 4030	809 \pm 0	962 \pm 495	9150 \pm 0	2030 \pm 0	600

^a - Canadian Environmental Quality Guidelines for Soil (CCME 1999).

The bioaccessible concentrations and average bioaccessibility in floor dust are shown (Table 6.4). Bioaccessibility (%) of Mn, Fe, Ni, Zn, Ba and Pb in the dust samples were < 100%, however, bioaccessibility of Cu was $\geq 100\%$ in roadside area dust. Bioaccessibility of Mn, Fe, Ni, Cu, Zn, Ba and Pb ranged from 3 to 33%, 0.3 to 3%, 0.1 to 23%, 0.3 to 221%, 1.6 to 95%, 0.4 to 9% and 0.1 to 24% respectively.

Table 6.4 Bioaccessible concentrations (mg/kg) and average bioaccessibility (%) of floor dust from the five different functional areas (mean \pm 1 standard deviation).

Element	Dismantling		Wire stripping		Roadside		Storage		Commercial area	
Unit	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)	(mg/kg)	(%)
Mn	74 \pm 35	12.0	108 \pm 76	19.6	48 \pm 22	11.5	24 \pm 0	3.1	68 \pm 0	12.6
Fe	1040 \pm 1490	1.7	864 \pm 480	1.7	668 \pm 478	1.7	293 \pm 0	0.4	1260 \pm 0	3.2
Ni	14 \pm 23	9.3	9 \pm 5	11.4	6 \pm 4	12.2	1 \pm 0	0.2	92 \pm 0	93.9
Cu	2140 \pm 2720	28.2	3210 \pm 3500	28.2	885 \pm 1150	82.7	13 \pm 0	0.3	664 \pm 0	17.6
Zn	2440 \pm 2950	43.6	2580 \pm 3120	71.7	464 \pm 298	34.4	78 \pm 0	1.6	1300 \pm 0	53.3
Ba	35 \pm 23	3.7	30 \pm 8	3.7	17 \pm 12	2.4	11 \pm 0	0.7	105 \pm 0	6.0
Pb	372 \pm 493	11.6	147 \pm 86	18.2	109 \pm 95	11.3	6 \pm 0	0.1	1210 \pm 0	59.6

6.3.2 Non-carcinogenic risks

Site-specific bioaccessibility factors were used in the calculation of the average daily intake for the oral exposure route. The average daily intake of dust from dermal contact and inhalation was calculated for adults and children who may be exposed through the contaminated dust. Exposure factors (Table 6.5) from USEPA and the literature was used for calculation of health risks using USEPA human health risk assessment model. The results are described (Table 6.6).

Table 6.5 Exposure factors and input parameters used for calculation of average daily intake.

Exposure factors	Unit	Children	Adult	Reference
Dust ingestion rate (SIR)	mg/day	200	100	USEPA 2011
Exposure frequency (EF)	Days	350	350	USDOE 2011
Conversion factor (CF)	Dimensionless	1×10^{-6}	1×10^{-6}	USEPA 2011
Exposure duration (ED)	Years	6	24	USEPA 2011
Body weight (BW)	kg	15	55.9	Lee-Steere 2009
Averaging time (AT)	Days	$365 \times ED$	$365 \times ED$	USEPA 2011
Dust inhalation rate (InhR)	m ³ /day	7.63	12.8	Li et al. 2001
Particle Emission factor (PEF)	m ³ /kg	1.36×10^9	1.36×10^9	USEPA 2011
Exposed skin surface area (SA)	cm ²	1600	4350	Lee-Steere 2009
Skin adherence factor (AF)	mg/cm ² /day	0.2	0.7	USEPA 1993
Dermal absorption factor (ABS)	Dimensionless	0.001	0.001	Chabukdhara and Nema 2013

Concentrations of Mn, Fe, Ni, Cu, Zn, and Ba did not present non-carcinogenic ingestion risks to children and adults (Table 6.6). The average daily intakes of these elements were smaller than their respective reference doses. Lead presented non-carcinogenic risks to children and adults because the hazard quotients (HQ) for Pb for children and adults were ≥ 1 . Lead contributed the greatest HQ in the dismantling area, followed by Cu, Zn, Fe, Ni, Mn and Ba in decreasing order: Pb > Cu > Zn > Fe > Ni > Mn > Ba. Lead and Cu contributed the highest percentage of the HQ of 62.3% and 31.3% respectively. Hazard index (HI) describes the summation of all exposure pathways (i.e. ingestion, dermal and inhalation). The HI of the elements is shown in Table 6.7. Lead had the greatest HI for both the child and adult e-waste worker. Lead contributed significantly to chronic health risks for children and adults in the dismantling areas. Children were more susceptible to non-carcinogenic ingestion risks than adults. HQ for non-carcinogenic dermal and inhalation risks for all other metals, except Pb were less than 1 for both children and adults. Therefore, exposure to Mn, Fe, Ni, Cu, Zn and Ba were assumed to be safe for children and adults.

Table 6.6 Health risks to dismantling e-waste worker (children and adults) from metals in the dismantling area. The greatest HQ for the three non-carcinogenic pathways for children and adults are highlighted in bold.

Element	C _d (mg/kg)	RfD (mg/kg/day)	ABS _{GI}	Rfc (inh)	BAF (%)	Exposure route	ADI (mg/kg/day)		HQ	
							Child	Adult	Children	Adult
Mn	615	0.14	1	0.00005	12	Ingestion	9.8×10 ⁻³	2.88×10 ⁻⁵	7.03×10 ⁻³	2.06×10 ⁻⁴
						Dermal	1.31×10 ⁻⁵	3.35×10 ⁻⁵	9.37×10 ⁻⁵	3.35×10 ⁻⁵
						Inhalation	2.21×10 ⁻⁷	2.48×10 ⁻⁸	4.41×10⁻³	4.96×10⁻⁴
Fe	57000	0.7	1		1.82	Ingestion	1.37×10 ⁻²	1.84×10 ⁻³	1.95×10 ⁻²	2.62×10 ⁻³
						Dermal	1.22×10 ⁻³	3.11×10 ⁻³	1.74×10 ⁻³	4.44×10 ⁻³
						Inhalation	2.04×10 ⁻⁵	2.30×10 ⁻⁶		
Ni	151	0.02	0.04		9.54	Ingestion	1.90×10 ⁻⁴	2.57×10 ⁻⁵	9.56×10 ⁻³	1.28×10 ⁻³
						Dermal	3.22×10 ⁻⁶	8.23×10 ⁻⁶	4.03×10 ⁻³	1.65×10 ⁻⁵
						Inhalation	5.42×10 ⁻⁸	6.09×10 ⁻⁹		
Cu	7600	0.04	1		28.2	Ingestion	2.86×10 ⁻²	3.83×10 ⁻³	7.14×10 ⁻¹	9.58×10 ⁻²
						Dermal	1.62×10 ⁻⁴	4.14×10 ⁻⁴	4.05×10 ⁻³	1.03×10 ⁻²
						Inhalation	2.73×10 ⁻⁶	3.07×10 ⁻⁷		
Zn	5590	0.3	1		43.6	Ingestion	3.25×10 ⁻²	4.36×10 ⁻³	1.08×10 ⁻¹	1.45×10 ⁻²
						Dermal	1.19×10 ⁻⁴	3.05×10 ⁻⁴	3.98×10 ⁻⁴	1.02×10 ⁻³
						Inhalation	2.00×10 ⁻⁶	2.26×10 ⁻⁷		
Ba	953	0.2	0.07		3.63	Ingestion	4.60×10 ⁻⁴	6.14×10 ⁻⁵	2.29×10 ⁻³	3.07×10 ⁻⁴
						Dermal	2.03×10 ⁻⁵	5.19×10 ⁻⁵	1.45×10 ⁻³	3.71×10 ⁻³
						Inhalation	3.42×10 ⁻⁷	3.85×10 ⁻⁸		
Pb	3210	0.0035	1		11.6	Ingestion	4.96×10 ⁻³	6.66×10 ⁻⁴	1.42×10⁰	1.90×10⁻¹
						Dermal	6.85×10 ⁻⁵	1.75×10 ⁻⁴	1.96×10⁻²	5.00×10⁻²
						Inhalation	1.15×10 ⁻⁶	1.30×10 ⁻⁷		

Table 6.7 Hazard indices (Σ HQ) of metals for assessed exposure pathways.

HI	Mn	Fe	Ni	Cu	Zn	Ba	Pb
Child	1.15×10^{-2}	2.12×10^{-2}	1.36×10^{-2}	7.18×10^{-1}	1.08×10^{-1}	2.41×10^{-1}	1.44×10^0
Adult	7.36×10^{-4}	7.06×10^{-3}	1.30×10^{-3}	1.06×10^{-1}	1.55×10^{-2}	2.34×10^{-1}	2.40×10^{-1}

6.3.3 Geoaccumulation index (Igeo)

Based on the mean Igeo values of metals (Table 6.8), the overall degree of contamination by metals in floor dust was in this decreasing order: Cu > Pb > Zn > Ba > Ni > Mn > Fe. In the dismantling areas, floor dust showed extreme contamination with Cu, Zn and Pb and uncontamination with Ni and Ba. Manganese and Fe showed uncontamination, as their Igeo value were less than 0. In the wire stripping area, floor dust showed extreme contamination with Cu (Igeo=7.05), Zn (Igeo=4.36) and Pb (Igeo=4.72). Igeo values for Mn, Fe, Ni and Ba were less than 0, indicating uncontamination for these elements. In roadside dust, Mn, Fe, Ni, and Ba showed uncontamination, because Igeo values for these metals were less than 0. Pb (Igeo=4.85) showed strong to extreme contamination while Cu and Zn with Igeo values of 3.73 and 3.10 respectively showed strong contamination. In the storage area, Cu, Zn, and Pb with Igeo values of 5.93, 5.06 and 8.25 respectively showed extreme contamination. Manganese and Fe showed no contamination, while Ni showed moderate to strong contamination (Igeo=2.58). Barium showed uncontamination to moderate contamination (Igeo=0.77). In the commercial area, floor dust was extremely contaminated with Cu and Pb with Igeo values of 5.80 and 6.08 respectively while Zn showed extreme to moderate contamination (Igeo=4.1). Manganese, Fe, and Ni showed no contamination, as Igeo values were less than 0 while Ba showed moderate contamination (Igeo=1.01).

Table 6.8. Mean Geoaccumulation indices for functional areas.

Functional area	Mn	Fe	Ni	Cu	Zn	Ba	Pb
Dismantling area	-1.28	-6.95	-0.45	6.25	4.68	-0.04	5.44
Wire stripping area	-1.25	-6.55	-0.45	7.05	4.36	-0.11	4.72
Roadside	-1.64	-6.97	-1.14	3.73	3.10	-0.29	4.85
Storage	-0.74	-7.92	2.58	5.93	5.06	0.77	8.25
Commercial area	-1.24	-5.81	-0.06	5.80	4.10	1.01	6.08

6.3.4 Floor dust toxicity

Toxicity of contaminated dust samples was assessed based on the total impact points of metal elements (ATSDR 2015). This environmental assessment model was originally applied in steelmaking sites (Strezov and Chaudhary 2017) to assess the toxicity of elements. To assess

element toxicity, the median concentration of each metal was multiplied by their total impact points and the product divided by the maximum value. The total impact points were obtained from the Agency for toxic substances and disease registry database. Manganese, Fe, Ni, Cu, Zn, Ba and Pb total impact points were 798, 0, 996, 806, 915, 802 and 1529 respectively (ATSDR 2015). The results showed that Cu, Zn and Pb had the greatest element toxicities. The most important metals which are of toxicity concern in the floor dust were in the order $Cu > Zn > Pb > Ba > Mn > Ni > Fe$. Copper is an important constituent of circuit wires and Zn as galvanising in alloys. Lead is important as solders used in printed circuit boards in computers. Open burning activities and breakage of older electronic components especially printed circuit boards may have contributed to the release of dust containing toxic metals in Agbogbloshie (Wong et al. 2007). In the dismantling area floor dust, the most important metal followed the order $Cu > Zn > Pb > Ba > Mn > Ni > Fe$, however in the roadside dust, the most important metals were in the order $Pb > Zn > Cu > Ba > Mn > Ni > Fe$. In the wire stripping area, the most important metals were in the same order as the dismantling area floor dust, i.e., $Cu > Zn > Pb > Ba > Mn > Ni > Fe$. The order of importance of metals in the commercial and E-waste storage area was $Pb > Cu > Zn > Ba > Mn > Ni > Fe$ and $Pb > Zn > Cu > Ba > Mn > Ni > Fe$. Floor dust samples from the e-waste storage area, which was an indoor dust sample was highly contaminated. Indoor dust samples from the wire stripping area were strongly contaminated with metals because, in an indoor environment, paint chips can be an additional contamination source in addition to contamination coming from the outdoor environment (Fergusson and Kim 1991; Rasmussen et al. 2001; Rasmussen 2004).

6.4 Conclusions

Dust collected from the largest informal e-waste recycling site in Ghana were analysed for total and gastric bioaccessibilities. Gastric bioaccessibility varied significantly for all metals studied from the floor dust ($p < 0.05$). Site-specific bioaccessibility values were used to refine exposure assessments. Non-carcinogenic risks due to dermal absorption and inhalation were negligible and are generally assumed to be safe for child and adult e-waste workers. Children were more susceptible to carcinogenic and non-carcinogenic risks of Pb through ingestion of contaminated floor dust. Children should be prevented from coming into direct contact with metal contaminated floor dust in Agbogbloshie to reduce their exposure to contaminated dust through inadvertent ingestion of dust.

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CHAPTER 7: Metals in an intensive vegetable production system along Korle Lagoon, Accra, Ghana, downstream of an e-waste recycling area: concentrations, transfer factors, and health risks



Figure 7.1 Vegetables growing in urban gardens along Korle Lagoon, downstream area.

Abstract

Total and bioaccessible concentrations of five metals –Mn, Fe, Cu, Zn and Pb – have been determined in soils and leafy vegetables from two urban gardens near Agbogbloshie, Accra, Ghana. Leafy vegetables had bioaccumulated Zn and other metals from soils. Transfer factors for Cu, Zn and Pb in leafy vegetables from garden 1 were smaller than garden 2, indicating that bioaccumulation was greater for garden 2. The bioaccessibility (%) reported for Mn, Fe, Cu and Zn in leafy vegetables in this study were comparable to those found in the literature.

Keywords: transfer factors, estimated daily intake, bioaccessibility hazard quotient.

7.1 Introduction

Metals occur naturally in soils, however anthropogenic activities such as wastewater irrigation, fertilizer application, and waste disposal can increase metal contamination in the environment and agricultural production systems, and subsequently impact human health (Khan et al. 2008; Shaheen et al. 2016). Excessive amounts of micronutrients including Fe, Co, Cu and Zn (Okoronkwo et al. 2005) can be toxic at larger concentrations, while other elements such as Cr (VI), As, Cd, Hg, and Pb have no known physiological function and are toxic to humans at low doses (Obiri et al. 2016).

Vegetables are important sources of carbohydrates, proteins, minerals and vitamins that are required by the human body (Keatinge et al. 2011; Eliku and Leta 2017). Vegetables grown on contaminated soils can bioaccumulate toxic metals from soils or dust deposited on plant surfaces exposed to polluted air (Wang et al. 2005; Harmanescu et al. 2011). Variability in bioaccumulation of toxic metals in soils depends on soil pH, organic matter, cation exchange capacity, binding to different soil components and species (Okoronkwo et al. 2005; Brady and Weil 1999; Kabata-Pendias and Pendias 1984). Transfer factors can be used to evaluate the capacity of plants to transfer metals from the soils into edible tissues. Greater transfer factors are an indication of strong metal accumulation by vegetables (Pal et al. 2017). The soil-water-food-human pathway, especially through ingestion, can be critical for human intake of metals. Atmospheric deposition and contamination of cultivated land may pose human health risks through contamination of locally grown vegetables (Larsen et al. 1992).

Urban and peri-urban agriculture are important sources of food production and employment (Maxwell 1999). Urban and peri-urban agriculture is practiced in open spaces near water sources to get access to water for irrigation (Amoah 2012). Studies in Ghana have focussed on microbial risks (Amoah et al. 2005; Amoah et al. 2007; Quansah et al. 2018), elemental composition (Baidoo et al. 2014), and risks posed by metals in vegetables (Lente et al. 2012; 2014; Ametepey et al. 2018).

Preliminary sampling of vegetables from some parts of Ghana indicated that concentrations of metals were within the Codex Alimentarius Joint Food and Agriculture/World Health Organisation (FAO/WHO) food standards (FAO/WHO 1995). In contrast, similar studies have revealed food crops with enhanced metal concentrations growing in contaminated urban soils (Nabulo et al. 2006; 2012). Metals released from salvaging useful materials and uncontrolled open burning of electronic waste can contaminate soil and these contaminants can bioaccumulate in vegetables and crops (Luo et al. 2011). Globally, data on dietary exposure risks in the food chain are lacking, compared with exposure risks from soil (Frazzoli et al. 2010). South-east Asian and west African nations are major hubs for informal e-waste recycling (Bisschop 2012; Schmidt 2006). In China, information on food contamination due to impacts of e-waste recycling activities have focussed on rice (*Oryza sativa*) (Fu et al. 2008), Green foxtail grass (*Setaria viridis*), peanuts (*Arachis hypogaea*) (Liu et al. 2013) and vegetables (Han et al. 2017; Luo et al. 2011). For example, contamination of vegetables by Cd and Pb from an e-waste incineration site in South China exceeded the Chinese food safety maximum permissible limits by 4.7 and 2.6 times respectively (Luo et al. 2011). In India, the common species scutch (couch) grass (*Cyanodon dactylon*) contained greater concentrations of metals

in an electronic waste recycling site than in residential areas (Pradhan and Kumar 2014). In Nigeria, few studies examined the impacts of e-waste recycling on vegetables (Olafisoye et al. 2013) and some plants species (Narrowleaf cattail - *Typha angustifolia*, the flowering shrub *Chromolaena odorata* and Desho grass - *Pennisetum pedicellatum*) (Tanee et al. 2018). In Ghana, concentrations of Cr, Ni, Cu, Zn, As, Cd, Sn, Hg and Pb were determined in vegetables (Lettuce - *Lactuca sativa* and Roselle hibiscus - *Hibiscus sabdariffa*) and plants (Guinea grass - *Panicum maximum* and Cogon grass - *Imperata cylindrica*) (Fosu-Mensah et al. 2017). Agricultural sites near Agbogbloshie e-waste recycling area were selected because there is a mix of industrial and agricultural land uses with the agricultural sites located close to abundant emissions from vehicular traffic, e-waste burning sites, and electric power generators (Donkor et al. 2017).

Information on metal contaminants in food crops grown in contaminated soils or near contaminated areas may help prevent human health risks from consumption of local produce that may exceed acceptable metal limits. I hypothesise that vegetables cultivated in urban gardens in a hotspot for e-waste recycling in Agbogbloshie, Accra, Ghana, contains elevated metal concentrations. As plants take up different amounts of contaminant, there will be different health risks caused to people consuming a range of vegetables. This study assesses total and bioaccessible metal contamination in agricultural soils and vegetables near a metal-contaminated informal e-waste recycling site and estimates the daily intake of vegetables as a basis of a human health risk assessment.

7.2 Methods

7.2.1 Study area

Vegetables and corresponding soils used to cultivate the vegetables were collected from two urban gardens in Accra, Ghana (Figure D1). Furthermore, control soil sample was collected in Korle Bu Teaching Hospital Doctor's flat area where there was no influence from any e-waste recycling activity. Sampling points were located to ± 5 m using a Garmin global positioning system receiver using the WGS84 geoid, 30 N projection zone. Garden 1 was a former municipal waste dump on the bank of Korle Lagoon and between 5°33'10.36"N, 0°13'50.60"W and 5°33'12.34"N, 0°13'51.46"W. Garden 2 was about 50 m from Garden 1 and between 5°33'05.02"N, 0°13'43.77"W and 5°33'12.70"N, 0°13'50.16"W. The reference site was in Korle Bu Teaching Hospital Doctor's flat area (5°32'21.88"N, 0°14'05.05"W). The control site was located about 1.3 km from the study area while Agbogbloshie e-waste recycling site was located about 500 m from the study area.

7.2.2 Field procedures

7.2.2.1 Sampling and sample preparation

Leafy vegetables (n=49) and soils (n=32) were collected during the dry season in December 2016 to January 2017 from two gardens located near Agbogbloshie e-waste site. Control soil samples were collected from a third garden at Doctor's flats, Korle Bu in Accra, Ghana in January 2017. Leafy vegetables comprised lettuce (*Lactuca sativa*), African eggplant (*Solanum macrocarpon*), hibiscus (*Hibiscus sabdariffa*), and Egyptian spinach (*Corchorus olitorius*) in garden 1, and lettuce, African eggplant, hibiscus, Egyptian spinach, and Amaranth (*Amaranthus spp.*) in garden 2. Soils were collected using a plastic trowel from the sides and centers of the beds to ensure representative sampling. Leafy vegetable portions were rinsed using deionized water to remove adhering soil and dust particles. Both soils and vegetables were placed into clean ziplock[®] bags and sent immediately to the laboratory. Vegetables were freeze-dried at -17 °C with a vacuum of 6.110 mbar for 48 h.

7.2.3 Laboratory procedures

Soil samples were irradiated with 50 kGy of gamma irradiation to satisfy Australian quarantine and import requirements. After air-drying the soil samples for five days at 40 °C, the gravels were removed by sieving at 2 mm. The < 2 mm soil fraction was then milled using a Retsch MM301 mill with tungsten carbide vials and balls for 10 min at 25 Hz. Vegetables were milled using a Retsch ZM200 mill with tungsten carbide rotor and titanium sieves. The tungsten carbide vials and balls were cleaned using acid-washed quartz (UNILAB Ajax Finechem B/No. 1510204652), and the ZM200 components with ethanol, after each milling, to prevent inter-sample contamination.

7.2.3.1 Acid digestion of leafy vegetable samples

Powdered leafy vegetable samples (0.50 g) were weighed into acid-cleaned Teflon vessels followed by the addition of 6.0 mL concentrated 65 % HNO₃ (Suprapur[®], Merck Millipore, Australia). The solution was digested for 35 min using a microwave digester (Anton-Paar Multi-wave 3000 Microwave digestion system). Procedural blanks were included in the digestion to check for contamination. Once digestion was complete, the digested solutions were quantitatively transferred into 50 mL polyethylene vials and topped up to 20 mL using 18 MΩ.cm (Type I) deionised water (Millipore Synergy, Merck Australia). Digested solutions were stored in a refrigerator at 2 °C until analysis.

7.2.3.2 Analysis of soils and vegetables for metals

Milled soils were analysed for Mn, Fe, Cu, Zn, and Pb using an Olympus Delta Pro X-ray fluorescence spectrometer with 50 kV Ta anode tube, with three measurement conditions of 60 s each in soil calibration mode. Measurement conditions were 50 kV, 4 W, 60 s with aluminum filter; 15 kV, 4 W, 60 s with no filter; and 5 kV, 4 W, 60 s with no filter. The analytical area was a 6 x 4 mm ellipse. Accuracy was constrained using repeated analysis of two United States National Institute of Standards and Technology Standard Reference Materials (NIST 2710a, 2711a), which showed inaccuracies better than 10% for elements more abundant than 0.1 weight (wt) % and better than 20% for trace elements more than double the limit of quantification.

Digested vegetables were analysed with total reflection X-ray fluorescence (TXRF) spectrometry using Ga as an internal standard. 50 µL of 20 mg/L Ga spike was added to 450 µL of sample and mixed on a vortex mixer for 15 s. 10 µL of spiked acidified sample was placed on a siliconised quartz disc and dried on a hot plate at 60 °C for 15 min. Elemental compositions of the evaporites on the discs were measured using a Bruker S2 Picofox total reflection X-ray fluorescence spectrometer with Mo anode tube, and measurement conditions of 30 kV, no filter and a measurement time of 600 s. Limits of quantification depend on the matrix but are typically ~5 µg/L for elements in this study. Inaccuracy, constrained using a Merck XVI multi-element standard, was better than 20% where concentrations exceeded 0.1 mg/L.

7.2.3.3 Soil pH determination

pH (CaCl₂) was determined on extracted soil solution ratio of 1:10 (v/v) using 0.01 M CaCl₂ solution with a calibrated pH meter (Denver Instrument 250 m), after shaking end-over-end for 1 h.

7.2.3.4 Bioaccessibility of metals in soils and vegetables

The gastric phase of the physiologically based extraction test (PBET) was employed for the determination of bioaccessible concentrations through in-vitro techniques. The preferred soil fraction for oral bioaccessibility is the < 250 µm soil fraction, as it is considered the soil fraction that adheres to the fingers of children and are more responsible for human health risks than the larger soil fraction, however using the < 2 mm soil fraction of the garden soils can provide a conservative estimate of human health risks (Attanayake et al. 2014). In vitro extraction was determined using surrogate fluids (Intawongse and Dean 2008). Gastric solution was prepared by adding 1.25 g pepsin (Sigma Aldrich, Australia), 0.5 g sodium citrate (Sigma Aldrich,

Australia), 0.5 g malic acid (Sigma Aldrich, Australia), 420 µL lactic acid (Sigma Aldrich, Australia), 500 µL acetic acid (Sigma Aldrich, Australia) to 1 L 18 MΩ.cm (Type I) deionised water (Millipore Synergy, Merck Australia). pH of the gastric solution was adjusted to 1.5 by adding 12 M trace metal grade HCl (Sigma Aldrich, Australia). Gastric solution (30 mL) was added to 0.3 g of the soil sample in a clean 50 mL HDPE bottle. The sample solution mixture was placed in a shaking water bath at 37 °C and rotated horizontally at 30 rpm for 1 h. Supernatants from the gastric phase were separated using 0.45 µm Sartorius MiniSart cellulose acetate filters, followed by total reflection X-ray fluorescence (TXRF) spectrometry to determine Mn, Fe, Cu, Zn, and Pb concentrations in the supernatants. The oral bioaccessible metal content was calculated from the measured concentrations using equation 7.1;

$$\text{Bioaccessible metal} \left(\frac{\text{mg}_{\text{metal}}}{\text{kg}_{\text{(matrix)}}} \right) = \frac{C \times V}{M} \quad (7.1)$$

Where C= concentration of metal in gastric solution (mg/L), V= volume of solvent (L) and M= mass of matrix (soil or vegetable) (kg).

7.2.4 Data analysis

Data analysis was performed using SPSS v.20.0 (IBM, USA). The Kolmogorov-Smirnov (K-S) method was used to test for data normality and homogeneity of variances was verified using Levene's test. Variance ($p < 0.05$) of total metal concentrations among the three gardens was performed using a one-way Analysis of Variance (ANOVA). Where significant interactions were found, a Tukey's post hoc test was used to examine which group created the difference.

7.2.4.1 Transfer factor (TF)

TF was defined as the ratio of metal concentration in vegetable tissues to the total metal concentrations in soils. TF was calculated using equation 7.2;

$$\text{TF} = \frac{M_v}{M_s} \quad (7.2)$$

where M_v = metal concentration in vegetable (mg/kg dry weight), and M_s = mean metal concentration in the corresponding soil in mg/kg dry weight (Luo et al. 2011; Mohammed and Inuwa 2017).

7.2.4.2 Estimated daily intake (EDI) and total hazard quotient (THQ)

The estimated daily intake (EDI) of metals through vegetable consumption was calculated using equation 7.3;

$$EDI = \frac{C_{\text{metal}} \times C_{\text{factor}} \times D_{\text{food intake}}}{BW} \quad (7.3)$$

where C_{metal} = concentration of metals in vegetables (mg/kg), C_{factor} = 0.085, the conversion factor from fresh weight to dry weight following Rattan et al. (2005), $D_{\text{food intake}}$ = daily amount of vegetables consumed (kg/day) and BW = body weight (kg) of the average adult. Health risk estimations were evaluated using the target hazard quotient (THQ), and compared with the reference doses, considered as the safe limit. The estimated daily intake (EDI) was divided by oral reference doses (RfDo) for each of the metals to calculate the total hazard quotient (THQ) (equation 7.4);

$$THQ = \frac{EDI}{RfDo} \quad (7.4)$$

The oral reference dose is the safe level of exposure over a lifetime for oral intake (USEPA 2000; Luo et al. 2011). If THQ is < 1 , it means there are no health risks due to consumption of metal-containing vegetables, however, if THQ is > 1 , then humans consuming metals in vegetables may suffer health effects. The multi-element hazard index (HI) which is the sum of the hazard quotients of the individual metals was used to calculate the potential risk through more than one metal (equation 7.5);

$$HI = \sum HQ = HQ_{Mn} + HQ_{Fe} + HQ_{Cu} + HQ_{Zn} + HQ_{Pb} \quad (7.5)$$

7.3 Results and Discussion

7.3.1 Elemental data of garden soils and soil pH

An initial assessment of the data showed the probability distribution of the data were highly skewed. The Kolmogorov-Smirnov test, applied to the data distribution showed that the total concentrations of Fe, Cu, Zn and Pb followed a normal distribution ($p < 0.05$), while Mn concentrations did not follow a normal distribution ($p > 0.05$) (Table 7.1). Manganese concentrations were log-transformed to bring the data distribution closer to normality. One-way analysis of variance of the data showed significant differences among soil samples ($P < 0.05$) for Mn, Cu, Zn and Pb (Table 7.2). There were no significant differences in concentrations of Fe ($p = 0.135$) (Table 7.2). A Tukey's post hoc test (level of significance set at 0.05) allowed multiple comparisons of Fe concentrations among different sites. There were no significant differences in soil Fe concentrations between gardens 1 and 2 ($p\text{-value} = 0.377$), garden 1 and the reference site ($p\text{-value} = 0.123$), and garden 2 and the reference site ($p\text{-value} = 0.907$). Mean (geometric and arithmetic) concentrations of Mn in soils of the two gardens were within the Australian Soil quality guideline of 500 mg/kg for the agricultural soil (Table 7.3), while mean

concentration of Cu in soils of garden 1 was within Australian, Canadian and United States of America soil quality guidelines of 100, 150 and 270 mg/kg respectively. Mean concentrations of Zn in soils of garden 1 were greater than the Australian soil quality guideline for agricultural soils of 200 mg/kg but within the Canadian and United States of America soil quality guideline of 500 and 1100 mg/kg respectively for agricultural soil. Mean concentration of Pb in soils of garden 1 was greater than Australian, Canadian and United States of America guideline limits of 300, 200 and 200 mg/kg respectively. pH of soils in the study areas was weakly acidic to weakly alkaline; gardens 1 and 2 ranged from 7.05 to 7.35 and 6.40 to 7.47 respectively, whereas the reference site ranged from 7.07 to 7.48.

Table 7.1 One-sample Kolmogorov-Smirnov test for normality to assess significant differences among metals.

	Mn ^a	Fe	Cu	Zn	Pb
Kolmogorov-Smirnov test (p value)	0.183	0.021	≤0.001	≤0.001	≤0.001

^a- log tranformation

Table 7.2 One-way analysis of variance for metals in soils.

Element		Sum of Squares	df	Mean Square	F	Significance
Mn ^a	Between Groups	1.191	2	0.595	22.33	≤0.001
	Within Groups	0.800	30	0.027		
	Total	1.991	32			
Fe	Between Groups	0.060	2	0.03	2.15	0.135
	Within Groups	0.418	30	0.014		
	Total	0.477	32			
Cu	Between Groups	31750	2	15880	19.35	≤0.001
	Within Groups	24620	30	821		
	Total	56370	32			
Zn	Between Groups	1029000	2	514579	27.32	≤0.001
	Within Groups	565000	30	18835		
	Total	1594000	32			
Pb	Between Groups	3020000	2	1510234	36.95	≤0.001
	Within Groups	1226000	30	40868		
	Total	4246000	32			

7.3.2 Metal bioaccessibility (%) of garden soils

Gastric bioaccessible fractions for soils varied among the metals in the gardens and the reference site. Average bioaccessible fractions for Mn and Fe were greatest for the soils from

the reference site. Smallest bioaccessibilities of Cu and Pb were recorded from soils from the reference site. Soils of garden 1 recorded the greatest bioaccessibility (%) for Pb. Soils of garden 2 recorded the greatest bioaccessibility (%) for Cu and Zn (Figure 7.1). The acidic nature of the gastric solution (pH 1.5) and organic acids in the gastric solution may have facilitated desorption and dissolution of metals, leading to greater bioaccessible fractions of garden soils (Cui et al. 2010).

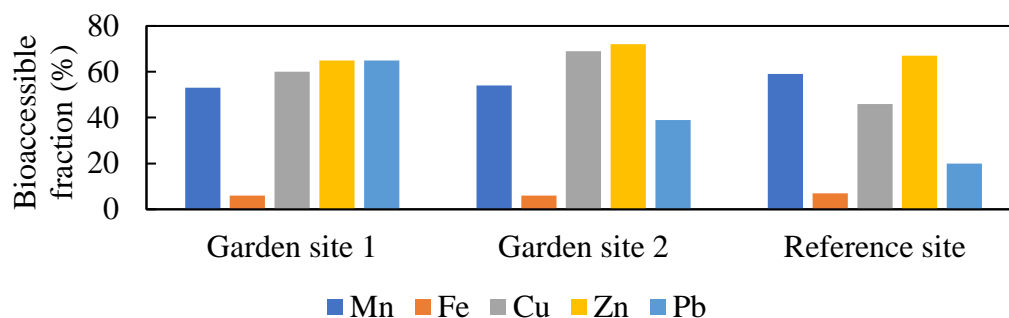


Figure 7.2 Bioaccessibility (%) for garden soil and reference site soils.

Table 7.3 Metal concentrations (mg/kg) of garden soils and their respective guideline values for agricultural soils in Australia, Canada and the United States of America.

Statistics	Garden soils near Agboglobloshie (Garden 1, n=11 soils)					Garden soils near Agboglobloshie (Garden 2, n=8 soils)					Reference garden soils in Korle Bu (n=14)				
	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb
Geometric mean	257	18100	67	444	573	144	15300	16	142	59	433	14500	13	108	30
Arithmetic mean	268	18500	81	498	685	177	15500	16	146	65	447	15400	14	113	32
Minimum	154	11800	20	147	109	90	11900	9	95	36	314	9770	7	75	19
Maximum	449	22400	162	922	1310	586	21000	26	199	150	697	23500	25	173	52
Median	268	19900	78	426	678	123	15700	16	142	52	417	12400	14	103	26
Standard deviation	85	3630	49	233	348	166	2760	5.8	37	38	118	5480	5	33	13
Australia ^{a,b}	500		100	200	300										
Canada ^a			150	500	200										
United States of America ^a			270	1100	200										

^aHe et al. 2015, ^bNEPC 1999.

7.3.3 Metal concentrations in vegetables

Metal accumulation in edible portions of vegetables is of toxicological importance to the health of consumers (Luo et al. 2011). The concentrations of Mn, Fe, and Cu in vegetables from garden 1 did not exceed the FAO/WHO Codex Alimentarius maximum allowable concentrations of metals in food substances (Table 7.4). The concentrations of Zn and Pb exceeded the FAO/WHO Codex Alimentarius maximum allowable concentrations for all vegetables from garden 1. For garden 2, the concentrations of Mn in all vegetables were within the FAO/WHO Codex Alimentarius maximum allowable limits. The concentrations of Cu were within the FAO/WHO Codex Alimentarius maximum allowable limits for African eggplant, hibiscus, Egyptian spinach and amaranth. The concentrations of Fe in hibiscus, Egyptian spinach, lettuce and amaranth were greater than the FAO/WHO Codex Alimentarius maximum allowable concentrations. The concentration of Fe in African eggplant was smaller than the FAO/WHO Codex Alimentarius maximum allowable concentrations. The concentrations of Zn and Pb in all leafy vegetables were greater than the FAO/WHO Codex Alimentarius maximum allowable concentrations for Zn and Pb. Zinc concentrations were 1-3 times greater than FAO maximum allowable limits (Table 7.5). The concentrations of Zn in vegetables from this study were greater than concentrations reported for vegetables in previous studies (Ackah et al. 2014; Lente et al. 2014). Elevated Zn concentrations found in vegetables in this study may be due to impacts from long-term wastewater irrigation (Wang et al. 2005). Mean concentrations of Mn, Fe, Cu, Zn and Pb in leafy vegetables were 38, 888, 22, 84, 4 mg/kg and 30, 780, 31,118 and 4 mg/kg respectively for gardens 1 and 2.

Table 7.4 Average total and bioaccessible metal concentrations (mg/kg) of vegetables in two urban gardens near Agbogbloshie e-waste recycling site.

Leafy vegetables	Garden 1 (n=19)										Garden 2 (n=19)									
	Total concentrations (mg/kg)					Bioaccessible concentrations (mg/kg)					Total concentrations (mg/kg)					Bioaccessible concentrations (mg/kg)				
	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb
African eggplant	16	390	27	76	2	24	44	16	140	<0.5	21	369	40	144	6	18	47	14	79	<0.4
Hibiscus	40	580	23	82	4	43	110	19	107	2	41	1130	16	103	4	11	32	5	32	0.2
Lettuce	52	1820	14	73	7	16	14	7	51	1	27	818	42	109	3	28	54	17	100	1
Egyptian spinach	39	762	24	104	4	26	52	9	72	1	37	943	20	78	3	33	115	14	85	1
Amaranth	a	a	A	a	a	a	a	a	a	a	22	638	39	158	3	16	88	12	63	0.4
Arithmetic mean	38	888	22	84	4	27	55	13	93	1	30	780	31	118	4	21	53	12	72	1
Recommended tolerable levels (WHO/FAO ^c)	500	450	40	60	0.3															

^c Joint FAO/WHO Expert Committee on Food Additives 1993, 1999. ^a Amaranth not sampled in garden 1.

7.3.4. Estimated daily intake (EDI), bioaccessible estimated daily intake (EDI_B), hazard quotient and bioaccessible hazard quotient

Estimated daily intake and hazard quotient of vegetables are shown (Table 7.6). The greatest mean hazard quotients of Mn, Fe, Cu and Pb were reported for lettuce while the greatest mean hazard quotient of Zn was reported for amaranth. Mean hazard quotients varied widely among the elements and vegetables. The greatest mean hazard quotient of Mn, Fe, Cu, Zn and Pb were reported for hibiscus, lettuce, hibiscus, African eggplant and hibiscus respectively. The reference doses used for this study were derived from the Integrated Risk Information System (IRIS) database, USEPA and the World Health Organization (Table 7.5).

Table 7.5 Oral reference doses for metals.

Metals	RfDo ^a (mg/kg dry weight/day)
Mn	1.4×10^{-1}
Fe	7.0×10^{-1}
Cu	4.0×10^{-2}
Zn	3.0×10^{-1}
Pb	3.5×10^{-3}

^a**Provisional tolerable daily intake (PTDI) for Pb is 3.5×10^{-3} mg/kg/day (USDOE (2011), JECFA 1993).**

7.3.5 Transfer factors (TF) of metals from soil to leafy vegetables

Metal concentrations between agricultural soils and vegetables showed variations in their total concentrations, as demonstrated by metal transfer factors (Figures 7.3-7.7). Metal concentrations in vegetables were smaller than soil metal concentrations and varied among the species. Metal uptake from soil was assessed by way of soil-plant transfer factors. Transfer factors differed among the vegetables and elements. Transfer factors were greater for Cu and Zn and smaller for Mn, Fe, and Pb. Copper and Zn exhibited greater transfer factors in the vegetables because of their essentiality and abundance in plants (Orisakwe et al. 2018). Vegetables with greater Cu and Zn transfer factors were lettuce, African eggplant and amaranth. Lettuce, African eggplant and amaranth have bioaccumulated Cu and Zn from the soils compared to other vegetables. The smallest transfer factor for Pb showed that vegetables bioaccumulated small concentrations of Pb from garden soils. Atmospheric deposition could be a potential source of contamination to leafy vegetables for Pb (McBride et al. 2014).

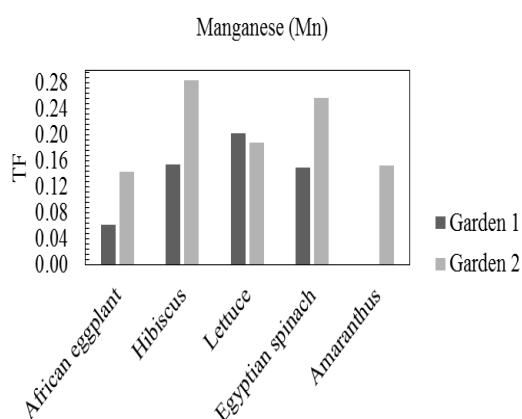


Figure 7.3 Transfer factors of Mn in vegetables.

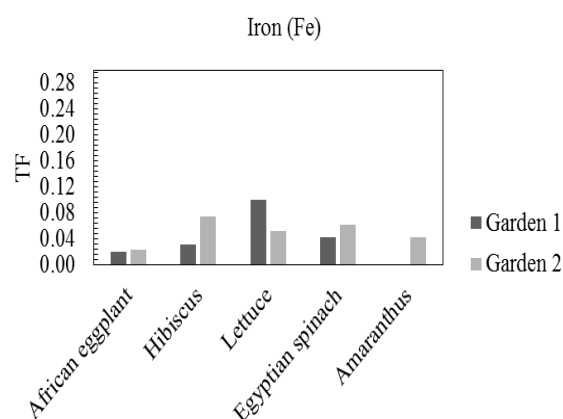


Figure 7.4 Transfer factors of Fe in vegetables.

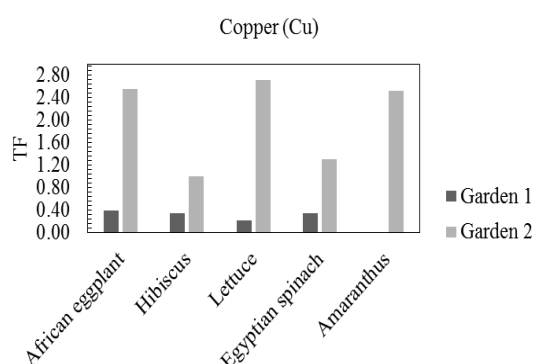


Figure 7.5 Transfer factors of Cu in vegetables.

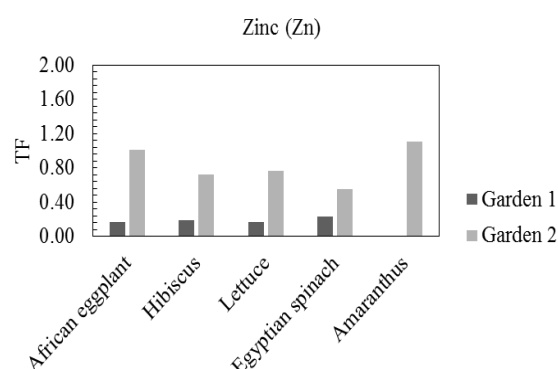


Figure 7.6 Transfer factors of Zn in vegetables.

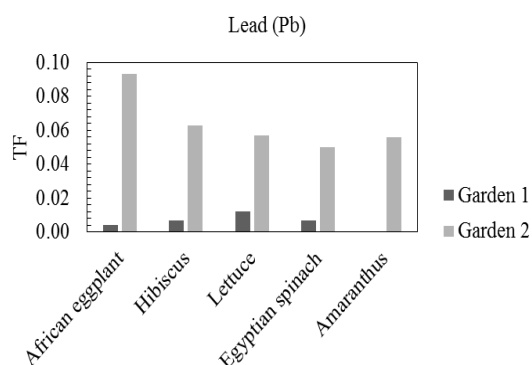


Figure 7.7 Transfer factors of Pb in vegetables.

Table 7.6 Mean values of estimated daily intake (EDI), bioaccessible estimated daily intake (EDI_B), hazard quotient (HQ) and bioaccessible hazard quotient (HQ_B).

Vegetables	Index	Mn	Fe	Cu	Zn	Pb	Index	Mn	Fe	Cu	Zn	Pb
Garden 1												
African eggplant	EDI	3.3×10 ⁻³	8.1×10 ⁻²	5.6×10 ⁻³	1.6×10 ⁻²	4.2×10 ⁻⁴	EDI _B	5.0×10 ⁻³	9.2×10 ⁻³	3.3×10 ⁻³	2.9×10 ⁻²	ND
	HQ	2.4×10 ⁻²	1.2×10 ⁻¹	1.4×10 ⁻¹	5.3×10 ⁻²	1.2×10 ⁻¹	HQ _B	3.6×10 ⁻²	1.3×10 ⁻²	8.3×10 ⁻²	9.7×10 ⁻²	ND
Hibiscus	EDI	8.3×10 ⁻³	1.2×10 ⁻¹	4.8×10 ⁻³	1.7×10 ⁻²	8.3×10 ⁻⁴	EDI _B	9.0×10 ⁻³	2.3×10 ⁻²	4.0×10 ⁻³	2.2×10 ⁻²	4.0×10 ⁻⁴
	HQ	6.0×10 ⁻²	1.7×10 ⁻¹	1.2×10 ⁻¹	5.7×10 ⁻²	2.4×10 ⁻¹	HQ _B	6.4×10 ⁻²	3.3×10 ⁻²	9.9×10 ⁻²	7.4×10 ⁻²	1.2×10 ⁻¹
Egyptian spinach	EDI	8.1×10 ⁻³	1.6×10 ⁻¹	5.0×10 ⁻³	2.2×10 ⁻²	8.3×10 ⁻⁴	EDI _B	5.4×10 ⁻³	1.1×10 ⁻²	1.9×10 ⁻³	1.5×10 ⁻²	2.1×10 ⁻⁴
	HQ	5.8×10 ⁻²	2.3×10 ⁻¹	1.2×10 ⁻¹	7.2×10 ⁻²	2.4×10 ⁻¹	HQ _B	3.9×10 ⁻²	1.5×10 ⁻²	4.7×10 ⁻²	5.0×10 ⁻²	6.0×10 ⁻²
Lettuce	EDI	1.1×10 ⁻²	3.8×10 ⁻¹	2.9×10 ⁻³	1.5×10 ⁻²	1.4×10 ⁻³	EDI _B	3.3×10 ⁻³	2.9×10 ⁻³	1.5×10 ⁻³	1.1×10 ⁻²	2.1×10 ⁻⁴
	HQ	7.7×10 ⁻²	5.4×10 ⁻¹	7.3×10 ⁻²	5.1×10 ⁻²	3.9×10 ⁻¹	HQ _B	2.4×10 ⁻²	4.2×10 ⁻²	3.6×10 ⁻²	3.5×10 ⁻²	6.0×10 ⁻²
Garden 2												
African eggplant	EDI	4.4×10 ⁻³	7.7×10 ⁻²	8.3×10 ⁻³	3.0×10 ⁻²	1.3×10 ⁻³	EDI _B	3.8×10 ⁻³	9.8×10 ⁻³	2.9×10 ⁻³	1.6×10 ⁻²	ND
	HQ	3.1×10 ⁻²	1.1×10 ⁻¹	2.1×10 ⁻¹	1.0×10 ⁻¹	3.6×10 ⁻¹	HQ _B	2.7×10 ⁻²	1.4×10 ⁻²	7.3×10 ⁻²	5.5×10 ⁻²	ND
Hibiscus	EDI	8.5×10 ⁻³	2.4×10 ⁻¹	3.3×10 ⁻³	2.1×10 ⁻²	8.3×10 ⁻⁴	EDI _B	2.3×10 ⁻³	6.7×10 ⁻³	1.0×10 ⁻³	6.7×10 ⁻³	4.2×10 ⁻⁵
	HQ	6.1×10 ⁻²	3.4×10 ⁻¹	8.3×10 ⁻²	7.2×10 ⁻²	2.4×10 ⁻¹	HQ _B	1.6×10 ⁻²	9.5×10 ⁻³	2.6×10 ⁻²	2.2×10 ⁻²	1.2×10 ⁻²
Egyptian spinach	EDI	7.7×10 ⁻³	2.0×10 ⁻¹	4.2×10 ⁻³	1.6×10 ⁻²	6.3×10 ⁻⁴	EDI _B	6.9×10 ⁻³	2.4×10 ⁻²	2.9×10 ⁻³	1.8×10 ⁻²	2.1×10 ⁻⁴
	HQ	5.5×10 ⁻²	2.8×10 ⁻¹	1.0×10 ⁻¹	5.4×10 ⁻²	1.8×10 ⁻¹	HQ _B	4.9×10 ⁻²	3.4×10 ⁻²	7.3×10 ⁻²	5.9×10 ⁻²	6.0×10 ⁻²
Lettuce	EDI	5.6×10 ⁻³	1.7×10 ⁻¹	8.7×10 ⁻³	2.3×10 ⁻²	6.3×10 ⁻⁴	EDI _B	5.8×10 ⁻³	1.1×10 ⁻²	3.5×10 ⁻³	2.1×10 ⁻²	2.1×10 ⁻⁴
	HQ	4.0×10 ⁻²	2.4×10 ⁻¹	2.2×10 ⁻¹	7.6×10 ⁻²	1.8×10 ⁻¹	HQ _B	4.2×10 ⁻²	1.6×10 ⁻²	8.9×10 ⁻²	6.9×10 ⁻²	6.0×10 ⁻²
Amaranth	EDI	4.6×10 ⁻³	1.3×10 ⁻¹	8.1×10 ⁻³	3.3×10 ⁻²	6.3×10 ⁻⁴	EDI _B	3.3×10 ⁻³	1.8×10 ⁻²	2.5×10 ⁻³	1.3×10 ⁻²	8.3×10 ⁻⁵
	HQ	3.3×10 ⁻²	1.9×10 ⁻¹	2.0×10 ⁻¹	1.1×10 ⁻¹	1.8×10 ⁻¹	HQ _B	2.4×10 ⁻²	2.6×10 ⁻²	6.2×10 ⁻²	4.4×10 ⁻²	2.4×10 ⁻²

7.3.6 Total metal concentrations in soils

The extent of soil metal contamination in the two gardens was evaluated by comparing soil metal concentrations with metal background values from a reference site. Metal concentrations in soils from the two gardens near the e-waste sites were greater than metal concentrations in soils from the reference site. Copper concentrations in soils of the two gardens were 1-5 times greater in gardens near the e-waste site than the reference site. Zinc concentrations in garden soils were greater than Zn concentrations in soils from the reference site. Lead concentrations in the soils from gardens located near Agbogbloshe e-waste recycling site was greater than Pb concentrations in soils from the reference area by 1-19-fold. Soils in gardens located near Agbogbloshe were affected by atmospheric deposition from considerable e-waste burning activities and this may have accounted for differences observed among soil metal concentrations in the two gardens and the reference area. Geometric mean concentrations of Fe, Cu, Zn, and Pb in soils were greater than the geometric mean from the control area, except for Mn. Maximum concentrations of Mn and Fe in gardens were smaller than the maximum concentration in the reference garden indicating Mn and Fe in the garden soils reflect background concentrations and may originate from the parent rocks. Maximum concentrations of Cu, Zn and Pb, were greater than the maximum concentrations in the reference garden. Manganese and Fe may have originated from the natural parent materials. The geometric mean of Zn (444 mg/kg) in the soils exceeded Australian NEPC soil quality Zn guideline of 200 mg/kg by 120%. Zinc concentrations in garden areas may be due to the use of wastewater containing Zn effluents for irrigation. The near neutral pH of the soils is important for reducing the ability of some metals such as Pb to be taken up by plants (McBride et al. 2014).

7.3.7 Total and bioaccessible metal concentrations in vegetables

Metal concentrations varied among vegetables. Iron contained the greatest mean concentrations in all vegetables, followed by Zn. Lead had the smallest metal concentrations in vegetables. The ranges and arithmetic mean of the BAF in vegetables from the study areas were; Mn (BAF = 70-71%, mean = 71%), Fe (BAF = 6-7 %, mean = 7%), Cu (BAF = 39-59%, mean = 49%), Zn (BAF = 61-111%, mean = 85 %) and Pb (BAF=8-276%, mean = 25%). The smallest BAF in vegetables was recorded for Fe (BAF = 6-7%, mean = 7%), while the greatest BAF was recorded for Zn (BAF = 61-111%, mean = 85%). The BAF reported for elements in this study, as Mn Fe, Cu and Zn respectively in this study is comparable to published values for Mn, Fe, Cu, Zn (30-77, 4-55, 36-74, 69-94% respectively) (Intawongse and Dean 2008; Khouzam et al. 2011; Hu et al. 2013; Zia et al. 2017).

7.3.8 Estimated daily intake and health risks

The degree of toxicity of metals to humans depends on their daily intake. EDI was calculated for each vegetable type (Table 7.6) by using the concentrations and daily intake of vegetables of 0.137 kg/person/day (Bempah et al. 2011). EDI was calculated for total and bioaccessible metal concentrations in vegetables (Table 7.6) using reference doses, defined as an estimate of daily oral exposure for the human population, which does not cause deleterious effects during a lifetime (Guerra et al. 2012). The hazard quotient for individual metals in the leafy vegetables was ≤ 1 . Metal concentrations in vegetables do not present non-carcinogenic risks to adult residents in the Agbogbloshie e-waste recycling area. However, when all five metals were combined, the hazard index was ≥ 1 for lettuce in garden 1 (HI=1.14). Hazard indices for vegetables from garden 1 were 0.45, 0.65 and 0.72 for African eggplant, hibiscus and Egyptian spinach respectively. Hazard indices for African eggplant, hibiscus, lettuce, Egyptian spinach and Amaranth in garden 2 were 0.81, 0.79, 0.76, 0.67 and 0.71 respectively. Contaminated lettuce presents more risks than the other vegetables. Lettuce bioaccumulates Pb naturally from contaminated soils (Smical et al. 2008). However, it is relieving to know that bioaccumulation of Pb from garden soils was small, from the transfer factors reported for Pb of 0.01 and 0.06 for garden 1 and 2 respectively. Atmospheric particulates containing Pb from open burning of e-waste in Agbogbloshie e-waste recycling site can travel over long distances to agricultural areas. Historical air samples contained elevated concentrations of Pb and other elements in the vicinity of Agbogbloshie e-waste recycling site (Caravanos et al. 2011).

7.4 Conclusions

Bioaccessible and total concentrations of Mn, Fe, Cu, Zn and Pb in African eggplant, hibiscus, Egyptian spinach, lettuce and amaranth were used to estimate non-carcinogenic ingestion risks health risk for vegetables cultivated near the Agbogbloshie e-waste recycling site in Accra, Ghana. Other exposure sources such as ingestion of contaminated soils, dermal contact, and inhalation, were not examined in this study. HI (\sum HQ) of African eggplant, Egyptian spinach, lettuce, amaranth and hibiscus do not present non-carcinogenic ingestion risks. HI of lettuce was greater than 1 in garden 1, meaning there are potential non-carcinogenic risks to population consuming lettuce from that garden. The BAF in this study is comparable to BAF values from other studies. Regular monitoring of metal contamination in leafy vegetables around Agbogbloshie is encouraged to ensure food safety.

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CHAPTER 8: Dissolved elemental concentrations and pollution assessment of Korle Lagoon sediments, downstream of an e-waste processing area in Accra, Ghana

Abstract

Enrichment factors and geoaccumulation indices indicate that Pb and Zn were priority pollutants in sediments of urban Korle Lagoon, in Accra, Ghana. Mean concentrations of the dissolved elements were within World Health Organisation guidelines for drinking water. The concentration of Pb in the sediments exceeded the Canadian Interim Sediment Quality Guideline (ISQG) threshold effect level for Pb and the Netherlands target value for Pb in sediments. Sediments posed low ecological risks, based on potential ecological risk index and modified degree of contamination (mC_d) pollution index values of 27.9 and 1.08 respectively. Lead presented the greatest potential ecological risk factor in sediments with potential ecological risk factor (Er^i) of 22, while Mn presented the smallest potential ecological risk factor in sediments with Er^i of 0.22. Principal component analysis of dissolved elements in surface waters showed that Mn, Zn and Pb had strong loadings in the first principal component, and these elements accounted for 61.4% of the total variance. Manganese, Zn and Pb in the waters were associated with effluent from industrial activities, urban wastewaters and agricultural activities. Principal component analysis of sediment metals showed that Cu, Zn and Pb had strong loadings in the first principal component, and these elements accounted for 47.8% of the variance. Manganese and Fe of the sediment were significantly correlated (r value = 0.458) at the 0.05 level. Similarly, Mn and Fe of the waters were significantly correlated (r value = 0.514) at the 0.05 level.

Keywords: dissolved metals, pollution indices, ecological risks.

8.1 Introduction

Natural processes and anthropogenic impacts can affect urban water quality through dilution or concentration of dissolved elements and suspended particulates (Khatri and Tyagi 2015). Natural processes include precipitation, erosion and weathering of crustal materials, whereas anthropogenic impacts may be from urban, industrial, domestic or agricultural activities (Simeonov et al. 2003). Trace metals can be important pollutants in the environment due to their persistence, toxicity and bioaccumulation (Wong et al. 2006; Diagomanolin et al. 2004). Zinc and lead are associated with smelting and metallurgical processes and discharge of metal-containing wastewaters from industries as well as landfill leachates and deposition of air-borne particulate matter (Bradl 2005). Sediments act as sinks for trace elements and may be potential sources of contaminants in the water column (Förstner and Müller 1974; Okay et al. 2008). Sediment trace metals may be available to benthic fauna or released to the water column

through sediment resuspension, adsorption and desorption reactions and reduction-oxidation reactions (Pekey 2006). Concentrations of metals dissolved in water are relatively small compared to sediment concentrations, and metals in the water can indicate recent inputs into the aqueous phase (Mutia et al. 2012).

Korle Lagoon supported a thriving fishery industry of fin and shellfish in the 1950s (Boadi and Kuitunen 2002). Korle Lagoon receives anthropogenic inputs from domestic, industrial and agricultural activities, and lagoonal sediments were contaminated with copper and cadmium from e-waste recycling (Chama et al. 2014). A recent study reported that dissolved elements - Ni, As, Cd and Hg - in surface waters of Korle Lagoon were within World Health Guidelines for drinking water (Essumang et al. 2012). In China, informal e-waste recycling had metal-contaminated pond water in Longtang (Wu et al. 2015), surface water (Wong et al. 2007a) and river sediments (Wong et al. 2007b) in Guiyu and shallow groundwater in Taizhou (Wu et al. 2014). Metals dissolved in natural waters can be absorbed by aquatic organisms and can bioaccumulate or biomagnify within the aquatic food web (Xia et al. 2018). Monitoring of dissolved contaminants can detect subtle changes in the aquatic environment and help water resource managers understand priority pollutants in aquatic environments and plan for remediation where necessary. Data on dissolved elements in the lagoon basin can assist environmental decision makers and water resource managers to understand pollution trends in surface waters and associated sediments.

Effluents from industrial activities situated along Odaw River can contaminate surface waters through runoff and may lead to elevated dissolved concentrations of metals in waters and sediments. Elevated concentrations in waters and sediments may present ecological risks to sensitive aquatic species. Lead is an important component of cathode ray tube (CRT) funnel glass (Gramatyka et al. 2007; Herat 2008). It will be of interest to assess the dissolved metal concentrations and ecological risks of the Korle Lagoon ecosystem. This study assesses the distribution of five dissolved metals – Mn, Fe, Cu, Zn and Pb in surface water samples from Odaw River and Korle Lagoon. Sediment contamination of Mn, Fe, Cu, Zn and Pb in Korle Lagoon was assessed using pollution indices and sediment quality guidelines.

8.2 Materials and methods

8.2.1 Study area

Odaw River is between Aburi Mountains 5° 52' N, 0°10' W and Korle Lagoon 5° 32' N, 0°15' W (Ansa et al. 2017). Odaw River empties directly into Korle Lagoon, located downstream of

Agbogloboshie. Odaw River consists of six main streams; Ntare, Obommirem, Dakobi, Buade, Onyasias and Odaw (Ansa et al. 2017). Odaw River is used as a source of domestic water supply in upstream and midstream while in downstream areas for commercial activities such as car washing and as irrigation water for vegetable production (Ansa et al. 2017). Mean annual rainfall is 810 mm (Abraham et al. 2006).

8.2.2 Pollution Indices

Pollution indices can provide a relative ranking of contamination levels by comparing the metal content in each sample with a background concentration (Chen et al. 2015; Christophoridis et al. 2009). Generally, pollution indices fall under single element indices (contamination factors, enrichment factor, geoaccumulation index) and multi-element pollution indices (modified degree of contamination (mCd) and pollution index (PI) (Duodu et al. 2016). Multi-element pollution indices improve the limitations encountered in the use of single element indices by offering a comprehensive assessment of the scale or degree of pollution by considering contamination from several metal contaminants in urban or industrial environments (Brady et al. 2015; Duodu et al. 2016). Pollution indices compare metal content in each sample with a background concentration, such as the average continental shale (Turekian and Wedepohl 1961) or the average continental crust abundance (Wedepohl 1995). An alternative approach is to use metal concentrations in deeper sediment samples as background concentrations (Christophoridis et al. 2009).

8.2.2.1. Geoaccumulation

Geoaccumulation index (Igeo) is used to assess contamination by comparing current and pre-industrial concentrations (Müller 1969). Igeo was computed using equation 8.1;

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 \times B_n} \right) \quad (8.1)$$

where C_n = total concentration of element 'n' in the surface layer of the sediment tested and B_n = concentration of element 'n' in the earth crust. A factor of 1.5 is used because of possible variations of the background data due to lithological variations. Geoaccumulation index is categorised into seven classes reflecting different grades of contamination (Müller 1981). Igeo values ≤ 0 show that sediment is uncontaminated. Igeo values 0 to 1 show sediment is uncontaminated to moderately contaminated, Igeo values 1 to 2 show sediment is moderately contaminated, Igeo values 2 to 3 show sediment is moderate to strongly contaminated, Igeo values 3 to 4 show sediment is strongly contaminated, Igeo values 4 to 5 show sediment is

strong to extremely contaminated and Igeo values ≥ 5 show sediment is extremely contaminated (Table 8.1).

Table 8.1 Geoaccumulation index (Igeo) for contamination levels in sediments (from Müller 1981).

Igeo class	Igeo value	Contamination level
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to strongly contaminated
4	$3 < I_{geo} < 4$	Strongly contaminated
5	$4 < I_{geo} < 5$	Strongly to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

8.2.2.2 Enrichment factor

Enrichment factor (EF) compares the ratio of the element of interest to a normalizing or reference element. The normalizing element is a “conservative” element which should be insensitive to inputs from anthropogenic sources. The conservative element should have a minimum variability of occurrence and neither show significant synergistic nor antagonistic effects towards the examined elements (Christophoridis et al. 2009). Enrichment factors were calculated for sediment pollution originating from anthropogenic sources. Iron was selected as the normalization element. EF is calculated using equation 8.2;

$$EF = \frac{\left(\frac{C_i}{C_{ref}}\right)_{\text{sample}}}{\left(\frac{C_i}{C_{ref}}\right)_{\text{background}}} \quad (8.2)$$

where C_i = concentration of the element of interest and C_{ref} = concentration of the normalization element. Generally, seven classes of contamination categories are distinguished (Chen et al. 2007) (Table 8.2). $EF \geq 1.0$ signifies anthropogenic inputs while $EF \leq 1.0$ indicates inputs from natural weathering processes (Taylor 1964). For EF evaluation, the following classification was used (Chen et al. 2007). $EF \leq 1$ indicates no enrichment, EF 1 to 3 indicates minor enrichment, EF 3 to 5 indicates moderate enrichment, EF 5-10 indicates moderately severe enrichment, EF 10 and 25 indicates severe enrichment, EF 25 and 50 indicates very severe enrichment and $EF \geq 50$ indicates extremely severe enrichment (Table 8.2).

Table 8.2 Enrichment factor classification of sediment (Chen et al. 2007).

EF Value	Sediment quality designation
<1	No enrichment
1-3	Minor enrichment
3-5	Moderate enrichment
5-10	Moderately severe enrichment
10-25	Severe enrichment
25-50	Very severe enrichment
>50	Extremely severe enrichment

8.2.2.3 Degree of Contamination Cd

The degree of contamination calculates an overall pollution factor, based on seven metals and one organic contaminant (Hakanson 1980; Christophoridis et al. 2009). The contamination factors for individual elements are calculated using equation 8.3;

$$Cf^i = \frac{M_x}{M_b} \quad (8.3)$$

where M_x = mean concentration of the target metal in at least five sub-samples and M_b = concentration of the metal in the selected reference background. The overall degree of contamination (C_d) is given by equation 8.4;

$$C_d = \sum_{i=1}^n Cf^i \quad (8.4)$$

The overall degree of contamination is the sum of all contamination factors for the respective elements. The modified degree of contamination was developed to account for the lack of feasibility to analyze all components used for this index (Abraham and Parker 2008). The modified degree of contamination is given by equation 8.5;

$$mC_d = \frac{\sum_{i=1}^n Cf^i}{n} \quad (8.5)$$

Thresholds for sediment quality classification for the modified degree of contamination are shown (Table 8.3).

Table 8.3 Modified degree of contamination classification of sediment (Christophoridis et al. 2009).

mC_d	Sediment status
$mC_d < 1.5$	Zero to very low degree of contamination
$1.5 < mC_d < 2$	Low degree of contamination
$2 < mC_d < 4$	Moderate degree of contamination
$4 < mC_d < 8$	High degree of contamination
$8 < mC_d < 16$	Very high degree of contamination
$16 < mC_d < 32$	Extremely high degree of contamination
$mC_d \geq 32$	Ultra-high degree of contamination

8.2.2.4 Potential ecological risk index (RI)

Potential ecological risk index (RI) measures the sensitivity of the biological community to the overall contamination of a site (Hakanson 1980). RI is the sum of the potential ecological risk of an individual element. It is evaluated based on the contamination factor of element i (Cf_i), potential ecological risk factor (Er_i), and the sediment biological toxic response factor (Tr_i). RI is evaluated using equation 8.6 following Hakanson (1980);

$$RI = \sum_{i=1}^n Er^i = \sum_{i=1}^n Tr^i \times Cf^i \quad (8.6)$$

where Tr^i = biological toxic response coefficient of an individual element, and Cf^i = contamination factor for every single element. RI is categorized into four classes (Hakanson 1980) (Table 8.4).

Table 8.4 Risk categories for potential ecological risk (Hakanson 1980).

Risk intensity	Er^i	Risk intensity	RI values
Low ecological risk	$Er^i < 40$	Low ecological risk	$RI < 150$
Moderate ecological risk	$40 \leq Er^i < 80$	Moderate ecological risk	$150 \leq RI < 300$
Considerable ecological risk	$80 \leq Er^i < 160$	Considerable ecological risk	$300 \leq RI < 600$
High ecological risk	$160 \leq Er^i < 320$	Very high ecological risk	$RI \geq 600$
Very high ecological risk	$Er^i \geq 320$		

8.2.2.5 Sediment quality guidelines (SQG)

Sediment quality guidelines are useful indicators of sediment contamination by comparing sediment concentration with the corresponding guideline value. SQG evaluate the extent to which the chemical status of sediment-associated chemicals impacts on aquatic organisms (Maanan et al. 2015). The Canadian interim sediment quality guidelines (ISQG) offer two levels as the basis for comparison of sediment quality. The lower level, referred to as the threshold effect level (TEL), is the concentration below which adverse biological effects are expected to occur rarely (CCME 1995; 2001). The upper level, referred to as the probable effect level (PEL), defines the level above which adverse biological effects are expected to occur frequently (CCME 2001). The Netherlands defines two Guideline levels, which are target values (TV) and intervention values (IV). Sediment concentrations lower than the target values requires no site investigation, while sediment concentrations larger than intervention values indicate remediation of the site is necessary. Sediment concentrations between the target values and intervention values suggest further site investigations (Swartjes 1999, VROM 2000). The Australian and New Zealand SQG offers two levels for each pollutant classification, which are Interim Sediment Quality Guidelines-Low (ISQG-L) and Interim Sediment Quality Guideline-High (ISQG-H) (Duodu et al. 2016). Three designations are defined for each pollutant concentration range. Concentrations smaller than ISQG-L values relates to the state whereby adverse biological effects rarely occur and/or are observed. Concentrations at or greater than ISQG-H relates to the state whereby adverse biological effects occurs frequently while concentrations between ISGH-L and ISGH-H relates to the state whereby biological effects occur occasionally (ANZECC/ARMCANZ 2000).

8.2.3 Sampling

Surface water samples ($n = 96$) including two control samples were collected along Odaw River and Korle Lagoon and its tributaries in the upstream, midstream, downstream and estuarine areas (Figure 8.1) in December 2016- January 2017. The two control samples (i.e., samples 1 and 2) (Figure 8.1) were also collected from a stream flowing in an undisturbed area near Comet Estates. Sampling points were located to ± 5 m using a Garmin global positioning system receiver using the WGS84 geoid, 30 N projection zone. Sediment samples ($n = 21$) were sampled from the upper reaches of Korle Lagoon near Agbogbloshie e-waste recycling area and placed in ziplock[®] bags. During the collection of surface water samples, there was ongoing dredging of the Korle Lagoon, so sediments were sampled alongside the water. The surface water samples were collected at a depth of ~ 10 cm using previously cleaned and acid-washed 500 mL high-density polyethylene (HDPE) containers. Water samples were filtered in situ

using 0.45 μm Sartorius MiniSart cellulose acetate syringe filters and acidified with 2 mL/L (vol/vol) ultrapure trace metal grade concentrated HNO_3 .

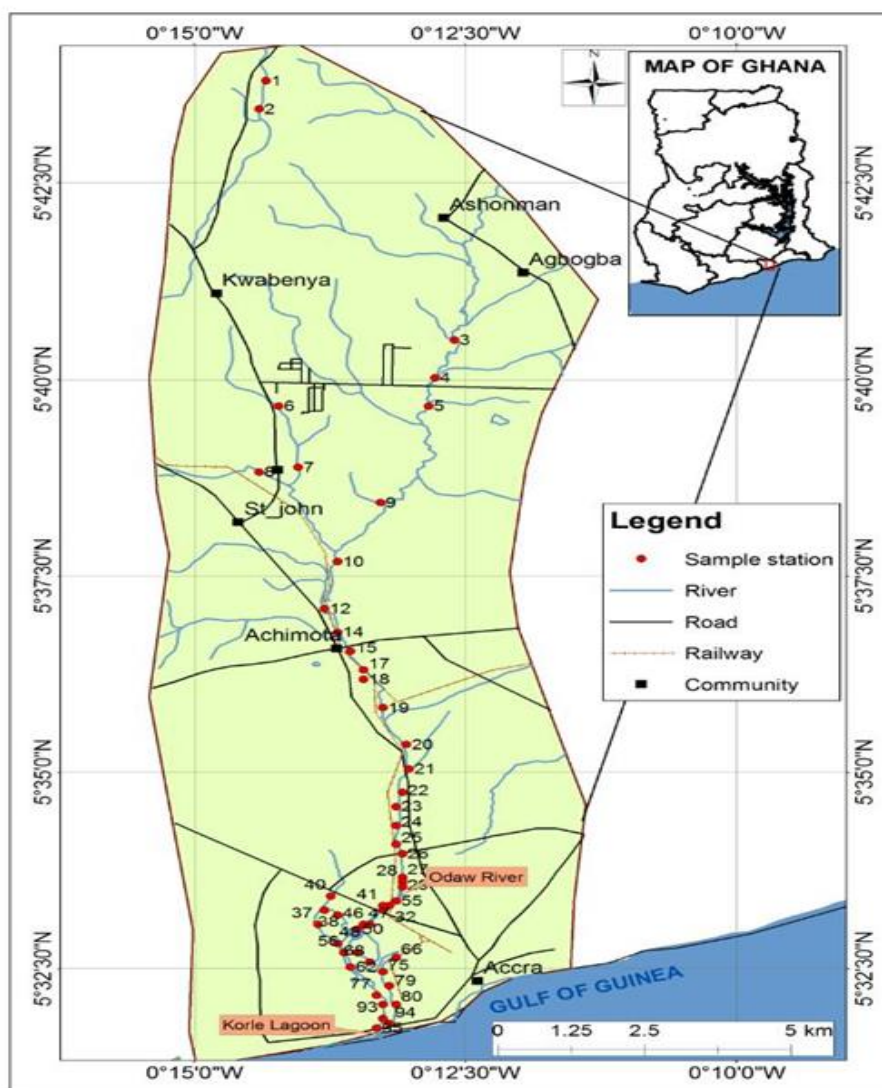


Figure 8.1 Location of sampling sites in Odaw River and Korle Lagoon.

8.2.4 Laboratory procedures

pH of water samples was measured using a calibrated Mettler Toledo Seven-Multi pH meter. The elemental composition of the water was then measured using total reflection X-ray fluorescence (TXRF) spectrometry. Sample preparation commenced with 450 μL of water sample pipetted into clean 5 mL plastic vials. 50 μL of 2 mg/L Ga spike was then added for internal quantification. The resultant mixture was homogenised thoroughly for 15 s on a vortex mixer and an aliquot of 10 μL transferred onto a pre-cleaned, acid-washed, siliconised and labeled polished quartz discs. A reagent blank was analysed to quantify and correct for signals arising from sources rather than the sample. Quartz discs containing blanks and samples were dried on a hotplate for 15 min before TXRF analysis. Elemental compositions of the evaporites

on the discs were measured using a Bruker S2 Picofox TXRF with Mo anode tube, and measurement conditions of 30 kV, no filter and a measurement time of 600 s. Limits of quantification depend on the matrix but are typically ~2-5+ µg/L for elements in this study. Inaccuracy, constrained using a Merck XVI multi-element standard, was better than 20% where concentrations exceeded 0.1 mg/L.

Sediments were oven-dried at 40 °C for 48 h. Dried sediments were then sieved to < 2 mm fraction using a stainless-steel sieve with nylon and powdered at 25 Hz for 10 min, using a Retsch MM-301 mixer mill with tungsten carbide vials and balls. The tungsten carbide vials and balls were cleaned by milling acid-washed quartz (UNILAB Ajax Finechem B/No. 1510204652) for 2 min, after each successive sample milling to prevent inter-sample cross-contamination. Approximately 10 g of < 2 mm powdered sediment was placed in a plastic cup and sealed using a 3.6 µm thickness mylar X-ray film. The sample was placed in a test stand and analysed for concentrations of Mn, Fe, Cu, Zn and Pb using an Olympus Delta Pro X-ray fluorescence spectrometer with 50 kV Ta anode tube, with three measurement conditions of 60 s each in soil calibration mode. Measurement conditions were 50 kV, 4 W, 60 s with aluminum filter; 15 kV, 4 W, 60 s with no filter; and 5 kV, 4 W, 60 s with no filter. The analytical area was a 6 x 4 mm ellipse, and measurements were made in air. Repeated measurement of an acid-washed quartz blank (SiO₂) showed the reported analytes (Mn, Fe, Cu, Zn and Pb) to be below detection limits for all measurements. Accuracy was constrained using repeated analysis of two United States National Institute of Standards and Technology Certified Reference Materials (NIST 2710a, 2711a), which showed inaccuracies better than 10% for elements more abundant than 0.1 wt% and better than 20% for trace elements more than double the limit of quantification.

8.2.5 Data analysis and treatment

Data analysis was conducted using SPSS version 25 and OriginPro version 9.0 software. A one-sample Kolmogorov-Smirnov (K-S) test was used to assess the distribution of the dataset. Kaiser-Meyer-Olkin (KMO) and Bartlett's tests were conducted on the dataset to determine suitability for PCA. High KMO values (close to 1), indicates that a PCA/Factor analysis (FA) may be useful (Pejman et al. 2015). In Bartlett's test, small values (< 0.05) indicate significant relationships among variables and that PCA/FA may be useful (Pejman et al. 2015). KMO value and significance value Bartlett's test was 0.647 and 0.00. Principal component analysis (PCA) was then performed on elemental data based on correlation matrix using Varimax rotation which ensured that variables with the greatest contribution were retained, while reducing those

variables with lesser contributions (Helena et al. 2000) respectively. Hierarchical cluster analysis (HCA) grouped variables based on their similarities using Ward's method and squared Euclidean distances as a measure of similarity (Pejman et al. 2015).

8.3 Results and Discussion

8.3.1 Summary of surface water and sediment data

pH and compositional data were compared with the WHO guidelines for drinking water. The average pH of surface waters ranged from 6.18 to 7.98. pH in water suitable for domestic use ranges from 6.5 to 8.5 (APHA 1989). Zinc and Pb concentrations among surface water samples varied widely, and this reflected in high standard deviations reported for these two elements (Table 8.5). Mean concentrations of Mn, Cu, Zn and Pb were within the respective WHO guidelines for drinking water and Ghana Standard Board (GSB) limits for drinking water (Table 8.5). The maximum concentrations of Mn, Fe, and Pb were eight, one, seven and four times greater than WHO guidelines for drinking water and GSB limits for drinking water respectively (Table 8.5). 48% of lagoon water samples exceeded the 300 µg/L WHO guideline value for Fe in drinking water. Mean concentrations of Zn and Pb in sediments were greater than the CCME ISQG threshold effect levels (TEL) (Table 8.6). Mean concentrations of Cu, Zn and Pb in sediments were smaller than CCME interim sediment quality guidelines predicted effect level (PEL) concentrations and the intervention values for metals in the Netherlands SQG (Table 8.6).

Table 8.5 Descriptive statistics of pH and dissolved metals in surface water.

Variable	Mean \pm 1 standard deviation	Minimum	Maximum	Drinking water guidelines
pH	7.24 \pm 0.50	6.18	7.98	8.5 ^a
Mn (µg/L)	230 \pm 112	<4	476	400 ^b
Fe (µg/L)	400 \pm 300	20	2000	300 ^b
Cu (µg/L)	10 \pm 8	<2	100	2000 ^a
Zn (µg/L)	40 \pm 125	<2	1000	5000 ^a
Pb (µg/L)	6 \pm 9	<2	40	10 ^a

^a WHO 2011, ^b GSB 2009.

Mean elemental concentrations of Mn, Fe and Cu were smaller than the elemental concentrations in average continental shale while mean elemental concentrations of Zn and Pb were greater than the elemental concentrations in the average continental shale (Table 8.6). Maximum Pb concentration of 197 µg/L in the sediment was greater than the Canadian ISQG PEL value but smaller than the Netherlands intervention value (IV) (Table 8.6). The mean

concentration of Pb in the sediment was smaller than the Canadian ISQG PEL guideline value, which is consistent with the Chama et al. (2014) study on Odaw River sediments.

Table 8.6 Descriptive statistics of elemental concentrations (mg/kg) in sediments.

Elements	Mean \pm 1 standard deviation	Minimum	Maximum	Average shale ^a	CCME		Netherlands		ANZECC	
					ISQG		SQG		ISQG	
					TEL	PEL	TV	IV	LOW	HIGH
Mn	190 \pm 19	161	236	850						
Fe	23000 \pm 2830	14700	28600	47200						
Cu	31 \pm 8	<11	56	45	35.7	197	36	190	65 ^b	270 ^c
Zn	221 \pm 30	119	249	95	123	315	140	720	200 ^c	410 ^c
Pb	86 \pm 36	34	197	20	35	91.3	85	530	50 ^c	220 ^c

^a Turekian and Wedepohl (1961), ^b Chapman et al. 1999, ^cLong et al. 1995. TEL-Threshold effect level. PEL-Predicted effect level. TV- Target value. IV-Intervention value.

8.3.2 Comparison of dissolved metals with that of control area

Ranges of dissolved metals in surface waters were compared to those in the control area. Comparison of the ranges of dissolved metals in Odaw River-Korle Lagoon and the control area can provide information on whether or not dissolved metals were of natural or anthropogenic origin. The concentrations of Mn in surface waters ranged from < 4 to 476 $\mu\text{g/L}$ while Mn concentrations in the waters from two control sites ranged from 4 to 10 $\mu\text{g/L}$. Concentrations of Fe ranged from 20 to 2000 $\mu\text{g/L}$ while the concentrations of Fe in the control area ranged from 79 to 194 $\mu\text{g/L}$. Copper is used widely in microelectronics and plumbing. Copper concentrations in natural water ranges from 0.5 to 1000 $\mu\text{g/L}$ (Bergqvist and Sundbom 1980). Copper concentrations in surface waters ranged from < 2 $\mu\text{g/L}$ to 100 $\mu\text{g/L}$ while Cu concentrations in the control waters ranged from < 1 to 2 $\mu\text{g/L}$. Zinc and its compounds are naturally present in most rocks, certain minerals and some carbonate sediments (Roney et al. 2005). Zinc is used widely in galvanizing and as a component of alloys including brass and bronze (Hem 1992). In e-waste, Zn sulfides are used as phosphors in fluorescent lamps and cathode ray tubes (Roney et al. 2005). Urban runoff, municipal and industrial effluents are important sources of Zn (Hem 1992).

The concentration of Zn in natural water is < 10 $\mu\text{g/L}$ (Elinder 1986). Zinc concentrations in this study ranged from < 2 $\mu\text{g/L}$ to 1000 $\mu\text{g/L}$ while Zn concentrations in the control waters ranged from 9 to 12 $\mu\text{g/L}$. Lead compounds such as lead carbonates and lead phosphates have low solubilities (Hem 1992). Adsorption of Pb onto organic and inorganic sediment surfaces as well as co-precipitation with iron and manganese oxides is a contributing factor to small Pb

levels in natural waters (Hem 1992). Lead concentrations in this study ranged from $< 2 \mu\text{g/L}$ to $40 \mu\text{g/L}$ while Pb concentrations in the control waters were below detectable limits of $1 \mu\text{g/L}$.

8.3.3 Correlation analysis

Correlation between elemental concentrations and pH in surface waters and among sediment elements were determined using Spearman-rho correlation method (Tables 8.7, 8.8). In the waters, correlations were very low compared with those in sediments. There were no significant correlations between pH and other elements including Mn, Fe, Cu, Zn and Pb (Table 8.7). pH has a narrow range in the study area as evidenced by the small standard deviation of the pH values. However, there was strong correlation between Mn and Fe ($r = 0.514$), signifying Mn and Fe may have originated from the weathering of parent materials (Kumar and Singh 2018). Significant correlation between Fe and Cu ($r = 0.298$) may suggest these element pair may have originated from similar sources. Correlation determined among metal concentrations in sediments indicate significant relationships ($p < 0.05$) between Mn and Fe ($r = 0.458$), Fe and Zn ($r = 0.540$) and Cu and Zn ($r = 0.547$). Strong correlations of Fe with other metals may be due to ability of Fe to scavenge other metals (Chao and Theobald 1976).

Table 8.7 Correlation matrix of five elements and pH of surface waters of Korle Lagoon.

Waters	pH	Mn	Fe	Cu	Zn	Pb
pH	1					
Mn	0.262	1				
Fe	-0.452	0.514^a	1			
Cu	-0.356	0.075	0.298^b	1		
Zn	0.024	-0.063	0.110	0.205	1	
Pb	0.039	0.257	0.212	0.149	0.249	1

Table 8.8 Correlation matrix of five elements in sediments of Korle Lagoon.

Sediments	Mn	Fe	Cu	Zn	Pb
Mn	1				
Fe	0.458^b	1			
Cu	-0.066	0.035	1		
Zn	0.266	0.540^b	0.547^b	1	
Pb	0.126	-0.015	0.049	0.123	1

^a Correlation is significant at the 0.01 level, ^bCorrelation is significant at the 0.05 level, Significant correlations are marked in bold.

8.3.4 Enrichment factor, Geoaccumulation index and potential ecological risks of sediments

Sediment elemental data were evaluated using pollution indices calculated using metal concentration in average shale following Turekian and Wedehpol (1961) (Christophoridis et al. 2009; Abraham and Parker 2008; Loska et al. 1997). Mean EF values for Cu, Zn and Pb were ≥ 1 (Table 8.9), indicating anthropogenic inputs by these elements. Mean EF value for Zn was 3 to 5 (Table 8.9), showing moderate enrichment. Mean EF value for Pb was 5 to 10 (Table 8.9), showing moderately severe enrichment. The degree of enrichment for elements was in the order $\text{Pb} > \text{Zn} > \text{Cu} > \text{Mn}$.

Table 8.9 Mean and ranges (minimum and maximum) of EF values for sediments.

EF	Mn	Cu	Zn	Pb
Minimum	0.40	0.85	3.04	3.96
Maximum	0.77	4.00	8.15	26.2
Mean	0.47	1.37	4.81	8.95

Minimum, maximum and mean Igeo values range from -2.99 to +2.72 (Table 8.10). Mean Igeo values for Fe, Mn and Cu (Table 8.10) were ≤ 0 showing sediments were uncontaminated with those elements. The mean Igeo value for Pb was ≤ 2 (Table 8.10), showing sediments were moderately contaminated with Pb. The decreasing order of geoaccumulation indices for elements was $\text{Pb} > \text{Zn} > \text{Cu} > \text{Fe} > \text{Mn}$.

Table 8.10 Mean and ranges (minimum and maximum) of Igeo values.

Igeo	Mn	Fe	Cu	Zn	Pb
Minimum	-2.99	-2.27	-1.91	-0.26	0.19
Maximum	-2.43	-1.31	-0.27	0.81	2.72
Mean	-2.76	-1.66	-1.16	0.58	1.36

Modified degree of contamination and potential ecological risks were calculated based on concentrations of Mn, Cu, Zn and Pb using background concentrations from the average shale (Turekian and Wedepohl 1961) (Table 8.11). The mC_d of sediments was ≤ 1.5 , indicating zero to very low contamination. The contribution to the overall degree of contamination was $\text{Pb} > \text{Cu} > \text{Zn} > \text{Fe} > \text{Mn}$. The RI value was < 150 , indicating low ecological risk.

Table 8.11 Potential ecological risks of sediments.

Potential ecological risk of each metal (Er^i)					
Mn	Cu	Zn	Pb	Ecological risk (RI)	Modified degree of contamination (mC_d)
0.22	3.31	2.36	22.0	27.9	1.08

The modified degree of contamination and risk index show that Korle Lagoon exhibits low ecological risks. Low ecological risks in sediments sampled during the study period may have resulted from the removal of contaminated surficial sediments at the time of sampling from dredging activities carried out to prevent the lagoon from flooding its banks. Dredging of sediments removed more contaminated surficial sediments but can allow desorption of metals from the solid to aqueous phase increasing metal bioavailability (Amezcuca-Allieri and Salazar-Coria 2008).

8.3.5 Source apportionment using principal component analysis

Principal component analysis (PCA) was applied to dissolved elements and sediment elemental data to identify sources of these elements by applying Varimax rotation with Kaiser Normalization. From the Eigen values in the correlation matrix, the number of significant levels and percentage variance explained by each component calculated. PCA of dissolved metal concentrations of surface waters revealed that two principal components with Eigen values > 1 explained 85.6% of the total variance (Tables 8.12). PCA 1 accounted for 61.4% of the total variance and was correlated (loading > 0.6) with Mn, Zn and Pb. PCA 2 accounted for 24.2 % of the total variance and was correlated (loading > 0.6) with Fe and Cu. The scores for the first two principal components are shown (Table 8.14). Greater scores occur for surface water samples with relatively greater concentrations of Mn, Zn and Pb. In aqueous systems, Mn, Zn and Pb are associated with intense anthropogenic activities from urban, industrial and agricultural effluents (Kumar and Singh 2018). Greater scores occur for samples with relatively greater concentrations of Fe and Cu in the second principal component (Table 8.14). Iron was abundant in majority of the sampling stations, with many of the surface water samples exceeding World Health Guidelines limit of Fe in drinking water of 0.3 mg/L in 44 sampling stations (Table A8, Appendix A). The underlying lithology of the study area, characterised by easily erodible lateritic soils are important sources of Fe in the basin. Effluents from domestic, commercial and industrial processes were anthropogenic sources contributing to Fe in surface waters, especially in the downstream areas where there is a large concentrations of metal processing industries including an informal electronic waste recycling site. The initial Eigen values, extraction sums of squared loadings, rotation sums of squared loadings, component matrix and communalities are shown (Tables 8.12, 8.14). The component plot, with element loadings are shown (Figure 8.2).

Table 8.12 Total variances explained for variables in surface waters.

Component	Initial Eigen values			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	3.07	61.4	61.4	3.07	61.4	61.4	2.36	47.2	47.2
2	1.21	24.2	85.6	1.21	24.2	85.6	1.92	38.4	85.6
3	0.51	10.3	95.9						
4	0.17	3.48	99.4						
5	0.03	0.64	100						

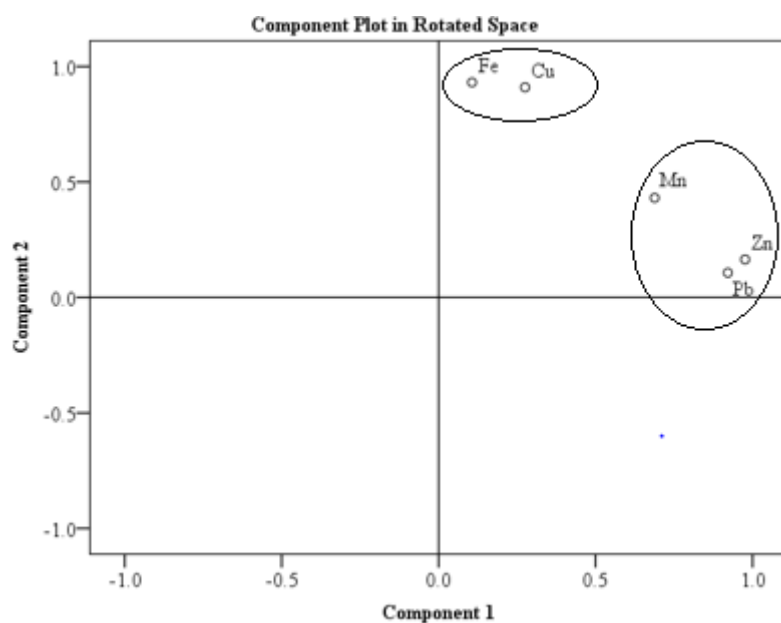
Extraction method: Principal components. Rotation method: Varimax rotation with Kaiser Normalization a. Rotation converged in 3 iterations. Bold values represent strong loadings (>0.6).

Table 8.13 Total variance explained for variables in sediments.

Component	Initial Eigen values			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	2.39	47.8	47.8	2.39	47.8	47.8	2.35	47.0	47.0
2	1.36	27.1	74.9	1.36	27.1	74.9	1.40	27.9	74.9
3	0.78	15.5	90.4						
4	0.43	8.59	99.0						
5	0.05	0.99	100						

Table 8.14 Rotated component matrices for variables in surface waters.

Element	1	2	Communality
Mn	0.688	0.431	0.659
Fe	0.106	0.931	0.878
Cu	0.275	0.910	0.903
Zn	0.976	0.165	0.980
Pb	0.921	0.107	0.860

**Figure 8.2 Factor loadings for components 1 and 2 of metal concentrations in surface water.**

Hierarchical cluster analysis (Ward's method) was applied to calculate cluster distances using the squared Euclidean distance as a similarity measure. The cluster distances show the degree of association between the elements. Hierarchical cluster analysis (HCA) was performed on the surface water compositional dataset and the output presented in a dendrogram (Figure 8.3). Equal weight was given to each variable and the calculated Euclidean distances were affected by variables with greater magnitude.

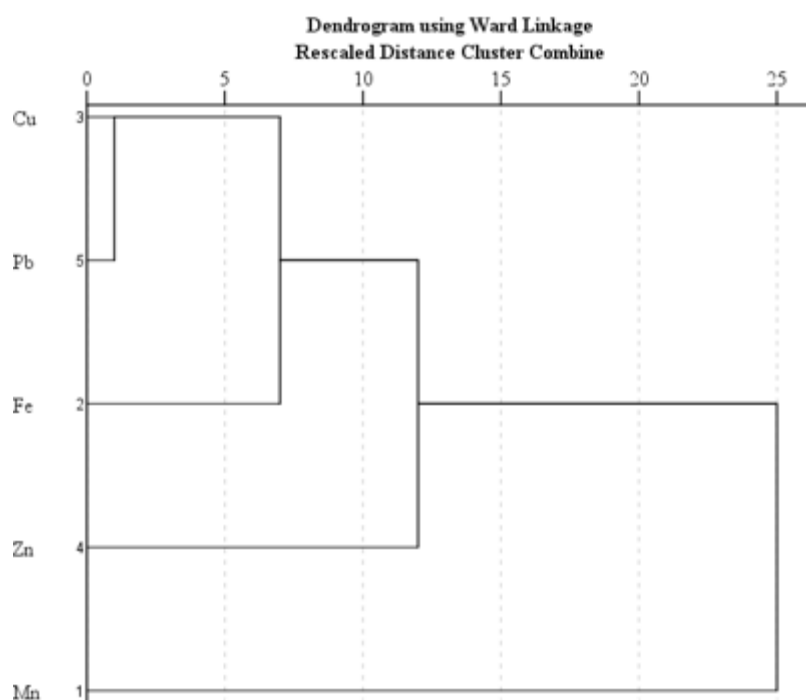


Figure 8.3 Dendrogram using Ward linkage (surface waters).

The dendrogram (Figure 8.3) shows five metals are grouped into two main clusters. The first cluster consisted of Cu, Pb, Fe and Zn. The second cluster consisted of Mn. Manganese originated from the weathering parent materials and subsequent pedogenesis while Cu, Pb, Fe and Zn were primarily from urban and industrial effluents from activities such as metal discharges, manufacturing processes and waste incineration (Li and Zhang 2010). Iron showed strong linear correlations with Cu, Zn and Pb, which were primarily from anthropogenic activities, therefore Fe could have originated from a mixed source of lithogenic and anthropogenic sources in the lagoon. Element loadings on the component plot is shown (Table 8.4). PCA performed on the elemental data of sediments showed two principal components were extracted with Eigen values >1 , accounting for 74.9% of the total variance (Table 8.14). PCA 1 accounted for 47.8% of the variance and had strong loadings (> 0.6) of Cu, Zn and Pb. PCA 2 accounted for 27.1% of the variance and contained strong loadings (> 0.6) of Mn and Fe (Table 8.15). Manganese and Fe were significantly correlated. Iron was significantly correlated with Zn. HCA of sediment elemental data, showing two main clusters (Figure 8.5). The first cluster was characterised by greater contributions from Cu, followed by Mn, Zn and Pb while the second cluster was characterised by Fe whose origin is related to natural processes (Yin et al. 2011).

Table 8.15 Rotated component matrices for variables in sediments.

Element	1	2	Communality
Mn	0.037	0.744	0.555
Fe	0.010	0.860	0.740
Cu	0.936	0.014	0.877
Zn	0.916	0.289	0.922
Pb	0.795	-0.140	0.652

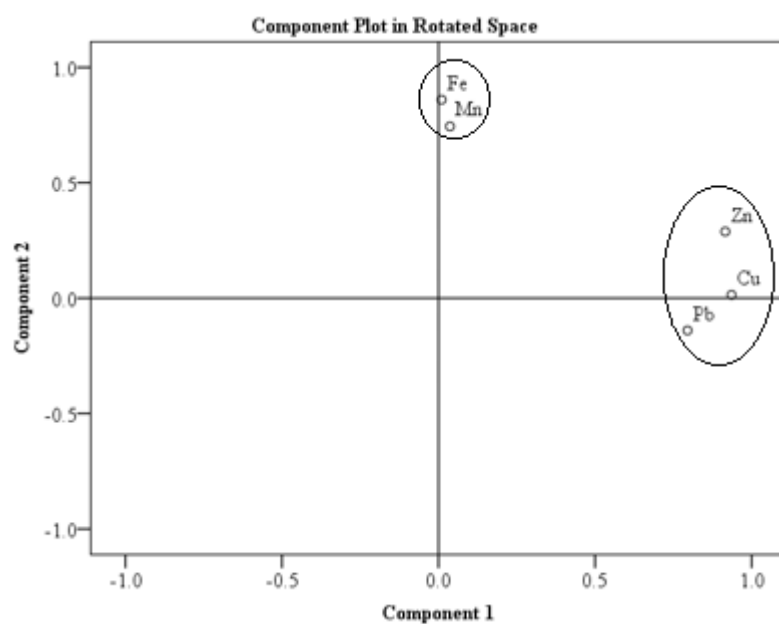


Figure 8.4 Factor loadings for components 1 and 2 of elemental concentrations in sediment.

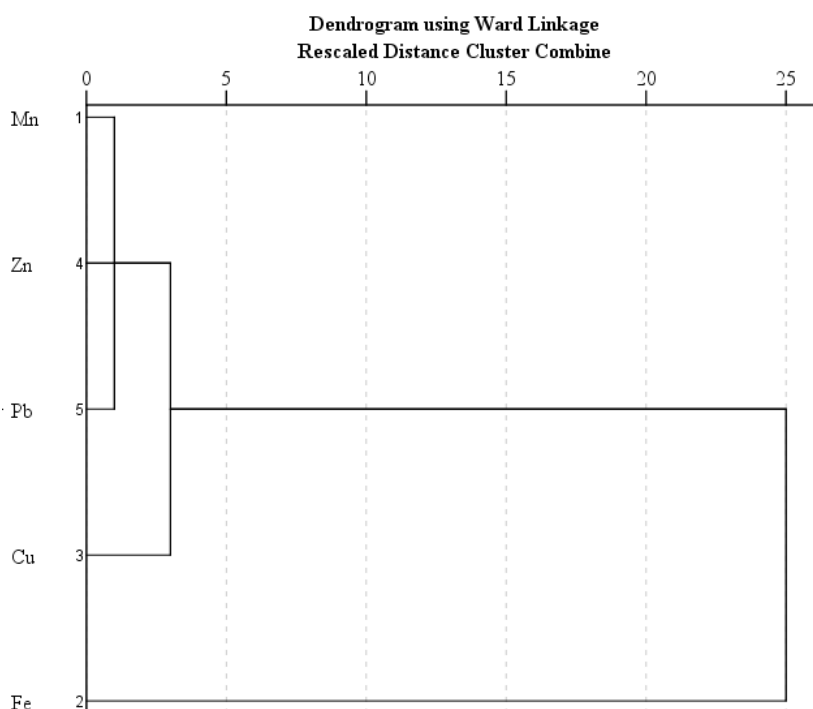


Figure 8.5 Dendrogram using Ward linkage (sediments).

8.3.6 Pollution sources in Odaw River/Korle Lagoon

Untreated industrial wastewaters from metal industries discharge into Odaw River and Korle Lagoon (Boadi and Kuitunen 2002). Dissolved elements in Odaw River-Korle Lagoon basin originated from diffuse sources. Land use in the upstream areas of the lagoon are mainly residential and there are fewer agricultural activities especially vegetable production. Usage of agrochemicals including fertilizers and pesticides are the pollutants in parts of the upstream areas. Metal concentrations in the upstream areas only exceeded metal concentrations of the control areas. Land-use in the midstream areas include a heavy industrial area and high-density commercial activities such as food markets, transport terminals, car washing and a network of roads. Traffic build-up is very high in these areas. Road-deposited dust containing metals, discharge of wastewaters from industrial areas, the use of detergents especially from car washing activities are some of the diffuse pollution sources in midstream areas of the lagoon. Dissolved metals in the downstream areas reflect inputs of untreated effluents from industries including an electronic waste recycling industry, a fresh food distribution market, commercial activities, agricultural activities and vehicle garages. Discharge of Cu may have originated from anti-fouling paints containing Cu used to paint fishing boats (Duodu et al. 2016). Health concerns are associated with usage of lagoon waters for irrigation of food crops and as drinking water by livestock including sheep and cattle.

8.3.7 Comparison of metal distribution with other studies

Dissolved metals in the Odaw River-Korle Lagoon basin are from natural and anthropogenic origin. Generally, dissolved metal concentrations in surface waters were small, compared with sediments. Some elements such as Fe and Mn were naturally present in parent rocks and reflect natural concentrations in water. Lead in the sediments originated mainly from industrial wastewaters discharged into the lagoon waters. Dissolved metals in Korle Lagoon were greater than dissolved elements in some rivers surrounding an informal e-waste recycling site in China (Wong et al. 2007a). Lead is toxic to aquatic organisms, which can suffer adverse effects due to exposure to Pb at 1 to 5 µg/L, exhibiting reduced survival, impaired reproduction, reduced growth and high bioconcentration (Eisler 1988). Odaw River receives effluents from industries, small business, road runoff, treated and untreated urban waste (Thorne et al. 2000). Pollutants discharged in midstream and downstream areas can affect aquatic life. Metal discharge from effluent and activities of informal e-waste recycling can contaminate the lagoon (Obiri et al. 2016). Surface waters showed small concentrations of dissolved metals, compared with Kpeshie Lagoon (Fianko et al. 2013). Sediment metal concentrations in this study presented low ecological risks and did not agree with previous findings on the pollution status in Odaw River (Chama et al. 2014). Pollution of sediments of Korle Lagoon has implications for aquatic fauna since sediments can act as a sink, releasing metals into the water column during sediment resuspension. It is possible that dredging may have removed the more contaminated surface sediments of Korle Lagoon. Dredging, though useful in improving the drainage channel can create further problems should the dredge spoil be dumped near the lagoon causing oxidation, leaching and remobilization of metals back into the lagoon affecting aquatic life. The low ecological risk index of sediments found in this study agrees with the sediment pollution status of the Yellow River in China (Guan et al. 2016).

Table 8.16 Comparison of dissolved metals concentrations in this study to other studies.

Study	Maximum concentrations (µg/L)					Reference
	Mn	Fe	Cu	Zn	Pb	
Korle Lagoon, Ghana	476	2000	100	100	40	This study
Kpeshie Lagoon, Ghana	1280	13200	-	-	11600	Fianko et al. 2013
Terminos Lagoon, Mexico	-	1200	77	97	-	Vazquez et al. 1999
MarChiquita Lagoon, Argentina	-	227	1000	1000	850	Beltrame et al. 2009
Lianjing River, China	246	106	10	34	2	Wong et al. 2007a
Nanyang River, China	217	358	67	117	2	Wong et al. 2007a
River Korotoa, Bangladesh	-	-	119	-	64	Islam et al. 2015

8.3.8 Management implications

Pollution mitigation should focus on the most important contaminants which present the greatest ecological risks to aquatic life and humans. In this study, the most important metal in sediments of Korle Lagoon was Pb. Industrial run-off from the largest e-waste recycling site is a contributor to Pb found in the sediments of Korle Lagoon. Lead is a constituent of Sn-Pb solders in printed circuit boards and other parts of many electric and electronic items including mobile phones, computers and CRT funnel glass. Runoff from residues containing CRT glass on the banks of Korle Lagoon could leach pollutants into Korle Lagoon and the pollutants can become trapped in the sediments. Collaborative efforts need to be implemented to remediate land areas contaminated in Agbogbloshie e-waste recycling site. Public education campaigns on the impacts of their activities on the lagoon should be targeted to informal recyclers. Furthermore, there should be the creation of buffer zones to prevent anthropogenic activities from harming the lagoon, especially from the impacts of informal e-waste recycling activities.

8.4 Conclusions

This study determined the baseline concentrations of dissolved elements in surface water and bulk elemental concentrations of sediments in Korle Lagoon. Pollution indices were used to assess the contamination of sediments. Sediments were enriched as follows: Pb > Zn > Cu > Mn. Geoaccumulation indices showed sediments were moderately contaminated with Pb and uncontaminated with Mn, Cu and Zn. Two pollution indices - modified degree of contamination (mCd) and risk index (RI) - showed sediments in the study area present low ecological risks.

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CHAPTER 9: Summary and Conclusion

This summary and conclusion integrate the findings of this study. This study is one of the first comprehensive assessments of metal contamination of Agbogbloshie and Ashaiman, and systematically investigated the contamination by assessing total concentrations in solid samples (180 and 13 urban soil samples for Agbogbloshie and Ashaiman respectively, 32 agricultural soil samples, 21 sediment samples, 88 dust samples, 49 leafy vegetables), dissolved (96 surface water samples) and bioaccessible concentrations of floor dust, garden soils and leafy vegetables. Furthermore, the human health and ecological risks were assessed in these sample matrices. The findings are summarised:

9.1 Metal distribution in solid matrices and health risk assessment

Agbogbloshie is known to be a hotspot for metal contamination in the Greater Accra Region of Ghana. Elevated metal concentrations were previously reported in Agbogbloshie without systematic investigation about the metal pollution in different environmental samples. Ashaiman, an emerging e-waste site has been scarcely investigated for metal contamination and health risks. In this study, the metal concentrations and health risks were assessed in these two e-waste recycling sites. The study sought to generate current information by collecting samples from different environmental matrices including surface dust, surface and deep soils and vegetables cultivated in urban gardens in Agbogbloshie and surface soils in Ashaiman. The health risk assessment of soil and dust indicated that ingestion rather than dermal exposure was the main pathway of chronic exposure in the two e-waste recycling sites. Of the metals present, Pb posed the most significant human health risk, contributing significantly to chronic health risks. Lead affects the cognitive development of children since a greater proportion of ingested Pb is absorbed from the gastrointestinal tract of children than adults. Besides, systematically circulating Pb can cross the blood-brain barrier of children, especially those five years of age or younger.

9.2 Bioaccumulation of metals by leafy vegetables grown in urban gardens downstream of Agbogbloshie

The transfer factor indicates the capacity of plants to transfer metals from soils to their edible tissues with greater transfer factors indicating strong metal accumulation. Transfer factors of Cu and Zn in vegetables (Lettuce - *Lactuca sativa*, African eggplant - *Solanum macrocarpon*, hibiscus - *Hibiscus sabdariffa*, Amaranth - *Amaranthus spp.* and Jute mallow (Egyptian spinach) - *Corchorus olitorius*) were greater than the transfer factors of Mn, Fe and Pb in urban gardens, downstream of Agbogbloshie. The transfer factor of Zn was considerably high and was a source of concern. Intensive irrigation using Zn impacted wastewaters in the area could

have resulted in greater Zn transfer factors. Geometric mean concentrations of Cu and Zn were within USEPA and Canadian limits of metals in agricultural soils, however, Pb was greater than USEPA and Canadian Guideline limits for Pb in garden soils of one of the two urban gardens. Lead in the two urban gardens may have come from different sources such as agrochemicals, atmospheric deposition and vehicular emissions. Lead concentrations were greater in Garden 1 than Garden 2. Garden 1 was a municipal waste dump, and greater Pb concentration may have resulted from that historical land use. Atmospheric deposition or vehicular emissions may be additional sources of metals in garden 1.

9.3 Bioavailability of metals in the dust, garden soils and vegetables

Bioavailability of metals was determined using a simulated gastric solution. In garden soils, the greatest bioaccessible fractions were recorded by Zn, Pb and Cu, Zn in gardens 1 and 2 respectively. Anthropogenic metal mineral reservoirs are more bioaccessible than lithogenic metal mineral reservoirs. Greater bioaccessibility of Cu, Zn and Pb indicated that these elements may have been released possibly from anthropogenic activities including long-term usage of wastewater containing metals for irrigation of the vegetables, application of fertilizers, vehicular emissions and atmospheric deposition.

Bioaccessible concentrations of Mn, Fe, Ni, Cu, Zn, Ba and Pb in the surface dust differed significantly in the sampling areas. Roadside dust recorded the greatest Cu bioaccessible fraction while the storage area dust recorded the greatest Pb bioaccessible fraction. In Agboglobshie e-waste recycling site, due to the unregulated nature of informal e-waste recycling activities, dismantling of electronic component is rampant near the roadside, so bioaccessible components such as CuO used as nanoparticles in electronics may be emitted from dismantling of CuO-rich electric or electronics. In the storage area, disused Pb-acid batteries were kept in the enclosure where dust was sampled and may have contributed to greater Pb bioaccessibility recorded.

Iron in garden soils was the least bioaccessible among the elements. Metal bioaccessibility is affected by pH, particle size and mineralogy of a sample matrix. Metals were soluble in the gastric solution with the acidic pH of 1.5. Incorporated site-specific bioaccessibility fractions helped estimate human health risks accurately. The results of human health risk assessment indicate floor dust in dismantling areas of Agboglobshie posed carcinogenic and non-carcinogenic risks through the oral exposure pathway for children and adults. Non-carcinogenic risks from floor dust metals through the dermal and inhalation exposure routes were assumed to be generally safe for children and adults in Agboglobshie. Consumption of leafy vegetables

represent an important pathway for contamination and human health risks for residents. Hazard quotients for leafy vegetables from the bioaccessible concentrations were smaller than hazard quotient from total concentration. Although, vegetables had greater percentage bioaccessibility than surface dust, metal intake through leafy vegetables consumption was assumed to be safe. Multi-element hazard index was greater for Pb in lettuce. Consumption of lettuce may pose chronic risks in the study area.

9.4 Dissolved metal contamination in surface waters and bed sediments

Dissolved metals in Odaw River-Korle Lagoon were affected by industrial activities and agricultural activities in the downstream areas than in the control area. The control area (i.e. Comet Estate) was 21 km upstream from Agbogbloshie. Control samples collected from a pristine stream in a natural preserve, showed background concentrations, with the dissolved metals in the Odaw River and Korle Lagoon reporting relatively greater concentrations than in the control area. Concentrations of dissolved elements in Odaw River Korle Lagoon basin were within the World Health Guideline limits for drinking water, except Fe, which was greater than the World Health Guideline for drinking water in 44 sampling stations. Iron in the waters of the Odaw River Korle Lagoon basin was from a mixed lithological and anthropogenic source. Copper exhibited greater concentrations in the waters of Korle Lagoon estuary and could have been associated with anti-fouling paints on boats used for fishing activities in the estuary. Sediments collected opportunistically in Korle Lagoon at a period of sediment dredging posed low ecological risks with a Hakanson Potential ecological risk index of 27.9. The most important metal in sediment was Pb with the greatest implications for aquatic life.

APPENDICES

APPENDIX A Metal concentration and mineralogical data

Table A1 Metal bearing minerals and phases in selected dust samples – D47, D49_3, D55, DS6, D66, D69, D88, DF5, D54, DS23_1, DS96, DS112, DS117, DS129_16, RES16 and ASH6B_15.

Mineral	Compound name	Chemical formula
Aktashite	Aktashite	$\text{As}_4\text{Cu}_6\text{Hg}_3\text{S}_{12}$
Albite	Sodium calcium aluminium silicate	$(\text{Na,Ca})\text{Al}(\text{Si, Al})_3\text{O}_8$
Analcime	Analcime	$\text{H}_4\text{A}_{11.806}\text{Na}_{1.71}\text{O}_{14}\text{Si}_{4.194}$
Anatacamite	Copper hydroxide chloride	$\text{Cu}_2(\text{OH})_3\text{Cl}$
Anglesite	Lead sulfate	PbSO_4
Anorthite	Anorthite	$\text{Al}_2\text{Ca}_{0.71}\text{Na}_{0.25}\text{O}_8\text{Si}_2, \text{Al}_2\text{Ca}_{0.94}\text{Na}_{0.06}\text{O}_8\text{Si}_2,$
Anorthoclase	Anorthoclase	$\text{Al}_{1.02}\text{K}_{0.3}\text{Na}_{0.7}\text{O}_8\text{Si}_{2.98}$
Barbosaltite	Iron phosphate hydroxide	$\text{Fe}_3(\text{PO}_4)_2(\text{OH})_2$
Blossite	Copper vanadium oxide	$\text{Cu}_2(\text{V}_2\text{O}_7)$
Bromargyrite	Silver bromide	AgBr
Calcite	Calcium carbonate	$\text{Ca}(\text{CO}_3)$
Clinoferrosilite	Clinoferrosilite	$\text{Fe}_1\text{O}_3\text{Si}_{1.5}$
Copper selenide	Copper selenide	CuSe
Corundum	Aluminum oxide	Al_2O_3
Covellite	Copper sulfide	CuS
Digenite	Digenite high	$\text{Cu}_{1.8}\text{S}$
Giniite	Iron phosphate hydroxide hydrate	$\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$
Glauconite	Potassium sodium iron aluminum magnesium silicate hydroxide	$(\text{K, Na})(\text{Fe, Al, Mg})_2(\text{Si, Al})_4\text{O}_{10}(\text{OH})_2$
Guidottiite	Manganese iron silicate hydroxide	$(\text{Mn}_2\text{Fe}^{+3})(\text{SiFe}^{+3})\text{O}_5(\text{OH})_4$
Gurimite	Barium vanadium oxide	$\text{Ba}_3(\text{VO}_4)_2$
Gypsum	Calcium sulfate hydrate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Hercynite	Iron aluminum oxide	$(\text{Fe}_{0.865}\text{Al}_{0.135})(\text{Al}_{1.865}\text{Fe}_{0.135})\text{O}_4$
Kaolinite	Aluminum silicate hydroxide	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Lead strontium telluride	Lead strontium telluride	$(\text{Pb}_{0.9}\text{Sr}_{0.1})\text{Te}$
Litharge	Lead oxide	PbO
Livingstonite	Livingstonite	$\text{Hg}_8\text{S}_8\text{Sb}_4$
Lopezite	Lopezite	$\text{Cr}_2\text{K}_2\text{O}_7$
Magnetite	Magnetite	Fe_3O_4
Metacinnabar	Mercury sulfide selenide	$\text{Hg}(\text{S}_{0.4}\text{Se}_{0.6})$
Microcline	Potassium aluminium silicate	KAlSi_3O_8
Oldhamite	Calcium sulfide	CaS
Orlandiite	Lead chloride selenite hydrate	$\text{Pb}_3\text{Cl}_4(\text{SeO}_3)(\text{H}_2\text{O})$

Paratacamite	Paratacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$
Penroseite	Nickel selenide	NiSe_2
Phillipsbornite	Lead aluminum arsenate hydroxide	$\text{PbAl}_3(\text{AsO}_4)(\text{AsO}_3\text{OH})(\text{OH})_6$
Potosiite	Lead tin iron antimony sulfide	$\text{Pb}_{24}\text{Sn}_9\text{Fe}_4\text{Sb}_8\text{S}_{56}$
Proustite	Arsenic silver sulfide	$\text{Ag}_3(\text{AsS}_3)$
Pyrochroite	Manganese hydroxide	$\text{Mn}(\text{OH})_2$
Quartz	Quartz	SiO_2
Rutile	Titanium oxide	TiO_2
Sinnerite	Sinnerite	$\text{As}_8\text{Cu}_{12}\text{S}_{18}$
Spinel	Copper iron oxide	$\text{Fe}(\text{CuFe})\text{O}_4$
Stoiberite	Copper vanadium oxide	$\text{Cu}_5\text{V}_2\text{O}_{10}$
Stolzite	Lead tungstate	$\text{Pb}(\text{WO}_4)$
Taenite	Iron nickel	(Fe, Ni)
Tenorite	Copper oxide	CuO
Titanium oxide	Titanium oxide	TiO_2
Trustedtite	Nickel selenide	Ni_3Se_4
Unnamed freshnoite	Rubidium vanadium oxide	$\text{Rb}_2(\text{V}_3\text{O}_8)$
Velikite	Copper mercury tin sulfide	$\text{Cu}_{3.75}\text{Hg}_{1.75}\text{Sn}_2\text{S}_8$
Whitneyite	Copper arsenide	Cu_9As
Wulfenite	Lead molybdenum oxide	$\text{Pb}_{3.76}\text{Mo}_{4.24}\text{O}_{16}$
Zinc oxide	Zinc oxide	ZnO
Zinc sulfide	Zinc sulfide	ZnS

Table A2 Qualitative dust mineralogy, using X-ray diffractometry.

Sample	Mineral phases (ICDD Reference codes)	Latitude (°N)	Longitude (°W)
D47	Calcite (98-004-0454), quartz (98-004-6012), lopezite (98-001-4267), microcline (00-019-0926), orlandite (01-073-7764), proustite (98-001-7590).	5°33'11.56"	0°13'32.02"
D49_3	Calcite (98-007-8925), corundum (01-071-1683), kaolinite (01-075-1593), livingstonite (98-002-1685), quartz (98-002-8389), spinel (01-082-8786).	5°33'11.02"	0°13'31.22"
D55	Anatacamite (01-078-7707), calcite (98-007-8925), litharge (00-005-0561), microcline (98-001-7276), quartz (01-085-0930), rutile (00-034-0180), tenorite (01-073-6372).	5°33'11.59"	0°13'28.02"
D54	Aktashite (98-004-5268), Anglesite (01-083-1720), Analcime (98-010-7633), calcite (01-075-6049), gypsum (00-036-0432), paratacamite (98-000-5759), phillipsbornite (00-051-1450), quartz (01-085-0930), stoiberite (00-027-1135), tenorite (01-089-5896).	5°33'06.95"	0°13'32.23"
D66	Calcite (01-083-0577), proustite (01-085-0972), quartz (01-085-0930), sinnerite (98-002-8605), stolzite (01-078-3063), taenite (00-018-0877).	5°33'12.06"	0°13'29.42"
D69	Anorthoclase (98-001-8005), calcite (01-085-1108), Copper Selenide (01-070-8577), microcline (98-001-7661), oldhamite (01-071-4760), potosiite (00-039-1364), quartz (01-070-8054), taenite (00-018-0877).	5°33'13.21"	0°13'29.64"
D88	Anorthite (98-002-2605), calcite (01-086-2334), clinoferrosilite (98-003-4669), pyrochroite (01-073-1133), quartz (98-010-5017).	5°33'12.74"	0°13'29.35"
DF5	Anorthite (98-004-6418), barbosallite (01-070-6442), calcite (01-086-2334), gurimite (00-029-0211), quartz (98-002-3313).	5°33'11.09"	0°13'33.96"
DS4	Calcite (01-085-1108), Copper selenide (01-070-8577), Lead strontium telluride (01-075-6448), proustite (01-085-0972), quartz (98-001-2466).	5°33'06.77"	0°13'31.94"
DS10	Bromargyrite (98-006-0438), calcite (01-083-1762), copper selenide (01-070-8576), hercynite (01-089-1679), quartz (01-086-1630), rutile (00-034-0180).	5°33'10.66"	0°13'23.48"
DS23_1	Anorthite (01-073-1435), blossomite (01-070-0831), giniite (00-045-1436), guidottiite (00-062-0737), quartz (01-075-8322), whitneyite (00-002-1215).	5°33'11.59"	0°13'27.05"
DS96	Calcite (01-085-1108), gypsum (00-006-0047), quartz (98-001-2468), zinc oxide (01-078-4607).	5°33'07.81"	0°13'37.06"

DS112	Albite (00-041-1480), anorthite (98-002-2605), covellite (03-065-3928), magnetite (98-007-7862), quartz (98-004-0810), titanium oxide (01-088-1174).	5°33'11.30"	0°13'37.06"
DS117	Albite (00-041-1480), anorthite (98-004-1924), penroseite (01-071-4944), quartz (98-004-0810), wulfenite (01-080-7503).	5°33'08.10"	0°13'34.07"
DS129_16	Calcite (01-089-1304), unnamed-fresnoite (01-072-9877), metacinnabar (01-071-9090), proustite (98-001-7590), quartz (98-006-5162), taenite (00-018-0877).	5°33'12.49"	0°13'34.18"
RES16	Albite (00-041-1480), calcite (01-086-0174), glauconite (00-058-2024), lopezite (98-001-4267), microcline (01-076-0918), quartz (98-010-5017).	5°33'05.40"	0°13'37.49"
ASH6B_1 5	Calcite (01-085-1108), digenite (98-006-7953), quartz (01-085-0794), taenite (00-018-0877), velikite (01-072-0457).	5°41'02.90"	0°1'42.24"

Table A3 Metal concentrations in burn area topsoils of Agboglobshie.

Site ID	Latitude (°N)	Longitude (°W)	Concentrations (mg/kg)										
			Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
A1	5°33'12.35"	0°13'26.54"	65	34900	442	558	<12	<2	3	<4	138	402	842
A2	5°33'12.10"	0°13'37.63"	47	17200	4370	2380	<12	<2	5	9	1260	442	2440
A3	5°33'11.12"	0°13'27.34"	159	161,000	1460	18800	<12	<2	36	7	245	1300	2510
A4	5°33'09.54"	0°13'29.06"	49	20000	10600	1090	<12	5	<3	5	648	561	3380
A5	5°33'12.10"	0°13'37.63"	51	90	23400	20800	<12	22	28	18	3000	1470	11600
A6	5°32'59.82"	0°13'34.07"	69	147	2510	1530	<12	<2	5	7	1440	342	2370
A7	5°33'04.10"	0°13'31.51"	75	65	17900	8000	<12	8	10	18	2040	895	11200
A8	5°33'08.60"	0°13'29.50"	52	153	859	1950	<12	<2	4	<4	92	761	526
A9	5°33'00.18"	0°13'32.48"	58	186	645	12600	<12	<2	<3	<4	401	298	436
A10	5°33'05.00"	0°13'35.44"	869	425	51000	7940	<12	17	19	44	842	1760	4360
A11	5°33'12.10"	0°13'37.63"	90	8570	27300	18400	<12	14	33	21	3350	1630	12000
A12	5°32'59.82"	0°13'34.07"	70	22300	2640	1800	<12	<2	22	11	1470	431	2630
A13	5°33'05.00"	0°13'35.44"	68	3470	18500	4390	<12	<2	9	16	2000	1090	11800
A14	5°32'59.82"	0°13'34.07"	75	23400	1660	1940	<12	<2	4	<4	600	363	1410
A15	5°33'05.15"	0°13'31.08"	48	20400	420	850	<12	3	4	<4	113	344	362
A16	5°33'06.70"	0°13'40.80"	83	24800	17100	8920	<12	<2	21	19	4370	1400	10600
A17	5°33'12.24"	0°13'44.94"	166	34400	698	55900	<12	6	<3	6	17	290	144
A18	5°33'12.10"	0°13'37.63"	69	7010	18800	4850	<12	<2	13	16	1830	981	13400
A19	5°33'12.35"	0°13'26.54"	59	31500	125	339	7	<2	11	<4	346	269	196
A20	5°33'06.70"	0°13'40.80"	62	25300	256	204	<12	<2	<3	<4	264	294	329
A21	5°33'12.10"	0°13'37.63"	43	17400	1250	1430	<12	<2	6	6	234	519	1200
A22	5°33'05.00"	0°13'35.44"	616	51700	38600	8090	<12	16	36	17	584	1590	6630
A23	5°33'09.54"	0°13'29.06"	62	26200	3730	865	<12	5	11	<4	757	990	3550
A24	5°33'12.28"	0°13'36.77"	57	17700	3710	1650	<12	5	6	6	777	572	2380
A25	5°33'08.60"	0°13'29.50"	60	28800	1120	2610	<12	<2	4	7	143	818	722

A26	5°33'00.18"	0°13'32.48"	57	26800	834	11900	<12	<2	<3	<4	124	489	525
A27	5°33'12.28"	0°13'36.77"	57	18100	1460	1000	<12	<2	18	5	452	356	1200
A28	5°33'05.15"	0°13'31.08"	57	29200	81	145	8	<2	<3	<4	20	231	85
A29	5°33'05.00"	0°13'35.44"	998	51200	43500	7740	<12	20	30	21	851	1370	4500
A30	5°33'08.60"	0°13'29.50"	64	28500	1880	3290	<12	<2	7	11	274	1500	1650
A31	5°33'12.10"	0°13'37.63"	95	8500	29900	16300	<12	11	31	28	6100	1780	15900
A32	5°33'12.10"	0°13'37.63"	95	19600	12400	4910	<12	<2	17	12	1740	812	5960
A33	5°33'04.10"	0°13'31.51"	96	8420	24200	6040	<12	10	6	17	1720	693	8970
A34	5°33'12.35"	0°13'26.54"	220	258,000	2520	8220	<12	<2	20	7	443	4490	9830
A35	5°33'12.31"	0°13'26.54"	21	238,000	2670	8360	<12	<2	20	7	437	4550	8960
A36	5°33'06.87"	0°13'29.69"	50	22200	557	829	<12	<2	<3	<4	101	269	1120
A37	5°33'01.32"	0°13'31.48"	84	6090	27400	6500	<12	10	21	27	3330	797	12600
A38	5°33'09.54"	0°13'29.06"	118	60600	7710	1940	<12	<2	39	7	923	2670	6370
A39	5°33'11.10"	0°13'27.34"	270	205,000	2990	8270	<12	<2	19	7	664	7670	13400

Table A4 Metal concentrations (mg/kg) in burn area subsoils of Agboglobshie.

Site ID	Latitude (°N)	Longitude (°W)	Concentrations (mg/kg)										
			Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
A40	5°33.05.15"	0°13'31.08"	60	27700	90	455	<12	<2	<3	<4	22	230	141
A41	5°33'12.35"	0°13'26.54"	40	17200	43	116	<12	<2	<3	<4	24	215	114
A42	5°33'12.10"	0°13'37.63"	23	8100	221	310	<12	3	<3	<4	27	136	191
A43	5°33'11.12"	0°13'27.34"	403	204000	2490	7680	310	<2	27	11	778	9980	29300
A44	5°33'12.10"	0°13'37.63"	83	9330	34700	13200	<12	<2	30	27	4810	1640	12300
A45	5°32'59.82"	0°13'34.07"	63	28100	546	1680	<12	<2	<3	<4	135	299	2550
A46	5°33'01.33"	0°13'31.48"	71	6430	33900	7860	<12	9	23	18	4060	788	9330
A47	5°33'08.60"	0°13'29.50"	79	26600	1980	3850	<12	<2	7	10	166	1800	2580
A48	5°33'09.54"	0°13'29.06"	87	43700	10700	1930	<12	6	14	<4	700	1070	5770
A49	5°33'08.60"	0°13'29.50"	89	32500	1690	2890	<12	<2	32	7	1120	2620	5030
A50	5°33'09.54"	0°13'29.06"	130	57700	11600	2390	<12	<2	19	9	711	1870	7500
A51	5°33'05.00"	0°13'35.44"	616	70800	38000	8660	<12	15	44	15	484	1400	3360
A52	5°33'05.72"	0°13'34.90"	59	40800	1490	2870	<12	<2	<3	<4	296	898	1480
A53	5°33'00.18"	0°13'32.48"	17	7150	216	942	<12	4	<3	<4	30	167	140
A54	5°33'07.34"	0°13'41.56"	41	17800	23	206	5	<2	<3	<4	<7	253	68
A55	5°33'05.15"	0°13'31.08"	65	26700	138	455	<12	<2	<3	<4	36	381	331
A56	5°32'59.82"	0°13'34.07"	51	22500	184	555	<12	<2	<3	<4	367	260	521
A57	5°33'12.10"	0°13'37.63"	39	14000	70	279	<12	<2	<3	<4	25	179	747
A58	5°33'11.12"	0°13'27.34"	302	165,000	3640	10200	273	<2	30	38	1050	9920	35300
A59	5°33'05.72"	0°13'34.90"	62	26500	640	1410	<12	<2	<3	<4	103	570	660
A60	5°32'59.82"	0°13'34.07"	64	25500	420	972	<12	<2	<3	<4	567	273	1320
A61	5°33'08.60"	0°13'29.50"	71	35600	1320	3040	<12	<2	8	5	188	2650	2810
A62	5°33'06.70"	0°13'40.80"	84	15700	22700	10500	<12	<2	21	20	2390	877	8720
A63	5°33'12.10"	0°13'37.63"	134	16500	30900	13200	<12	11	23	35	5240	2240	15700

A64	5°33'04.10"	0°13'31.51"	200	26600	661	250	<12	<2	<3	<4	169	261	419
A65	5°33'00.18"	0°13'32.48"	18	4660	177	726	<12	7	<3	<4	60	162	97
A66	5°33'05.00"	0°13'35.44"	546	47000	37300	6860	<12	22	17	17	493	1350	3150
A67	5°33'07.34"	0°13'41.56"	36	18700	20	164	<12	4	<3	<4	13	213	205
A68	5°33'12.35"	0°13'26.54"	40	14000	<11	34	<12	<2	<3	<4	8	274	42
A69	5°32'59.82"	0°13'34.07"	48	22200	44	763	<12	<2	<3	<4	16	204	169
A70	5°33'05.15"	0°13'31.08"	61	26000	48	174	7	<2	<3	<4	48	271	104
A71	5°33'05.00"	0°13'35.44"	527	45800	37900	6770	<12	14	21	20	706	1340	3030
A72	5°33'05.72"	0°13'34.90"	43	18500	271	499	<12	3	<3	<4	42	343	242
A73	5°33'00.18"	0°13'32.48"	9	2970	64	553	5	10	<3	<4	9	107	40
A74	5°33'04.10"	0°13'31.51"	47	24300	1560	778	<12	3	<3	<4	296	333	1100
A75	5°33'07.34"	0°13'41.56"	44	14000	38	334	<12	2	<3	<4	11	240	44
A76	5°33'00.18"	0°13'32.48"	13	3270	70	543	<12	7	<3	<4	19	109	45
A77	5°33'01.33"	0°13'31.48"	18	6120	2060	717	<12	<2	4	<4	274	192	1210
A78	5°33'01.33"	0°13'31.48"	22	6310	2110	742	<12	5	<3	<4	290	179	1100
A79	5°33'00.18"	0°13'32.48"	50	18000	21	176	<12	<2	<3	<4	9	246	100
A80	5°33'0.18"	0°13'32.48"	15	3020	109	541	<12	4	<3	<4	10	104	55
A81	5°33'05.15"	0°13'31.08"	65	25900	36	165	4	<2	<3	<4	12	238	91
A82	5°33'05.72"	0°13'34.90"	36	20100	216	659	<12	3	<3	<4	54	352	253
A83	5°33'07.34"	0°13'41.56"	39	12600	26	400	<12	<2	<3	<4	8	202	36
A84	5°33'05.00"	0°13'35.44"	492	46200	34400	5890	<12	9	28	19	646	1150	2870
A85	5°32'59.82"	0°13'34.07"	46	23400	49	1600	<12	<2	<3	<4	6	202	429
A86	5°33'05.15"	0°13'31.08"	50	25200	30	120	<12	<2	<3	<4	9	248	68
A87	5°33'01.33"	0°13'31.48"	46	18800	620	429	<12	3	<3	<4	90	263	314
A88	5°33'05.15"	0°13'31.08"	50	26900	33	203	<12	<2	<3	<4	10	263	145
A89	5°33'00.18"	0°13'32.48"	6	2920	59	412	4	12	<3	<4	14	72	39
A90	5°33'04.10"	0°13'31.51"	51	14600	11200	3520	<12	5	4	9	2020	583	5730
A91	5°33'05.11"	0°13'37.27"	41	13600	32	94	<12	<2	3	<4	9	194	75
A92	5°33'05.00"	0°13'35.44"	48	21700	218	591	<12	<2	4	<4	33	306	253
A93	5°33'05.15"	0°13'31.08"	48	17600	987	771	<12	<2	<3	<4	186	306	541
A94	5°33'05.15"	0°13'31.08"	56	25800	68	578	<12	<2	<3	<4	20	248	145
A95	5°32'59.82"	0°13'34.07"	59	26900	123	524	<12	<2	<3	4	117	242	196
A96	5°33'07.34"	0°13'41.56"	53	14200	24	313	<12	2	<3	<4	<7	201	36
A97	5°33'00.18"	0°13'32.48"	11	4360	160	645	<12	6	<3	<4	21	109	75
A98	5°33'05.00"	0°13'35.44"	50	19900	156	164	<12	<2	<3	<4	16	264	96
A99	5°32'59.82"	0°13'34.07"	64	28800	133	201	<12	<2	<3	3	53	374	216
A100	5°33'07.34"	0°13'41.56"	67	22500	22	508	4	2	<3	<4	<7	257	44
A101	5°33'05.72"	0°13'34.90"	69	28700	904	2300	<12	<2	5	<4	220	724	1030
A102	5°33'05.72"	0°13'34.90"	40	9560	97	99	3	2	4	<4	19	189	38

Table A5 Metal concentrations (mg/kg) in dismantling area topsoils of Agbogbloshie.

Site			Concentrations (mg/kg)
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ID	Latitude (°N)	Longitude (°W)	Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
A103	5°33'11.27"	0°13'29.57"	50	21900	716	623	<12	4	4	5	306	487	697
A104	5°33'06.34"	0°13'36.01"	43	21000	426	590	<12	<2	3	<4	104	445	1600
A105	5°33'09.43"	0°13'34.57"	210	120,000	11100	4160	<12	7	83	42	3830	3910	4710
A106	5°33'06.34"	0°13'36.01"	<55	242	<11	20	11	<2	38	<4	<7	<161	<10
A107	5°33'11.34"	0°13'31.55"	58	19200	24400	1050	<12	7	6	<4	293	262	2960
A108	5°33'07.96"	0°13'34.14"	50	22500	679	466	<12	4	7	<4	318	407	830
A109	5°33'08.64"	0°13'33.24"	27	12600	87	135	<12	3	<3	<4	10	152	54
A110	5°33'09.54"	0°13'32.56"	70	23400	603	502	<12	<2	<3	<4	191	786	421
A111	5°33'08.59"	0°13'35.29"	86	197	3640	1160	<12	<2	15	<4	261	704	1250
A112	5°33'05.72"	0°13'34.90"	78	42400	831	847	<12	<2	6	5	226	453	443
A113	5°33'11.27"	0°13'29.57"	119	69700	4310	1960	<12	<2	17	7	1250	665	2560
A114	5°33'12.57"	0°13'31.15"	34	16300	69	368	<12	<2	4	<4	24	253	164
A115	5°33'10.66"	0°13'23.48"	213	19100	695	1010	<12	<2	14	24	148	566	1810
A116	5°33'06.34"	0°13'36.01"	202	80600	306,000	9690	531	<2	33	21	3160	696	33800
A117	5°33'09.58"	0°13'30.29"	85	38300	1230	2580	<12	<2	8	<4	285	1210	1940
A118	5°33'12.57"	0°13'31.15"	241	311,000	820	3650	<12	<2	10	<4	99	2020	575
A119	5°33'11.85"	0°13'29.86"	159	104,000	5440	2790	<12	9	16	10	244	920	2320
A120	5°33'12.57"	0°13'31.15"	129	95900	744	1800	<12	<2	6	6	128	792	1710
A121	5°33'10.66"	0°13'23.48"	85	17500	228	379	<12	<2	4	10	64	506	229
A122	5°33'11.85"	0°13'29.06"	69	27900	818	1330	<12	<2	5	<4	175	566	1340
A123	5°33'12.57"	0°13'31.15"	44	17100	260	381	<12	<2	<3	<4	30	359	177
A124	5°33'12.57"	0°13'31.15"	48	17000	275	369	<12	3.3	<3	<4	31	375	174
A125	5°33'09.58"	0°13'30.29"	159	113,000	4280	2660	<12	7	8	12	263	657	2120
A126	5°33'09.43"	0°13'34.57"	206	189,000	10600	3680	<12	<2	75	17	2760	3320	3910
A127	5°33'08.64"	0°13'33.24"	59	21800	1770	898	<12	3	7	<4	560	535	939
A128	5°33'08.59"	0°13'35.29"	70	29000	3530	660	<12	<2	6	<4	94	471	470
A129	5°33'09.58"	0°13'30.29"	92	39700	1720	3430	<12	<2	12	8	555	1320	2290
A130	5°33'05.72"	0°13'34.90"	61	41500	647	572	<12	<2	7	<4	127	411	792
A131	5°33'11.27"	0°13'29.57"	51	24300	1210	617	<12	5	8	<4	597	467	683
A132	5°33'11.27"	0°13'29.57"	93	56000	3560	1360	<12	<2	31	<4	840	769	1540
A133	5°33'11.85"	0°13'29.86"	50	28500	642	455	<12	2	3	3	54	232	441
A134	5°33'11.27"	0°13'29.57"	91	58800	2280	1530	<12	<2	15	5	425	568	1430
A135	5°33'07.96"	0°13'34.14"	85	47300	4950	2090	<12	<2	9	7	829	812	2220
A136	5°33'09.43"	0°13'34.57"	162	217,000	5250	3510	<12	<2	38	11	1050	3000	3390
A137	5°33'09.54"	0°13'32.56"	167	51200	1790	1140	<12	4	18	5	145	556	1150
A138	5°33'10.66"	0°13'23.48"	60	25900	27700	1850	<12	<2	10	<4	764	458	4230
A139	5°33'09.58"	0°13'30.29"	142	47700	3500	4260	<12	<2	23	7	1470	3740	3190
A140	5°33'08.64"	0°13'33.24"	60	16100	992	596	<12	<2	6	<4	340	545	590
A141	5°33'09.54"	0°13'32.56"	178	64100	4150	5480	<12	<2	15	7	852	2800	3430
A142	5°33'10.66"	0°13'23.48"	65	20300	207	263	<12	<2	<3	<4	45	348	274
A143	5°33'11.34"	0°13'31.55"	178	139000	4060	3680	<12	<2	16	7	466	1060	2240

Table A6 Metal concentrations (mg/kg) in dismantling area subsoils of Agbogbloshie.

Site ID	Latitude (°N)	Longitude (°W)	Concentrations (mg/kg)										
			Cr	Fe	Cu	Zn	As	Se	Ag	Cd	Sn	Ba	Pb
A144	5°33'07.96"	0°13'34.14"	89	52400	2240	1210	<12	<2	12	6	880	677	1630
A145	5°33'11.85"	0°13'29.86"	57	30800	148	364	<12	3	2	<4	24	286	467
A146	5°33'08.64"	0°13'33.24"	50	15700	650	488	<12	3	4	<4	334	394	394
A147	5°33'10.66"	0°13'23.48"	50	20600	116	260	<12	<2	<3	<4	44	300	302
A148	5°33'07.96"	0°13'34.14"	89	52400	2240	1210	<12	<2	12	6	880	677	1630
A149	5°33'12.57"	0°13'31.15"	41	15100	82	148	7	4	<3	<4	10	242	128
A150	5°33'11.70"	0°13'31.55"	53	43100	1280	761	<12	4	7	<4	97	368	643
A151	5°33'11.34"	0°13'31.55"	110	82300	2850	4410	<12	<2	21	<4	308	759	1330
A152	5°33'09.58"	0°13'30.29"	90	41100	3180	2400	<12	<2	16	<4	1030	1560	2060
A153	5°33'09.43"	0°13'34.57"	161	163,000	5040	2920	<12	<2	37	10	1810	2370	2770
A154	5°33'09.54"	0°13'32.56"	77	27400	922	1220	<12	3	6	<4	132	824	900
A155	5°33'06.34"	0°13'36.01"	68	24800	29400	1980	<12	<2	12	<4	636	404	2810
A156	5°33'11.85"	0°13'29.86"	68	20100	9	49	3	<2	<3	<4	<7	195	35
A157	5°33'11.70"	0°13'31.55"	85	66500	866	983	<12	<2	8	11	157	423	1060
A158	5°33'10.66"	0°13'23.48"	37	13500	177	155	<12	<2	<3	<4	70	254	158
A159	5°33'08.64"	0°13'33.24"	50	14800	495	350	<12	<2	<3	<4	156	551	446
A160	5°33'08.64"	0°13'33.24"	32	11700	60	140	<12	3	<3	<4	79	238	198
A161	5°33'09.43"	0°13'34.57"	78	68400	3180	1580	<12	<2	22	6	1280	1860	2480
A162	5°33'08.64"	0°13'33.24"	51	30800	1570	1020	<12	<2	5	<4	143	421	966
A163	5°33'09.58"	0°13'30.29"	38	25200	401	621	<12	<2	3	<4	67	466	383
A164	5°33'11.70"	0°13'31.55"	40	14100	63	94	<12	<2	<3	<4	10	211	81
A165	5°33'08.64"	0°13'33.24"	30	12900	128	359	<12	2	<3	<4	54	319	162
A166	5°33'09.58"	0°13'30.29"	35	14000	101	232	<12	<2	<3	<4	34	300	130
A167	5°33'09.43"	0°13'34.57"	69	43100	2570	1210	<12	4	22	7	802	1390	1380
A168	5°33'11.34"	0°13'31.55"	44	23600	1300	655	<12	<2	9	<4	332	345	2970
A169	5°33'10.66"	0°13'23.48"	23	6560	725	111	<12	3	<3	<4	23	174	177
A170	5°33'09.58"	0°13'30.29"	23	14800	119	284	<12	<2	<3	<4	32	297	177
A171	5°33'10.66"	0°13'23.48"	25	7990	22	55	<12	3	<3	<4	<7	308	35
A172	5°33'09.43"	0°13'34.57"	50	29800	1040	752	<12	3	12	<4	305	949	865
A173	5°33'11.70"	0°13'31.55"	34	13000	15	54	5	<2	<3	<4	<7	192	33
A174	5°33'09.58"	0°13'30.29"	29	15800	190	278	<12	<2	<3	<4	26	258	133
A175	5°33'09.43"	0°13'34.57"	57	33500	1210	625	<12	<2	9	<4	446	1360	872
A176	5°33'10.66"	0°13'23.48"	27	8040	119	58	<12	<2	<3	<4	13	182	28
A177	5°33'09.58"	0°13'30.29"	47	32100	440	1220	<12	6	<3	<4	49	311	314
A178	5°33'10.66"	0°13'23.48"	25	7680	62	93	<12	<2	<3	<4	13	240	30
A179	5°33'09.43"	0°13'34.57"	95	42300	1040	1230	<12	<2	9	<4	253	3920	808
A180	5°33'09.43"	0°13'34.57"	182	94800	2730	2490	<12	<2	16	13	960	1480	2330

Table A7 Metal concentrations in surface dust (mg/kg) of Agbogloboshie.

Sample ID	Latitude (°N)	Longitude (°W)	Concentrations (mg/kg)									
			V	Cr	Mn	Ni	Cu	Zn	Mo	Cd	Ba	Pb
DS137	5°33'08.21"	0°13'31.69"	43	50	245	29	1660	587	2	2	377	339
CO1	5°33'12.24"	0°13'44.94"	75	89	401	58	1820	1810	10	5	804	935
RC	5°33'15.91"	0°13'29.46"	110	187	753	92	24300	8260	6	9	853	702
DS125	5°33'10.01"	0°13'29.42"	102	115	577	151	10200	3040	12	12	825	9790
C06	5°33'14.04"	0°13'28.60"	45	49	285	34	338	551	3	3	577	414
DS6	5°33'06.95"	0°13'32.23"	101	214	561	452	26300	7930	14	30	1240	4670
DS100	5°33'08.64"	0°13'33.78"	124	125	1090	226	9380	17200	89	5	1620	3110
D65	5°33'12.46"	0°13'29.57"	85	64	418	23	4750	4210	4	6	989	271
DS20	5°33'09.14"	0°13'30.36"	56	48	391	15	1980	3330	3	2	463	179
DS101	5°33'08.35"	0°13'34.00"	83	269	3590	234	3840	6740	13	7	588	1690
DF7	5°33'11.09"	0°13'33.96"	103	73	527	93	3890	2520	12	7	1740	1950
DS28	5°33'08.68"	0°13'30.29"	78	77	468	60	3370	2650	5	6	926	1450
C05	5°33'14.44"	0°13'29.17"	80	94	466	47	1030	1700	6	6	775	1420
RES3	5°33'01.66"	0°13'35.47"	33	22	145	6	30	127	3	2	495	50
D54	5°33'11.81"	0°13'28.31"	51	76	350	27	1070	2300	7	8	463	338
D83	5°33'13.50"	0°13'30.72"	76	126	456	65	2150	2690	20	4	761	1170
D46	5°33'11.63"	0°13'31.91"	84	123	610	80	4530	2930	26	10	841	1320
DS19	5°33'09.40"	0°13'31.01"	52	78	397	53	13600	2170	26	5	477	696
DS141	5°33'07.24"	0°13'30.61"	66	91	394	63	1640	2590	19	5	576	644
DS135	5°33'11.16"	0°13'32.09"	64	76	454	53	3090	2340	13	9	739	870
DS12	5°33'08.60"	0°13'31.15"	93	215	666	149	6020	3420	25	10	908	1870
DS21	5°33'11.95"	0°13'26.72"	67	91	458	80	2440	2050	9	10	614	1190
DS1	5°33'11.27"	0°13'29.57"	61	100	495	85	3660	2010	9	5	645	689
D51	5°33'11.23"	0°13'30.83"	56	85	652	105	2080	2300	12	8	603	880
D31	5°33'10.44"	0°13'36.98"	101	96	482	101	3230	3460	9	6	1230	1950
RES32	5°33'02.66"	0°13'25.68"	43	35	242	9	97	351	3	3	695	169
DS144	5°33'08.60"	0°13'31.04"	83	146	680	121	4270	3930	29	25	873	1500
DS11	5°33'11.56"	0°13'29.24"	71	85	513	90	6680	4280	9	10	741	1260
D55	5°33'11.59"	0°13'28.02"	248	239	1440	83	18000	3220	12	5	3830	1140
DS95	5°33'07.92"	0°13'37.09"	93	117	3380	926	4400	4510	42	4	871	1130
DS118	5°33'07.45"	0°13'32.81"	98	119	538	178	12400	4520	16	20	1110	3140
D76	5°33'13.43"	0°13'30.61"	67	145	457	97	32800	3820	31	71	661	7690
DS115	5°33'08.96"	0°13'33.89"	56	66	395	84	13800	2430	52	7	656	2910
D48	5°33'11.23"	0°13'31.91"	69	88	400	53	1930	1700	10	4	771	751
RES13	5°33'05.72"	0°13'37.20"	38	47	217	20	624	1190	9	2	387	178
D42	5°33'12.78"	0°13'34.90"	116	239	1770	283	8550	13300	18	12	1310	2860
D44	5°33'12.85"	0°13'35.00"	104	160	688	136	11000	5790	37	9	1100	1630

DS2	5°33'09.58"	0°13'30.29"	75	136	430	58	3730	3240	21	8	846	1020
RP3	5°32'57.55"	0°13'23.92"	46	50	234	5.5	82	413	2	2	631	156
DS127	5°33'15.26"	0°13'31.22"	72	166	1170	110	1720	3620	11	8	771	808
DS130	5°33'12.42"	0°13'34.54"	88	215	1090	249	6800	4250	17	12	1010	1930
DS3	5°33'06.01"	0°13'31.94"	67	79	238	48	2840	1460	6	20	406	898
DS9	5°33'07.42"	0°13'30.86"	77	100	637	113	5250	4150	8	6	733	1590
DS7	5°33'06.80"	0°13'31.08"	96	140	742	177	4310	3870	43	15	704	1440
DS138	5°33'08.17"	0°13'31.94"	224	157	1170	414	19100	6060	27	24	3220	4310
D79	5°33'14.04"	0°13'29.17"	84	194	828	81	2160	5020	15	11	806	2810
D89	5°33'12.31"	0°13'29.14"	102	168	2410	208	7680	5830	19	12	1230	2090
D85	5°33'13.00"	0°13'29.96"	103	187	632	149	2010	5980	25	11	622	634
D36	5°33'11.12"	0°13'35.26"	114	158	595	87	2970	3690	15	12	1160	1570
D84	5°33'13.28"	0°13'29.93"	124	214	967	46	968	2360	18	4	1010	324
DS103	5°33'07.99"	0°13'32.74"	115	114	613	102	8910	3510	24	10	1260	2440
D58	5°33'12.13"	0°13'28.16"	135	170	909	267	4510	4360	21	9	1100	1530
DS112	5°33'11.30"	0°13'37.06"	35	51	249	31	610	564	2	2	379	365
D49	5°33'11.02"	0°13'31.22"	97	217	2540	265	10300	6190	39	10	738	3060
RES54	5°32'52.73"	0°13'25.93"	57	55	256	6	144	3650	2	2	790	169
RES16	5°33'05.40"	0°13'37.49"	38	46	230	18	376	738	2	2	367	193
DS117	5°33'08.14"	0°13'34.03"	70	120	1020	86	2870	3190	45	2	632	610
D47	5°33'11.56"	0°13'32.02"	90	127	845	89	6620	4490	42	9	984	1330
D88	5°33'12.74"	0°13'29.35"	84	119	478	122	6000	3210	11	6	741	1760
DS4	5°33'06.77"	0°13'31.94"	87	86	493	62	5940	3420	8	11	581	1370
DS10	5°33'10.66"	0°13'23.48"	83	97	443	74	4750	6660	10	7	807	1550
D55	5°33'11.59"	0°13'28.02"	153	286	745	2280	91600	12400	24	20	1510	7860
DS96	5°33'07.81"	0°13'37.06"	86	124	2180	213	6930	2690	13	2	848	1600
D66	5°33'12.06"	0°13'29.42"	95	150	1050	111	13300	5290	29	22	1040	1850
DS129	5°33'12.49"	0°13'34.18"	107	149	725	166	11000	4610	20	11	1190	2820
DF4	5°33'07.09"	0°13'34.18"	36	37	225	26	351	488	3	2	330	468
ST4	5°33'10.33"	0°13'33.38"	72	96	445	99	1630	3010	8	7	842	4240
C04	5°33'14.51"	0°13'29.28"	77	118	473	44	999	1980	7	4	752	1420
DF13	5°33'08.17"	0°13'31.94"	129	132	449	131	5950	2530	7	8	2110	1500
DS94	5°33'08.82"	0°13'30.11"	92	207	13700	554	4050	16300	10	9	904	5200
DS131	5°33'12.92"	0°13'34.90"	63	121	540	91	8090	3260	13	10	889	1680
DS121	5°33'10.19"	0°13'30.25"	79	112	518	198	2940	3670	8	14	689	1210
DF9	5°33'06.84"	0°13'37.13"	59	65	330	38	3690	1300	6	2	610	786
DS97	5°33'07.96"	0°13'36.88"	58	114	3170	118	11700	2280	16	9	820	2260
DS134	5°33'10.26"	0°13'34.28"	112	177	737	289	8120	7840	18	13	1230	1610
D162	5°33'12.28"	0°13'28.96"	72	281	6010	140	8910	9910	14	10	822	1390
RES33	5°32'56.44"	0°13'24.53"	54	32	252	14	55	314	2	2	754	90

DS119	5°33'07.16"	0°13'32.16"	100	138	578	233	32100	6540	18	21	1220	6200
D161	5°33'12.31"	0°13'28.13"	95	193	709	371	5780	3890	17	13	1280	1990
DS123	5°33'11.74"	0°13'28.02"	110	168	678	70	2960	2810	15	4	692	1110
ST2	5°33'12.71"	0°13'34.72"	108	230	1040	328	44600	6020	38	10	849	4870
RES2	5°33'02.56"	0°13'35.69"	56	57	355	22	1220	834	2	5	469	444
D81	5°33'13.64"	0°13'29.75"	122	116	464	58	5020	2240	18	7	2420	898
DS139	5°33'06.80"	0°13'32.23"	93	146	634	382	35500	6040	21	15	929	3740
D58	5°33'12.13"	0°13'28.16"	126	159	394	2485	16600	3890	93	8	1420	8010
D78	5°33'14.00"	0°13'29.17"	103	171	895	73	6940	3060	23	4	501	1190
DF15	5°33'07.99"	0°13'35.11"	91	169	985	259	12400	3780	20	15	972	3070
D41	5°33'12.74"	0°13'34.64"	112	125	552	274	9410	4180	22	17	1180	2680

Table A8 Metal concentrations (mg/L) in surface waters of Odaw River and Korle Lagoon.

Site ID	Latitude (° N)	Longitude (° W)	Mn	Fe	Cu	Zn	Pb
C01	5°43'40.22"	0°14'17.63"	0.004	0.194	<0.001	0.012	<0.001
C02	5°43'40.22"	0°14'17.63"	0.010	0.079	<0.001	0.009	<0.001
OR85	5°40'03.86"	0°12'50.44"	<0.003	0.144	0.002	0.017	<0.001
OR89	5°40'03.97"	0°12'50.54"	0.221	0.288	<0.002	0.013	<0.002
OR63	5°40'03.86"	0°12'50.62"	0.203	0.167	0.004	0.036	<0.002
OR41	5°38'52.33"	0°14'11.15"	<0.004	0.153	0.007	0.082	0.015
OR92	5°38'52.26"	0°14'10.81"	0.004	0.097	<0.001	0.010	0.001
OR18	5°38'51.58"	0°14'09.38"	0.164	0.209	0.008	0.052	<0.001
OR37	5°38'25.76"	0°13'16.90"	<0.004	0.281	0.006	0.025	0.004
OR68	5°37'16.25"	0°13'44.83"	0.006	0.141	0.003	0.006	0.004
OR88	5°37'16.26"	0°13'44.81"	<0.003	0.141	<0.002	<0.002	0.002
OR27	5°37'16.35"	0°13'44.83"	<0.004	0.055	<0.002	0.013	0.005
OR17	5°36'44.57"	0°13'35.40"	0.003	0.084	0.005	0.030	<0.002
OR51	5°36'44.57"	0°13'35.51"	0.265	0.281	<0.002	0.015	<0.002
OR90	5°36'44.64"	0°13'35.04"	<0.004	0.230	<0.002	<0.002	0.002
OR79	5°36'11.52"	0°13'15.31"	<0.003	0.146	0.005	0.014	0.002
OR16	5°36'10.80"	0°13'15.74"	<0.004	0.096	0.004	0.028	<0.002
OR48	5°36'10.87"	0°13'15.89"	0.016	0.132	<0.002	0.011	<0.001
OR69	5°35'21.08"	0°13'02.60"	0.161	0.180	0.003	0.048	0.004
OR91	5°34'45.55"	0°13'06.17"	0.313	0.355	<0.002	0.021	<0.002
OR15	5°34'45.49"	0°13'06.05"	0.225	0.313	0.003	0.036	0.004
OR56	5°34'06.96"	0°13'03.43"	0.372	0.257	0.006	0.094	<0.002
OR57	5°34'00.08"	0°13'03.00"	0.311	0.868	0.016	0.028	0.003
OR26	5°34'06.74"	0°13'03.47"	0.231	0.175	<0.002	0.026	0.002
OR58	5°33'48.31"	0°13'03.18"	0.340	0.643	0.005	0.011	<0.001
OR6	5°33'38.52"	0°13'04.12"	0.284	0.327	0.004	0.014	0.002
OR52	5°33'38.05"	0°13'04.22"	0.363	0.784	0.003	0.010	<0.001
OR9	5°33'30.89"	0°13'07.36"	0.282	0.470	<0.003	0.009	<0.002
KL64	5°33'10.62"	0°13'48.97"	0.172	0.214	0.007	0.023	<0.001
KL38	5°33'27.68"	0°13'12.11"	0.390	0.528	0.005	0.011	<0.002
KL81	5°33'22.10"	0°13'18.23"	0.042	0.017	<0.003	0.004	<0.002
KL67	5°33'21.17"	0°13'17.18"	0.458	0.840	0.004	0.016	<0.002
KL1	5°33'20.52"	0°13'17.76"	0.338	1.030	0.004	0.021	<0.002
KL50	5°33'16.45"	0°13'52.32"	0.127	0.172	0.004	0.016	<0.001
KL72	5°33'16.45"	0°13'52.46"	0.155	0.149	0.004	0.021	<0.002
KL44	5°33'17.42"	0°13'19.99"	0.476	0.839	0.004	0.027	<0.001

KL14	5°33'16.74"	0°13'20.57"	0.264	0.313	0.004	0.007	<0.002
KL5	5°33'13.25"	0°13'51.24"	0.154	0.893	0.008	0.058	0.004
KL2	5°33'14.90"	0°13'21.94"	0.150	0.087	<0.002	0.037	<0.002
KL62	5°33'13.28"	0°13'51.35"	0.155	0.376	0.008	0.015	0.003
KL10	5°33'11.70"	0°13'25.82"	0.315	0.164	0.002	0.031	<0.002
KL60	5°33'11.81"	0°13'24.74"	0.216	0.33	0.004	0.022	0.003
KL11	5°33'11.81"	0°13'24.31"	0.264	0.651	<0.002	0.008	0.002
KL55	5°33'11.27"	0°13'25.36"	0.206	0.342	0.005	0.035	0.002
KL75	5°33'09.97"	0°13'48.07"	0.171	0.394	<0.002	0.021	<0.001
KL39	5°33'09.14"	0°13'47.89"	0.200	0.466	0.007	0.030	<0.002
KL86	5°33'04.39"	0°13'44.51"	0.158	0.414	<0.002	0.015	<0.002
KL82	5°33'00.14"	0°13'37.78"	0.155	0.283	0.006	0.023	<0.002
KL65	5°32'58.02"	0°13'34.97"	0.162	0.231	0.003	0.105	<0.002
KL83	5°32'57.52"	0°13'34.21"	0.119	0.140	0.002	0.017	<0.001
KL74	5°32'54.96"	0°13'31.55"	0.145	0.224	0.002	0.025	<0.001
KL49	5°32'46.90"	0°13'31.94"	0.469	1.91	0.008	0.018	<0.003
KL31	5°32'44.92"	0°13'32.41"	0.391	0.415	<0.002	0.041	<0.002
KL35	5°32'41.42"	0°13'33.35"	0.248	0.165	<0.002	0.031	0.002
KL80	5°32'40.70"	0°13'33.38"	0.453	0.695	0.012	1.14	0.009
KL36	5°32'39.26"	0°13'33.20"	0.237	0.240	<0.003	0.005	0.003
KL73	5°32'38.94"	0°13'33.35"	0.274	0.339	0.008	0.02	<0.004
KL42	5°32'38.94"	0°13'33.35"	0.294	1.79	0.004	0.024	<0.002
KL59	5°32'33.83"	0°13'29.82"	0.301	0.466	0.004	0.019	<0.003
KL25	5°32'31.52"	0°13'26.04"	0.316	0.195	<0.003	0.016	<0.002
KL19	5°32'31.85"	0°13'19.34"	0.271	0.107	<0.002	0.010	<0.002
KL70	5°32'31.70"	0°13'19.42"	0.210	0.293	<0.003	0.067	<0.002
KL40	5°32'31.72"	0°13'19.42"	0.173	0.188	0.004	0.012	<0.003
KL46	5°32'31.06"	0°13'25.10"	0.212	0.469	0.005	0.096	<0.004
KL34	5°32'30.77"	0°13'19.99"	0.239	0.164	<0.003	0.011	0.006
KL28	5°32'30.34"	0°13'22.87"	0.337	0.317	<0.004	0.014	<0.002
KL33	5°32'30.19"	0°13'20.35"	0.286	0.490	<0.003	0.036	0.003
KL4	5°32'23.71"	0°13'18.91"	0.304	0.647	<0.002	0.006	<0.002
KL54	5°32'23.17"	0°13'18.66"	0.088	0.422	<0.007	0.011	<0.005
KL71	5°32'23.17"	0°13'18.66"	0.265	0.055	<0.009	0.008	<0.008
KL87	5°32'22.63"	0°13'18.19"	0.042	0.574	<0.011	0.078	<0.010
KL7	5°32'21.73"	0°13'17.83"	0.341	0.599	<0.003	0.014	0.020
KL13	5°32'19.50"	0°13'16.43"	0.342	0.624	0.004	0.012	<0.003
KL93	5°32'30.16"	0°13'20.57"	0.207	0.346	<0.004	0.016	<0.004
KL30	5°32'17.23"	0°13'14.92"	0.237	0.420	<0.003	0.005	<0.002
KL12	5°32'15.86"	0°13'10.34"	0.274	0.181	<0.004	0.013	<0.004

KL61	5°32'15.65"	0°13'11.39"	0.138	0.391	0.006	0.015	<0.005
KL22	5°32'15.76"	0°13'11.24"	0.286	0.317	<0.003	0.016	<0.003
KL24	5°32'15.58"	0°13'12.22"	0.371	0.434	<0.004	0.014	0.007
E43	5°31'57.43"	0°13'16.28"	<0.033	0.342	0.017	0.015	<0.014
E21	5°31'57.54"	0°13'16.36"	<0.062	0.094	<0.032	<0.029	<0.028
E8	5°31'55.45"	0°13'16.79"	<0.053	0.718	0.053	<0.025	<0.023
E45	5°31'54.62"	0°13'10.60"	0.022	0.299	<0.010	<0.009	<0.009
E32	5°31'53.69"	0°13'17.44"	<0.08	0.476	<0.042	<0.038	<0.037
E84	5°31'53.40"	0°13'17.69"	<0.038	0.198	<0.020	<0.017	<0.017
E23	5°31'53.90"	0°13'11.10"	<0.046	0.127	<0.023	0.024	<0.020
E78	5°31'53.62"	0°13'11.39"	<0.066	0.463	<0.036	0.143	<0.032
E47	5°31'52.50"	0°13'17.87"	<0.037	0.267	<0.019	<0.017	<0.017
E20	5°31'52.46"	0°13'13.94"	<0.057	0.124	0.029	<0.027	<0.026
E76	5°31'52.46"	0°13'13.30"	<0.057	0.097	<0.030	<0.028	<0.027
E53	5°31'52.00"	0°13'14.52"	<0.022	0.252	<0.011	0.017	<0.010
E77	5°31'52.14"	0°13'14.52"	<0.053	0.245	<0.028	0.031	<0.026
E29	5°31'48.29"	0°13'17.80"	<0.091	0.969	<0.047	0.217	<0.043

APPENDIX B Parameters for semi-variogram fitting

Table B1 Parameters for semi-variogram fitting for spatial distribution of elements in surface dust.

Elements	Model	Nugget (C ₀)	Partial Sill (C+C ₀)	Sill (C ₀ /C+C ₀)	Range (m)
Cr	Exponential	0.022	0.227	0.249	21.31
	Gaussian*	0.022	0.228	0.25	13.18
	K-Bessel	0.022	0.240	0.262	15.47
	Spherical	0.017	0.263	0.28	21.31
V	Exponential	0.087	0.106	0.193	683.43
	Gaussian*	0.105	0.112	0.217	511.60
	K-Bessel	0.105	0.012	0.117	558.93
	Spherical	0.094	0.104	0.198	554.46
Mn	Exponential	0.218	0.398	0.616	738.32
	Gaussian*	0.289	0.380	0.669	519.06
	K-Bessel	0.289	0.393	0.682	563.38
	Spherical	0.245	0.418	0.663	658.30
Ni	Exponential	1.400	0.001	1.400	971.74
	Gaussian*	0.753	3.803	4.556	971.74
	K-Bessel	0.753	3.395	4.148	971.74
	Spherical	0.800	1.3440	2.144	971.74
Cu	Exponential	0.736	0.515	1.251	70.66
	Gaussian*	0.823	0.420	1.243	75.44
	K-Bessel	0.825	0.422	1.247	94.89
	Spherical	0.768	0.456	1.224	77.96
Zn	Exponential	0.284	0.195	0.479	82.00
	Gaussian*	0.318	0.150	0.468	56.89

	K-Bessel	0.319	0.152	0.471	60.46
	Spherical	0.293	0.170	0.463	60.46
Mo	Exponential	0.442	0.191	0.633	28.77
	Gaussian*	0.392	0.243	0.635	16.02
	K-Bessel	0.395	0.241	0.636	17.07
	Spherical	0.464	0.153	0.617	22.16
Cd	Exponential	0.340	0.165	0.505	93.27
	Gaussian*	0.355	0.150	0.505	68.59
	K-Bessel	0.355	0.153	0.508	73.30
	Spherical	0.345	0.153	0.498	78.34
Ba	Exponential	0.188	0.032	0.220	15.24
	Gaussian*	0.156	0.077	0.233	11.12
	K-Bessel	0.155	0.076	0.231	11.12
	Spherical	0.170	0.051	0.221	11.12
Pb	Exponential	0.698	0.013	0.711	22.24
	Gaussian*	0.588	0.156	0.744	14.11
	K-Bessel	0.593	0.153	0.746	15.14
	Spherical	0.661	0.055	0.716	14.98

*Gaussian models were selected for fitting the semivariogram

APPENDIX C Diffractogram of surface dust samples

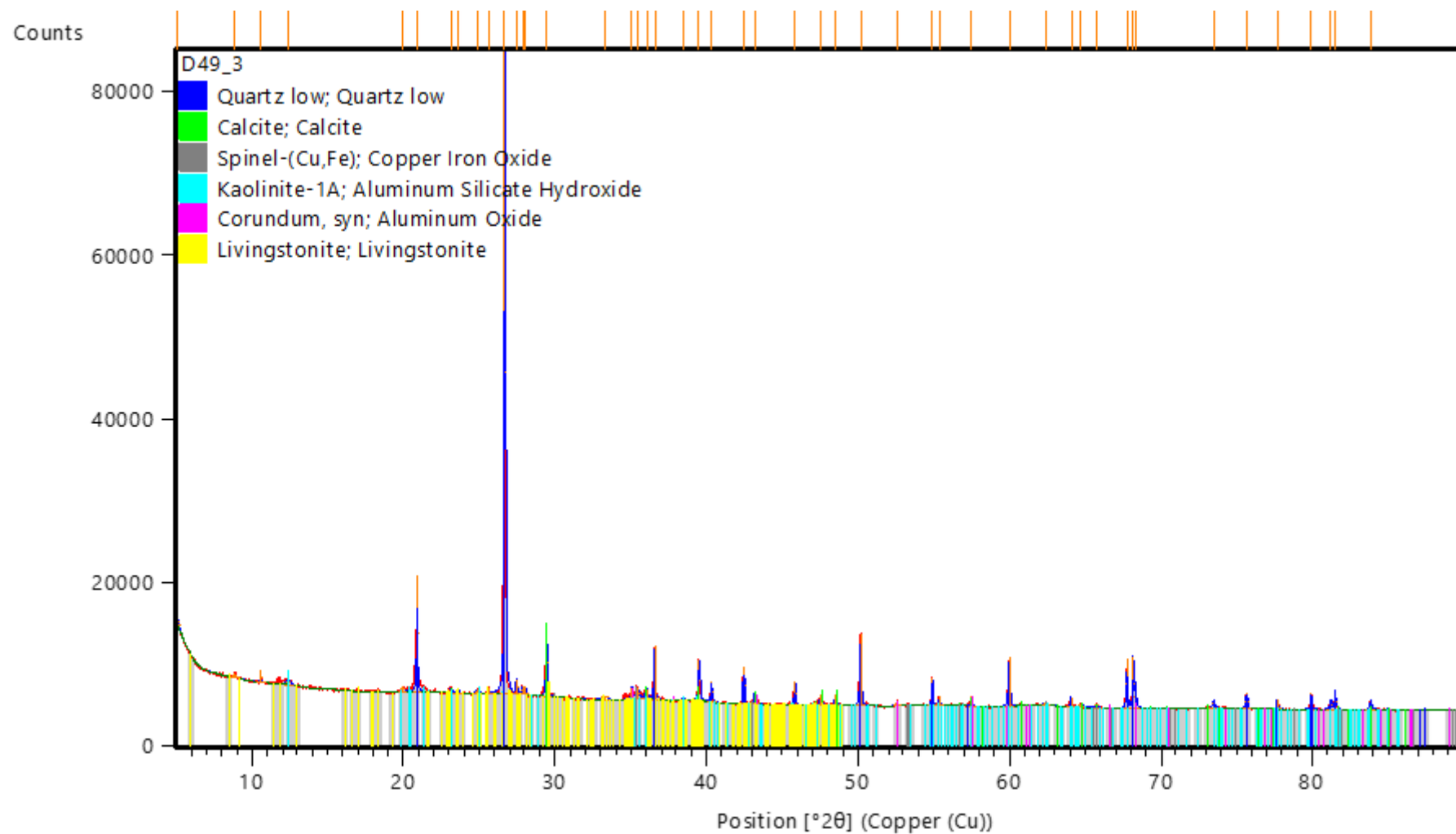


Figure C1 Diffractogram of surface dust sample (D49_3).

APPENDIX D Location of urban gardens near Agboglobloshie e-waste recycling site

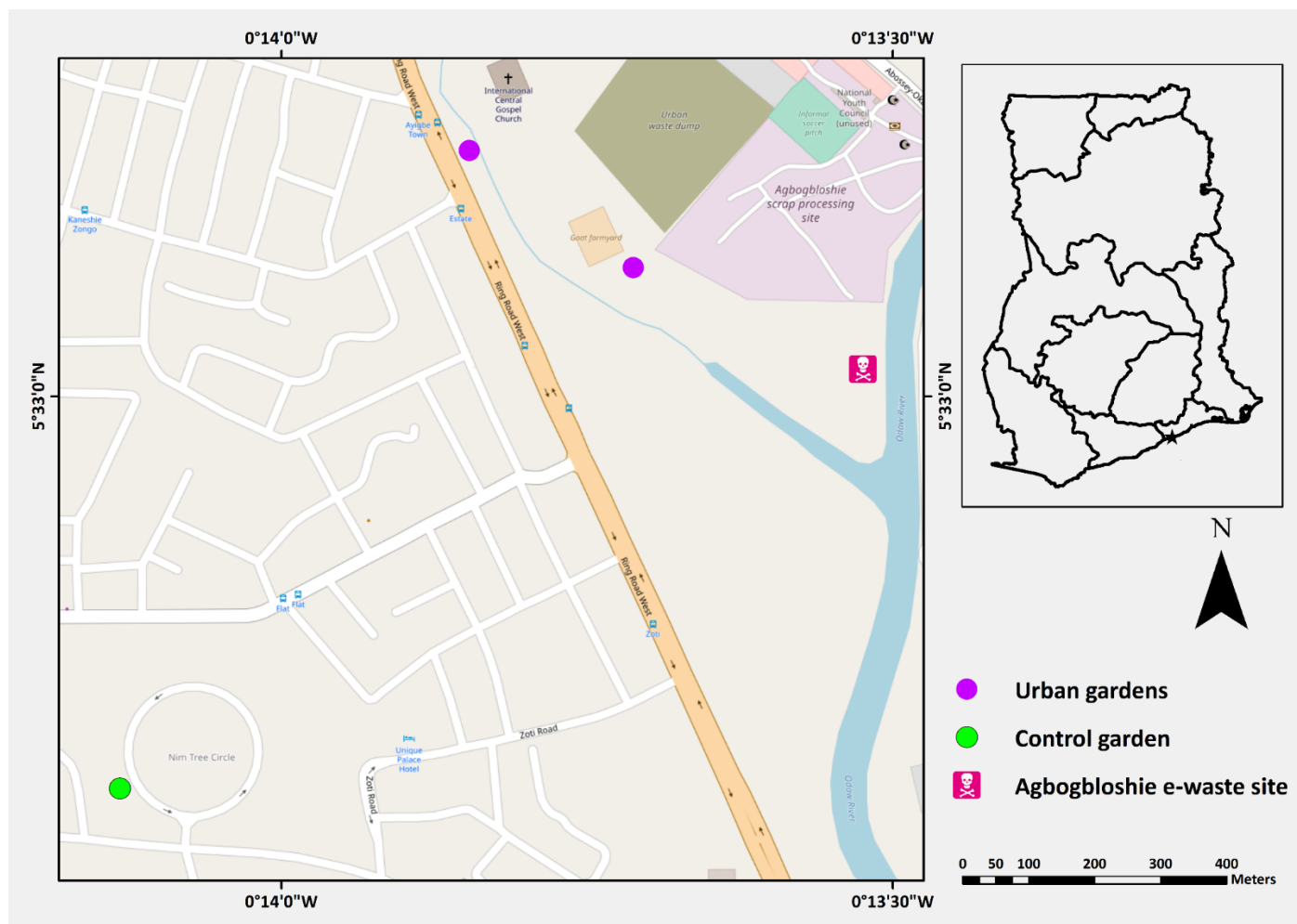


Figure D1 Location of urban gardens near Agboglobloshie e-waste recycling site

APPENDIX E Bioaccessibility (%) of metal(loid)s in vegetables in two urban gardens near Agbogbloshie e-waste recycling site

Table E1 Bioaccessibility (%) of metal(loid)s in vegetables in two urban gardens near Agbogbloshie e-waste recycling site.

	Garden 1					Garden 2				
Vegetables	Mn	Fe	Cu	Zn	Pb	Mn	Fe	Cu	Zn	Pb
African eggplant	150	11	59	184	<25	86	13	35	55	<7
Hibiscus	108	19	83	130	50	27	3	31	31	5
Lettuce	31	1	50	70	14	104	7	40	92	33
Egyptian spinach	67	7	38	69	25	89	12	70	109	33
Amaranth	a	a	a	a	a	73	14	31	40	13

^a Amaranth not sampled for garden 1. Bioaccessibility (%) was not measured in Amaranth for garden 1.

Pages of this thesis have been removed as they contain published material. Please refer to the following citation for details of the articles contained in these pages.

Ackah, M. (2017). Informal e-waste recycling in developing countries: review of metal(lloid)s pollution, environmental impacts and transport pathways. *Environmental Science and Pollution Research* 24(31) p. 24092-24101.

doi: 10.1007/s11356-017-0273-y

Ackah, M. (2019). Soil elemental concentrations, geoaccumulation index, non-carcinogenic and carcinogenic risks in functional areas of an informal e-waste recycling area in Accra, Ghana. *Chemosphere*, 235 p. 908-917

doi: 10.1016/j.chemosphere.2019.07.014