Waste management and impact on people's health when cultivating on sites contaminated with heavy metals
– Minor field study made in Zomba, Malawi

Sofie Orvestedt

Master's Thesis in Environmental Science
Soil and Water Management – Master's Programme

Abstract

This minor field study was executed in Zomba, Malawi, where land for cultivation is scarce, resulting in cultivation at potentially contaminated sites. Waste dumps are one of the main sources of heavy metal contamination and excessive levels in soil might lead to elevated levels in crops which can cause severe health effects. The objective of this study was to investigate how the current waste management affects the health of the local inhabitants when cultivating at contaminated sites, focusing on heavy metals. Two sites were studied: one field on a waste dump (WD) and one field close to a waste water treatment plant (WWTP). The hypothesis was that soil and crops contained higher concentrations of heavy metals close to these sites compared to a reference site. Samples of soil and crops were collected and analysed for cadmium, chromium, copper, iron, lead and zinc. The daily intake of these metals via maize was further calculated for the farmers to investigate possible health effects.

Comparing the results to The Swedish Environmental Protection Agency's generic guideline values, levels are exceeded for copper, cadmium and lead at the waste water treatment plant, and cadmium at the waste dump. This does not classify the sites as contaminated but indicates excessive levels. It is also important to emphasize the uncertainty of the gained results which are inaccurately high. However, comparing the sites in the study, the concentration of zinc was significantly higher at both sites compared to the reference site regarding both soil and maize. A significant difference was also found for copper at WWTP regarding soil and at WD regarding maize. In general, there were tendencies for higher amounts of heavy metals at the study sites compared to the reference site, indicating that farming at the study sites has a higher probability to affect human health compared to farming at the reference site. Regarding tolerable daily intake, consumption was exceeded for cadmium and lead at all sites including zinc for children. Copper consumption was also exceeded for children at the waste dump.

Unfortunately, this study was limited by several factors such as broken equipment and the results must be interpreted with this in mind. Recommended future actions are to perform a thorough risk assessment at the locations with improved methods and also include other hazards such as pathogens. In general, waste management should be made a higher priority where waste is disposed in a better way, e.g. a landfill, and cultivations at contaminated sites are avoided.

Popular summary

Eating contaminated food or not eating at all

Malawi is a fantastic country with incredibly friendly people but unfortunately it is one of the poorest countries in the world. The population density is high which results in a lack of farmland for the people. People grow crops and plants everywhere, making Malawi fantastically green and beautiful during the rainy season. However, this has also led to people growing crops at sites where waste or waste water is disposed. These sites might be contaminated with heavy metals. People should not grow crops on these sites since heavy metals in the ground might make their way into the plants thereby creating a risk of heavy metals being consumed. Unfortunately, not all people in the world can decide whether to avoid eating contaminated food or not. In Zomba, one of Malawi's four cities, people are farming on the official waste dump and close to a waste water treatment plant. The farmers have no protective clothes, no boots and sometimes not even shoes when walking on fields with plenty of broken glass. Not many people in Malawi are aware of the risks they are exposed to and instead consider these sites good locations for farming since it brings nutrients to the field, increasing their harvests.

Heavy metals are naturally found in the soil but mankind increases these levels in some places through industry or by placing waste in big piles. Some heavy metals are necessary for humans, but only in very small amounts. In general, they are toxic pollutants and dangerous to humans. Cadmium, chromium and lead are three of the most environmentally hazardous heavy metals since they are very toxic and frequently used in the society. A consumption of these kinds of metals, a large variation of health effects can arise ranging from reduced learning ability, increased blood pressure to promotion of cancer. Humans are mainly exposed to heavy metals by food and air but since there is not much we can do about the air, we therefore have to focus on what we eat. To find out if these farmers health is effected or not, soil and crops from the fields were examined so see if the levels of heavy metals were above the limits set by e.g. the World Health Organization.

Unfortunately, this study showed indications of high levels of heavy metals and that the farmers might be consuming too high levels of cadmium and lead from maize at all sites and also copper at the waste dump. Children eating the same amount of maize also consumed too much zinc. Hopefully, the local government will help the people to better fields for farming in the future and at least inform them about the risk they are exposed to.

Preface

This master thesis was a Minor Field Study financed by the Swedish International Development Cooperation Agency (Sida). The field work was carried out during February and March 2015 at the Department of Chemistry, Chancellor College in Zomba, University of Malawi. This master thesis was partly written in collaboration with fellow student Sabina Braun. All planning and performance of sampling and analysing were performed together which is why some parts presented in appendices were written together. This was done in an attempt to approach a problem from two different angles, one environmental aspect and one agricultural. The idea is that our master theses will, in some ways, complement each other. While my aim was environmental and focused on waste management and food safety, Sabina's focus was on agricultural history, use of fertilizers and food security. Therefore, if there is interest regarding those topics, Sabina Braun's mater thesis "The impact of solid waste and waste water on small-scale farming in Malawi" is further recommended.

Table of content

1. Introduction

Malawi is one of Africa's most densely populated countries and one of the poorest countries in the world (Swedish Institute for International Affairs 2011; United Nations Development Programme 2014). The life expectancy is very low and has during the later decades decreased due to poverty, malnutrition and HIV/AIDS. However, with the high birth rate of 3.33 %, the population is still increasing rapidly (The Central Intelligence Agency 2014; Swedish Institute for International Affairs 2011). About 85 percent of the population live in rural areas depending on rain-fed agriculture where droughts and floods lead to poor crop yields or no yields at all (National Statistical Office 2012; Magrath and Sukali 2009). In fact, only weeks before this study, a devastating flood affecting nearly a quarter of a million people ripped through Malawi. Hundreds of people died, crops were destroyed, livestock killed, homes swept away and the President declared half the country a disaster zone (Chonghaile, 2015). In countries like Malawi where the food supply is insufficient, people have a tendency to shift to more unsafe food (World Health Organization, 2014). In Zomba, this can be observed by farmers growing crops at potentially contaminated sites such as on the official waste dump and close to the waste water treatment plant.

The use of open dumps is the most common way to dispose waste in developing countries where waste is simply put in piles. In Malawi, this is the second most common way of disposal after waste pits, where waste is instead dug down in the backyard (Guerrero et al. 2013; National Statistical Office 2012). Vegetables usually accounts for about 60 percent of the waste in low-income countries and only 8 percent in total is plastics, glass and metals (Baird and Cann 2008). However, increasing population, rapid urbanization and higher living standards accelerates the waste generation in developing countries and changes the composition of the waste (Minghua et al. 2009; Baird and Cann 2008). Many heavy metals can be found in waste and waste water and it is well recognized that heavy metals can be toxic pollutants and even though several are essential for humans, excessive levels can be harmful (Naseri et al. 2014; Sajidu 2008; Berggren Kleja et al. 2006). The primary exposure to heavy metals is by food and air, and metals cannot be detoxified by the human body but instead tend to accumulate in different tissues (Sajidu 2008; Naseri et al. 2014). Cadmium, chromium and lead are three of the most environmentally hazardous heavy metals due to their extensive use in the society, toxicity and widespread distribution, and consumption of these toxic metals causes severe health effects ranging from neurological damage to cancer (Baird and Cann 2008; Naseri et al. 2014; Sajidu 2008).

1.1 General and specific objective

The general objective of this study was to investigate how the current waste management affects the health of the local inhabitants in Zomba, Malawi, cultivating at contaminated sites, with a focus was on heavy metals.

The specific objectives were:

i. To study the major environmental issues
ii. To investigate the current waste management
iii. To sample and analyse for heavy metals at fields close to a waste dump and a waste water treatment plant in Zomba to find out if they are contaminated with heavy metals and might possess a health related threat
iv. Through this aspire to make contributions in creating a more sustainable waste management system

1.2 Hypothesis

The hypothesis was that soil and crops contained a higher concentration of heavy metals at fields close to the waste dump and waste water treatment plant compared to a reference site.

Null hypothesis: There are no significantly higher heavy metal concentrations between the study sites compared to the reference site.

> Indicating that farming on the study sites *does not* affect human health compared to farming on the reference site.

If rejected: The study sites have significantly higher concentrations of heavy metals.

> Indicating that farming on the study sites *does* affect human health compared to farming on the reference site.

1.3 Limitations and delimitations

The sampling in this study was delimited to be performed at one waste dump, one waste water treatment plant and one reference site due to that Zomba only has one waste dump and one waste water treatment plant. The reference site is only meant to be used as a simplified comparison to an area not intentionally contaminated. This is important since no information about background levels or previous contaminations at the reference site are known and the natural variation might be significant. Since no drinking water was found at either site, this part had to be omitted.

The study was planned to investigate several heavy metals by using Microwave Plasma - Atomic Emission Spectroscopy (MPAES) but since the instrument was broken, this had to be omitted. Instead Atomic Absorption Spectroscopy (AAS), using a Buck Scientific Model 200A instrument, was used. Due to further limitations in functioning lamps, the study was delimited to Cd, Cu, Fe, and Zn. Unfortunately, even the functioning lamps were old and overused which is why Cd was controlled at SLU using AAS. To secure the data quality, Cr and Pb were analysed at SLU as well. Therefore, the heavy metals discussed in this thesis are Cd, Cr, Cu, Fe, Pb and Zn with focus on Cd, Cr and Pb due to their toxicity.

The Swedish Environmental Protection Agency's (SEPA) tolerable daily intake (TDI) limits were used since they have complied values from World Health Organization (WHO), United States Environmental Protection Agency (USEPA) etc. SEPA's generic guideline values for contaminated soil were also used since Malawi did not have any values of their own. It was intended to use modelling for estimating exposure but this was not possible due to a lack of information for several parameters. Further, the project was designed with the aim to be possible to repeat in the future. Therefore, methods possible to perform at the university in Zomba were chosen even if they might not be optimal. This was further limited by a lack of chemicals and equipment. Since the study took place during the rainy season, weather contributed as a limitation, shortening the time for sampling and following analyses.

1.3.1 Earlier research

No earlier research with the same objectives was found. As far as known, no heavy metal analyses have been done at the sites. Earlier research regarding Malawi and waste management is presented under each section in *Background* (chapter 2). Earlier studies and results regarding metal content in maize are found under section *3.2.3 Plant uptake in maize* in *Theory*.

2. Background

2.1 Malawi – The warm heart of Africa

Malawi is a small landlocked country located in Southeast Africa with an area of 118 484 km^2 of which surface water bodies covers about 20 percent (Food and Agriculture Organization of the United Nations, 2006). With a population of 17,4 million people, Malawi is one of Africa's most densely populated countries (The Central Intelligence Agency 2014; Swedish Institute for International Affairs 2011). This study took place in Zomba City, one of Malawi's four cities, located in the southeast. The south is the most densely populated region and particularly regarding the rural areas (Swedish Institute for International Affairs 2011; National Statistical Office 2012). About 85 percent of the population live in rural areas which leaves only 15 percent living in urban areas (National Statistical Office, 2012). The agricultural sector is Malawi's most important sector where about 85 percent of the economically active population are engaged. This sector is mainly constituted of small scale subsistence farming. The most important crop is maize, which is cultivated by almost all farmers (Rundquist, u.d.). The landholdings are in general small with an average of 0.23 ha arable land for the smallholding farmers. These lands are densely cultivated, causing overuse and degradation of agricultural land (World Food Programme, 2015). Instantly after arriving in Zomba, it was observed that all areas possible for cultivating were used for that purpose.

Malawi is one of the poorest countries in the world. The Human Development Index Value for Malawi is 0.414 which ranked the country 174th out of 187 countries in 2013 (United Nations Development Programme, 2014). The life expectancy is very low and has during the later decades decreased due to poverty, malnutrition and HIV/AIDS. However, with the high birth rate of 3.33 %, the population is still increasing rapidly (see Figure 1a) (The Central Intelligence Agency 2014; Swedish Institute for International Affairs 2011). In 2000, Malawi's population was 11.3 million people and with the current birth rate, the population is expected to increase to 22.8 until 2025 (The World Bank, 2013). Malawi also has a very young age composition, with almost 50 percent of the population below the age of 15 (see Figure 1b) (The Central Intelligence Agency, 2014).
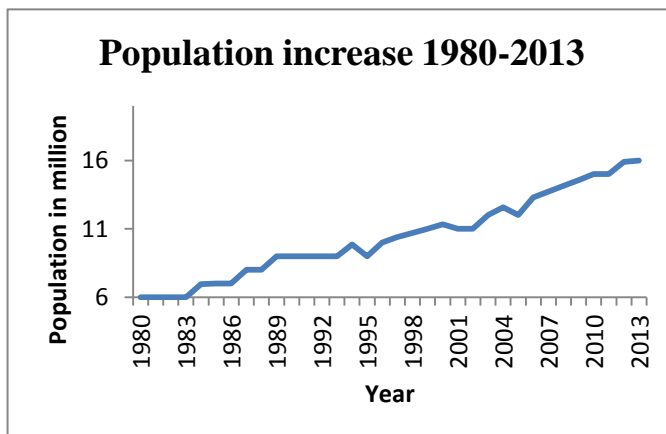
Figure 1a- Malawi's population increase from 1980 to 2013 (The World Bank Group, 2013)
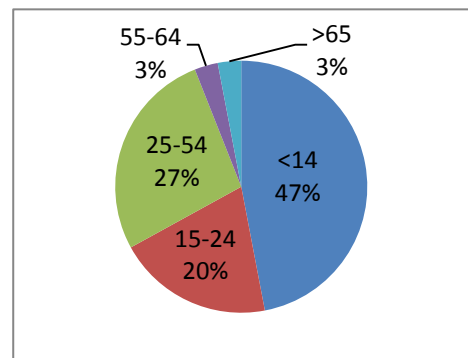
Figure 1b - Age distribution in Malawi in percent of total population (The Central Intelligence Agency, 2014)

2.1.1 Geology and climate

The topography is characterized by extreme diverse physical features, divided into four major physiographic zones: (Food and Agriculture Organization of the United Nations, 2006)

- − The highlands in the south;
- − The plateau of the central and northern regions;
- − The rift valley escarpment;
- − The rift valley plains along the lakeshores of Lake Malawi

The climate in Malawi is tropical continental with large influences from the considerable water mass of Lake Malawi. There are three seasons throughout the year: (Food and Agriculture Organization of the United Nations, 2006)

- − Rainy season from November to April
- − Cold dry season from May to July
- − Hot dry season from August to October

The annual rainfall ranges from 700 to 2400 mm with a mean annual rainfall of 1180 mm. The rainfall distribution is mainly influenced by topography and distance to Lake Malawi. Since Zomba is located on a higher altitude and mountainous area, the rainfall is at the highest here (Food and Agriculture Organization of the United Nations, 2006). In Figure 2 to the right, the massive Zomba Plateau located just above Zomba can be seen.

Temperature is also predominantly influenced by the topography and decreases with increasing altitude. The mean temperature has a maximum and minimum of 28 and 10°C in the plateau areas (such as Zomba) and 32 and 14°C in the rift valley plains (Food and Agriculture Organization of the United Nations, 2006).
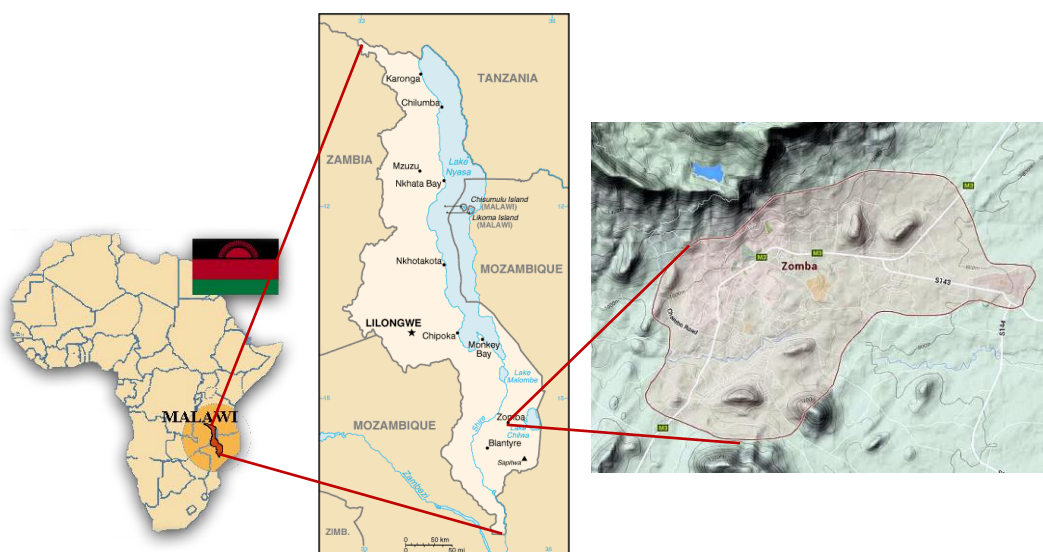
Figure 2 – To the left: A map of Africa showing the location of Malawi. In the middle: A more detailed map over Malawi where Zomba is located in the south. To the left: An elevation map of Zomba (highlighted) showing the massive Zomba Plateau just above (Malawi Orphan Care Project, 2015) (The Central Intelligence Agency, 2014) (Google, 2015).

2.1.2 Environmental issues

Malawi's rapid population growth results in a high pressure on land. Cultivation is expanding and fallow periods for restoring soil fertility have been significantly reduced. This leads to severe deforestation, soil erosion and an overall degradation of nature's reserves (Food and Agriculture Organization of the United Nations, 2006). According to CIA, Malawi's current environmental issues are, deforestation, land degradation, water pollution from agricultural runoff, sewage, industrial wastes and siltation of spawning grounds endangering fish populations (The Central Intelligence Agency, 2014). During the study, observations of eutrophication in Shire River were also made. A probable cause is the high soil erosion and surface runoff bringing nutrients into the river.

Magrath and Sukali reported in 2009 that the people in Malawi have noticed changes in the climate for the last decades. According to them people states that the temperature is getting hotter, rain season is becoming more unpredictable where rain arrives later and is more intense. This results in shorter growing seasons and triggers more droughts and floods. The Malawians does not connect these changes with greenhouse gases but with environmental changes close to home – deforestation (Magrath and Sukali 2009). Malawi has the highest deforestation rates in southern Africa with 2.8 percent and a decline of nearly 13 percent between 1990 and 2015 (World Food Programme 2015; Magrath and Sukali 2009). This is primarily due to the increasing population's lack of any other form of fuel than charcoal for cooking. As in many poor societies, the burning of trees is the key to livelihood and often the difference between having food on the table or not. Unfortunately, when forests are cut down, people also lose access to forest grown food (World Food Programme 2015; Magrath and Sukali 2009). Even if it will not stop global warming, there are current efforts for planting more trees. This might help people to cope with the impacts by shading the soil and reducing evaporation, act as wind breakers, reducing soil erosion and also increase the access to fruits and timber. One of the most important aspects is that an increased tree cover is likely to soak up groundwater and smooth out water flows, thus reducing sudden flooding and soil erosion (Magrath and Sukali 2009). Since the majority of the population is dependent on agriculture, the people are highly vulnerable to the effects of natural disasters such as annual dry spells and flooding (World Food Programme, 2015). Therefore, it is also important to mention Malawi's dangerous over-dependency on maize which is the staple crop practically everyone depends on. It is hence important to boost agricultural productivity and diversity of crops to build resilience to climate change (Magrath and Sukali 2009).

Malawi's government has developed and desires to implement a list of priority in order to start adapting to climate change. Malawi's National Adaptation Programmes of Action aim is to improve community resilience, restore forests, improve agricultural production, and improve preparedness for floods and droughts and boost climate monitoring. Unfortunately, so far as 2009, this has not been funded. However, more and more tree nurseries are springing up, local governance on cutting down trees is being tightened up and environmental awareness is rapidly spreading among the population (Magrath and Sukali 2009).

2.2 Municipal solid waste

Municipal solid waste (MSW) is defined as "Wastes generated by households, and wastes of a similar nature generated by commercial and industrial premises…" (United Nations Human Settlements Programme, 2010). The great majority of MSW is simply garbage and not hazardous at all. Generated waste and its composition vary greatly between countries and depend mainly on economic development. In North America, domestic and commercial waste generates about 2 kg/capita/day which are twice as much as Europe's average. As can be seen in Figure 3, the fraction of the waste being vegetable matter declines as the level of economic development rises while the opposite occurs for paper. In industrialized countries, food waste accounts for 25 percent while plastic, glass and metal accounts for almost 30 percent in total. Vegetables accounts for about 60 percent of the MSW in low-income countries and only 8 percent in total is plastics, glass and metals (Baird and Cann 2008). However, increasing population, rapid urbanization and higher living standards accelerates the MSW generation in developing countries and changes the composition of the waste as well (Minghua et al. 2009; Baird and Cann 2008).
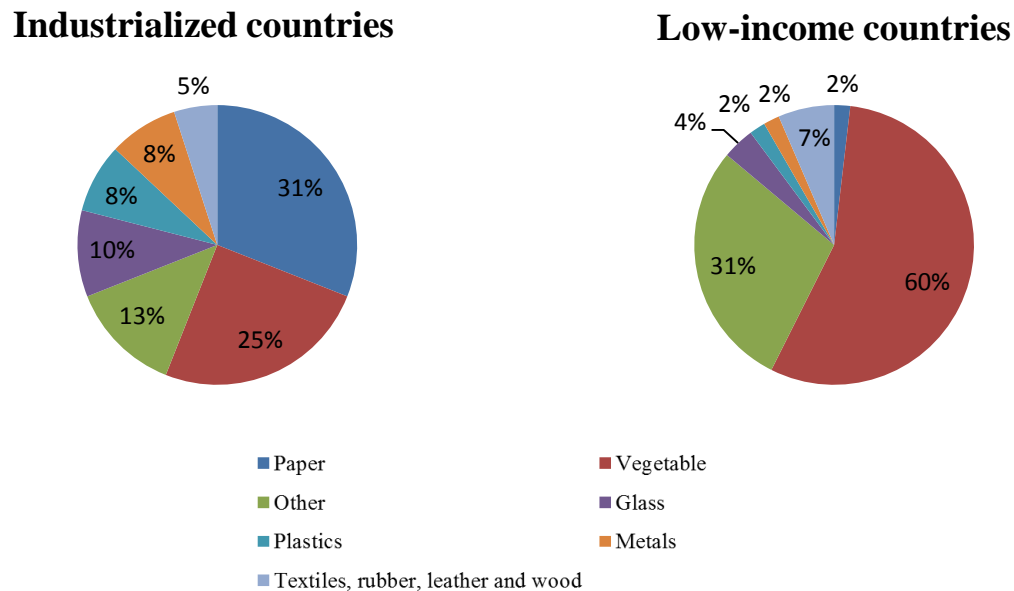
Figure 3 - Typical composition of solid waste at different levels of economic development (Baird and Cann 2008)

2.2.1 Solid waste management

In an attempt to conserve natural resources, including energy, and to reduce the volume of waste for incineration or deposition, the waste management philosophy is to reduce the amount of material used, reuse materials already produced, recycle material to recover components that can be refabricated, recover the energy content of the materials and finally disposal as a last option (see Figure 4) (Baird and Cann 2008; Swedish Environmental Protection Agency 2012).

Metal recycling is reasonable from both economical and energy conserving point of views. Almost all metals in Earth's crust are present in oxidised form and the reduction process requires energy that is not needed again when the metallic form of the element is recycled. For example, if aluminium cans are recycled, 95 % of the energy needed to produce aluminium metal from bauxite ore is saved and aluminium can be recycled endlessly without any loss in quality. One problem with recycling is the collection of material, especially in developing countries. In Sweden this is solved by deposits on beverage containers that are refunded upon their return resulting in an 85 % collection of aluminium cans (Baird and Cann 2008).

Incineration is the second most common way of disposal, especially organic and biological waste, where materials are oxidised by controlled burning to simple, mineralized products such as carbon dioxide and water. The main intention of incineration is to reduce the volume of waste to be deposited, resulting in about 1/3 of the initial waste volume. The second intention is the possibility to recover heat from the combustion and to convert it into steam, hot water or electricity. The main environmental concern about incineration is air pollution consisting of both gases and particles. Heavy metal emissions from waste management accounts for a high percentage of the total heavy metal discharge into the atmosphere. However, emission controls on MSW incinerators can control a large fraction of the toxic substances emitted. Even though fly ash only accounts for 10-25 percent of the total ash mass, it is generally the more toxic component, since heavy metals condense onto the small particles. The ashes low density and small-particle character gives a significant risk of unintentional emissions into the environment where heavy metals are of particular concern since they can pollute nearby surface waters and groundwater (Baird and Cann 2008).
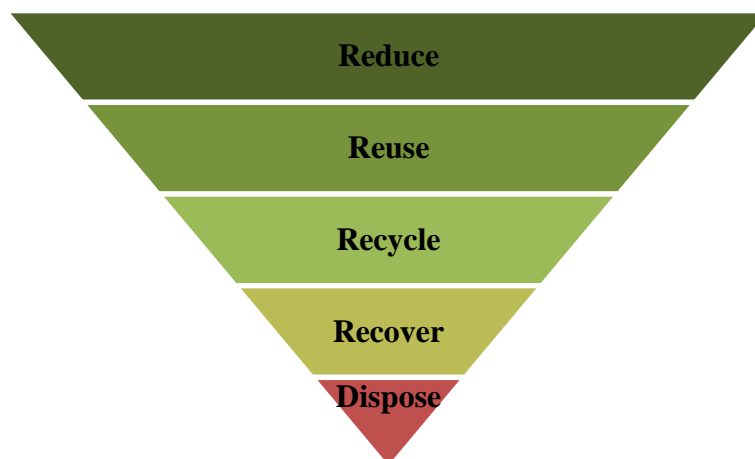
Figure 4 - The five steps of the waste hierarchy

8

Mainly due to substantially lower costs, the most common way of disposal are landfills which are basically holes in the ground that are usually covered with soil after filling (Baird and Cann 2008). Even though the technology is simple, landfills involve a complex organic process. To make sure the operation is efficient and the environmental impact as low as possible, landfills need to be carefully sited, correctly designed and well operated (Schübeler, 1996). Landfills result in a concentration of contaminants in a limited area. These substances will eventually leach into the surroundings, causing a risk to human health and the environment through pollution of soil and water. The extent of the effects from a landfill on human health and environment depend on its location, safety measures and the properties of the waste (Swedish Environmental Protection Agency, 2012). Modern landfills have a much more advanced design and often no hazardous waste is accepted. It is preferably placed on top of clay or plastic to avoid leakage and possibly even have a leachate collection system (Baird and Cann 2008). Open dumps are even less advanced where waste is basically just placed in a pile without any protection. This is an environmental hazard causing ecological imbalances in respect to land, water and air pollution (Sharholy et al. 2006).

Solid waste management in developing countries
Most disposal sites in developing countries are open dumps without treatment, bottom protection or other necessary infrastructure. Besides official disposal sites, cities often suffer from illegal disposal of waste in rivers, lakes, channels, empty lots and roadsides (Guerrero et al. 2013). Municipal Solid Waste Management (MSWM) is a big responsibility for local governments and includes collection, transfer, treatment, recycling, resource recovery and disposal of solids waste in urban areas (Schübeler, 1996). Providing an effective and efficient system in developing countries is difficult and problems beyond their ability often occur, mainly due to a lack of organization and financial resources (Sujauddin 2008; Burnley 2007). The main goal of MSWM is to protect the health of the population, especially the low-income population which are those who suffer most from poor waste management. Secondly, the aim is to promote environmental protection by controlling pollution. Further, MSWM supports economic development by providing waste management services and conserving valuable material and resources. MSWM also aims to generate employment and profits to the sector itself (Schübeler, 1996).

Unfortunately, MSWM in most cities of developing countries are highly unsatisfactory where a large part of the population have no access to waste collection services at all resulting in only a fraction of the generated waste being collected (Schübeler, 1996). In a literature review made by Guerrero, a variety of factors affecting waste management were presented. Technical factors are related to a lack of technical expertise among employees, inadequate technologies, insufficient infrastructure and poor roads and vehicles. Improper collection systems are also often affected by poor route planning and lack of information. The absence of financial support, resource limitations, people's unwillingness to pay for the service and a lack of proper use of economic instruments hampers proper waste management services. Another important factor influencing the waste management in developing countries is the environmental factor, mainly a lack of environmental control systems and evaluations of environmental and health impacts (Guerrero et al. 2013).

To achieve the goals of MSWM, it is essential to establish a sustainable waste management system where the entire urban population's needs are met, including the poor whom suffer most from poor waste management. The most important factor is the collaboration between the population and the local government. The authorities should enhance public awareness and educate the importance of MSWM and environmental protection. The system must be suitable for the city's particular circumstances and demanding services. In developing countries, the technical equipment etc. must be chosen carefully with regard to function and cost where a special attention is paid to repair possibilities and availability of spare parts. Identifying sources of hazardous material is important and that waste should be registered and targeted for appropriate management and kept out of municipal waste systems. The financial limitation is best solved with user charges, local taxes and intergovernmental transfers, where the first stated is of clear preference. However, collecting a fee is often difficult to achieve but can be solved by attaching the fee to some other service, like water supply (Schübeler, 1996).

The highest priority of MSWM must be given to effective collection and disposal but waste reduction and recycling etc. needs to be seen as equally important in the long-term objective. The most suitable method for final disposal in developing countries is practically always a sanitary landfill. To reduce the environmental impact as much as possible, the landfill should be carefully sited, correctly designed and well operated. It is hardly ever possible to go from open dumps to a fully sanitary landfill in one step. Instead, a transformation process can be planned, where dumping of waste is gradually improved and present sites updated. This should actually be encouraged instead of waiting for possibilities to construct a completely new and properly designed landfill (Schübeler, 1996).

Recycling might seem far away but recycling companies have appeared in some cities in developing countries due to an increase in prices on secondary materials which in turn seems to have promoted separation at household level. This was presented in a review done by Guerrero et al. where findings also suggest that when people learn about the benefits of recycling, how waste should be sorted and possibilities to take part in designing of the programs, people are more likely to participate in recycling campaigns. Of course, the accomplishment of a functioning recycling system does not only rely on participation levels but also on the efficiency of the equipment and infrastructure. However, the review also found that when municipal leaders are interested and prioritise waste issues, they support strategies including more efficient collection systems, better infrastructure and low cost recycling technologies (Guerrero et al. 2013).

Waste management in Malawi

In a study made in Malawi's capital Lilongwe in 2009, it was shown that waste origin arriving at the official disposal site was only household waste. The waste generation rate in 2009 was estimated to 0.50 kg/capita/day (Guerrero et al. 2013). As seen in Table 1, the most common method of waste disposal in households in Malawi is waste pits, where the waste is dug down at home. During a household survey 2010-2011, 49 percent of the rural households reported using waste pits while it was 55 percent in urban households. The second highest means of disposal is public waste heaping where about 20 percent of the households reported using this method. This was also observed at many locations in Zomba, especially at trading centres. About 17 percent of the households reported using no means of disposing their waste. This is more severe in rural areas than urban areas. 7.7 percent burn their waste while only 4.4 percent of the waste in Malawi is collected to a waste dump (Fee figure 5) (National Statistical Office, 2012).

Table 1 - Percentage distributions of households by kind of waste disposal used by residence in Malawi 2011 (National Statistical Office, 2012)

Residence	Kind of waste disposal (%)					
	Collected from waste bin	Waste pit	Burning	Public waste heap	Other	None
Malawi	4.4	49.0	7.7	20.1	1.9	17.1
Urban	17.7	55.4	2.6	13.9	1.0	9.4
Rural	1.9	47.8	8.6	21.2	2.0	18.5
Zomba	1.4	48.8	15.5	19.4	0.8	14.1
Zomba City	12.2	57.9	6.6	17.6	0.0	5.7

Figure 5 - The official waste dump in Zomba, Malawi (Orvestedt, 2015)

2.3 Food safety

Food safety means that people should be guaranteed that the food will not cause harm when consumed according to its intended use (Codex Alimentarius Commission, 2003). This is in some ways included or at least connected to food security which exists when a person has permanent physical and economical access to sufficient, safe and nutritious food to meet his or hers dietary needs and preferences for an active and healthy life (National Statistical Office, 2012). Malawi still suffers from food insecurity in large parts of the country and starving events occurred as late as 2007-2009 (World Food Programme 2015; Ellis and Manda 2012). The food shortages in Malawi are predominantly occurring during the lean season, usually December to March (World Food Programme, 2015). During this season, the vulnerable population requires food assistance and has according to Malawi's Vulnerability Assessment Committee's update 2013 increased from 1.4 to 1.8 million people. The main factors contributing to food insecurity includes low maize harvest leading to high food prices and insufficient household crop production. This is manly caused by extended dry spells, flooding and input shortages. Secondary factors include low food stocks, delayed import and unstable maize supply (World Food Programme 2014; World Food Programme 2015; Ellis and Manda 2012).

Access to sufficient amounts of safe and nutritious food is essential to sustain life and promote good health. As the world population increases and with it, the demand for food, intensification and industrialization of agriculture creates both opportunities and challenges for food safety. In countries where the food supply is insufficient, people have a tendency to shift to less healthy diets and consume more unsafe food, where chemical or other hazards might possess a health risk. Foodborne illnesses are commonly caused by pathogens or chemical substances that enter the body through contaminated food or water. Unsafe food causes more than 200 diseases ranging from diarrhoea to cancers. Chemical contamination can lead to acute poisoning or long-term diseases, such as cancer, and might lead to long-lasting disabilities and even death. The most concerning chemicals are naturally occurring toxins and environmental pollutants such as persistent organic pollutants and heavy metals (World Health Organization, 2014).

3. Theory

3.1 Soil properties

The soil environment can be described as consisting of three phases, the soil atmosphere (air), the soil solution and the soil solids. However, unlike the other two phases, the solid phase is not a single phase but a composite of several. These compartments are mineral (inorganic compounds), humus (soil organic matter), and biotic (living organisms). Minerals are the predominate material in practically all soils and have a large influence on the chemistry of the soil solution (Essington, 2004).

3.1.1 The charge of soil particles

The charge on a mineral surface can be permanent or pH-dependent. The permanent charge is developed when the mineral is formed and this property cannot be altered by the chemistry of the environment. This is a result from the process of isomorphic substitution during the formation. The development of permanent charge is specific to the phyllosilicates and does in general result in a net negative charge. The pH-dependent charge is developed from the combined influence of the mineral surface and the environment the mineral occurs in. This development is characterized pH-dependent since the charge is a result from the protonation and deprotonation of surface hydroxyl groups where the charge can become negative, positive or neutral (Essington, 2004). When pH increases, $\equiv$MOH groups dissociate (gives away H^+) and more negative charge sites emerge ($\equiv$MO$^-$). If pH decreases, $\equiv$MOH groups will take up H^+ and more positive charge sites emerges ($\equiv$M-OH$_2^+$) (Eriksson et al. 2011). These types of groups are commonly found on phyllosilicates and metal oxides, hydroxides and oxyhydroxides (Essington, 2004). In most soils, the of amount negative charges is in majority. With increasing age and degree of weathering of the soils, the number of negative charges decreases. In very old and strongly weathered tropical soils, the positive charges can be of quantitative meaning. Humus only has pH-dependent charge, which mainly emerges through the acid-base properties of carboxylic acid groups dissociating. Since humus has a very high charge per kg, only a few percent humus can considerably increase the negative charge and thereby the soils ability to bind cations (Eriksson et al. 2011).

3.1.2 Cation exchange capacity

Cation exchange capacity (CEC) is the soils total capacity to electrostatically bind cations in exchangeable form as outer sphere complexes. CEC corresponds to the sum of negative charges at the particle surfaces and is expressed in centimol charges per kg dry soil ($cmol_c$/kg). CEC is pH dependent since the amount of negative charges increases with increasing pH (Eriksson et al. 2011).

3.2 Heavy metals

Heavy metals are defined as metals with a density higher than 5 g/cm^3 (Eriksson et al. 2011). Even though they are naturally occurring in the soil, increased levels can be found due to anthropogenic sources such as industry, agriculture and sewage works (Sajidu, 2008).

3.2.1 Toxicity

It is well recognized that heavy metals can be toxic pollutants and even though several are essential for humans, excessive levels can be harmful (Naseri et al. 2014; Sajidu 2008). Non-essential heavy metals such as cadmium, chromium and lead are toxic metals and consumption can cause severe health effects (Naseri et al. 2014). Acute toxicity is the rapid onset of symptoms instantly after intake of a substance. Chronic exposure is long-term effects at relative low individual doses of a substance (Baird and Cann 2008). Rather than acute poisoning, heavy metals mainly cause toxic effects from chronic exposure which can lead to a great variation of conditions depending on the exposure route and the metal's metabolism and storage (Sajidu, 2008). This is why, in environmental toxicology, continuing chronic exposures are usually of most concern. The same chemical may give rise to both acute and chronic effects, although usually by different physiological mechanisms. The toxicity of heavy metals depends on their chemical form, i.e. their speciation. Insoluble or almost insoluble substances will pass through the human body without doing much harm, while the most devastating metals will cause immediate sickness, or even death, or pass through the membrane protecting the brain or the placenta protecting the foetus (Baird and Cann 2008).

Metals cannot be detoxified by the human body and tends instead to bio-accumulate in different tissues since they are added faster than removed (Naseri et al. 2014). The harmfulness of heavy metals is not only of major concern to humans but correspondingly to plants and other living organisms (Sajidu, 2008). Cd, Cr and Pb are three of the most environmentally hazardous heavy metals due to their extensive use, toxicity and widespread distribution. None of these metals are particularly toxic in their form as condensed free elements but all are dangerous in the form of chemical compounds. The cations have a strong affinity for sulphur, which is usually the cause for toxicity biochemically. Sulfhydryl groups exist in the human body's enzymes that control the speed of critical metabolic reactions. When heavy metals are ingested, the sulfhydryl groups attach themselves. This changes the entire enzyme and results in the enzyme not functioning normally and the human health is adversely affected (Baird and Cann 2008).

The primary exposure to heavy metals is by food and air but contaminated drinking water can also be a major source, above all in developing countries where water may be contaminated by poorly treated industrial or agricultural effluents (Sajidu, 2008). There is also a risk via direct contact to the contaminated soil, ingestion or inhalation as viewed in Figure 6 (Berggren Kleja et al. 2006; Swedish Environmental Protection Agency 2009).

3.2.2 Mobility
Heavy metals are commonly thought of as pollutants in aqueous systems but are mainly transported through the air, either as gases or as species adsorbed on or in suspended particulate matter (Baird and Cann 2008). Humans can inhale these small particles spread from the contaminated soil or air polluted by traffic, combustion or other distant sources (Swedish Environmental Protection Agency, 2009). The size and shape of the particles varies and determines where in the respiratory tract they will deposit. The resulting health effects are affected by several parameters such as size and surface area of the particles and composition. There are strong evidence supporting the fact that smaller particles are more dangerous in terms of cardiovascular and respiratory effects and even death (Kampa and Castanas 2007). Particles with a size <10 μm are considered to be able to reach the lungs (Swedish Environmental Protection Agency, 2009). Metals are among the major components in air pollution and one of the main contributions of the particulate matter toxicity (Kampa and Castanas 2007).
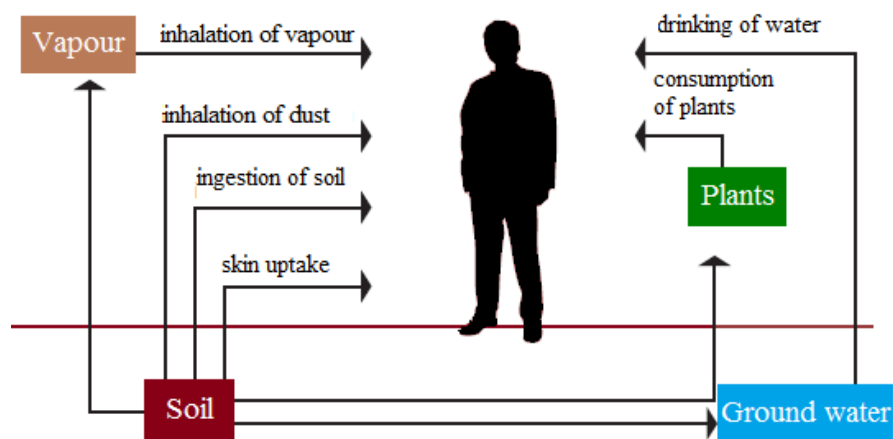
Figure 6 - Illustration of exposure pathways (Swedish Environmental Protection Agency, 2009)

Mobility in soil

Heavy metals are transported slower than water on their way through the soil since they "get stuck" on the way. The most important chemical mechanisms are precipitation and adsorption. These are reversible mechanisms where precipitated metals can eventually be dissolved, and adsorbed metals desorbed, resulting in an increase of metal concentration in the soil solution long after the contributing source has ceased (Berggren Kleja et al. 2006). The most important parameters controlling these mechanisms are clay type, metal speciation, metal concentration, soil pH, solid:solution mass ratio and contact time. Of all these, pH is considered the most important variable (Pare et al. 2013).

Adsorption

Adsorption is a surface process where a dissolved substance is accumulated at the interface of a solid (Essington, 2004). The process amounts to a chemical equilibrium between the dissolved concentration of the substance and the surface bound concentration (Eriksson et al. 2011). A complex is a central ion, usually the metal ion, surrounded with ligands which are molecules or anions (Elding, u.d.). An important characteristic of a complex is that the compound does not change when the complex is formed, that would instead mean that a new compound is formed (Eriksson et al. 2011). There are two kinds of surface complexes; inner-sphere and outer-sphere (ion-pairs). When the metal ion and ligand are directly bound without water molecules in between it is an inner-sphere complex. When the metal ion and ligand are attached outside the hydration sphere it is an ion-pair complex (Essington, 2004).

One important adsorption mechanism regarding the discussed metals is outer-sphere surface complex where at least one water molecule is between the charged surface and the adsorbed ion, preventing electron exchange. Surface complex formation occurs when a surface functional group reacts with an ion or molecule dissolved in the soil solution. (Essington, 2004). Many cations can form complexes with the oxygen in hydroxyl group on particle surfaces or carboxylic groups in humus which is why they are easily adsorbed to surfaces with these groups (Berggren Kleja et al. 2006). Adsorption is highly pH-dependent which is why pH is the most important factor controlling the adsorption of metals, where cation adsorption is more effective at a high pH (Berggren Kleja et al. 2006; Pare et al. 2013).

Precipitation

Precipitation is the process contrasting adsorption, meaning that the crystal structure of a secondary mineral increases in volume as a result of the three-dimensional growth of the structure (Essington, 2004). This process takes place when the ions occur in sufficient concentrations in the soil solution and regulates the concentration of free metal ions. The total concentration is also affected by other substances in the water forming complexes with metals. Both adsorption and precipitation are strongly affected by the concentration dissolved organic carbon (DOC) in the soil solution. The higher concentration DOC, the lower sorption since the metals in a larger extent is complex bound to the dissolved organic material (Berggren Kleja et al. 2006).

Mobility in water

Soil water is the most important phase in the soil where substances move and almost all chemical reactions occur, where the interface solid-water is even more important. The soil solution also mediates many of the reactions controlling the retention of substances such as adsorption etc. mentioned above. In the soil solution, metals can exist as dissolved complexes or free ions (Essington, 2004). The dissolved forms are strongly dominating in soil solution and groundwater while the particulate fraction can be of importance for the metal transport in water bodies. Metals in soil solution, ground- or surface water occur in different forms, so called species (Berggren Kleja et al. 2006). Even with a given concentration of a heavy metal, the toxicity depends on factors such as the water's pH and the amounts of dissolved and suspended carbon. This is due to interactions such as complexation and adsorption that may remove some of the metal ions from potential biological activity (Baird and Cann 2008). The transport to ground- and surface waters also depends on the soils hydraulic properties, e.g. macro pores giving rise to preferential flow (Berggren Kleja et al. 2006).

Free hydrated ions

The water molecule is a dipole where one side has a positive charge (the hydrogens), attracted to the anions, and the other has a negative charge (the oxygen), attracted to the cations. A charged ion dissolves in the water by forming week bonds to the water molecules in close proximity forming a shell around the ion. This process called hydration and occurs for all dissolved substances in water with varying numbers of water molecules depending on the ions charge and composition. The effect of the shell is an insulation of the ion where the charge is dissipated and the ion becomes shielded from other ions in the water (Berggren Kleja et al. 2006; Essington 2004). The cations can also form new ionic metal species (a hydroxide or an oxide) by hydrolysis. This is possible as most metal cations form strong bonds with oxygen and when in water, the interaction can split the water molecule. Hydrolysis may have a significant impact on the metal speciation and may change the reactivity to other species and soil solids (Essington, 2004).

Dissolved complexes

Some substances can form dissolved complexes with other substances in the water. For instance, many metals can form complexes with commonly occurring anions in the water, e.g. hydroxide, carbonate, fluoride, sulphate and organic acids (Berggren Kleja et al. 2006). Except hydration, inner-sphere and outer-sphere complexes with ligands present in the solution can also be formed (Essington, 2004). Sulphide ions form relatively strong complexes to several metal ions, including Cd^{2+} and Pb^{2+}, and many metals can form strong inner-sphere complexes to organic ligands. Similar complexes can also be formed between metals and humus substances which in general has a large content of carboxylic and phenolic groups. Humus occurs as both dissolved in water, where they contribute to metal transport through complex formation with metals, and aggregated as particles, where they instead bind the metals through adsorption (Berggren Kleja et al. 2006).

3.2.3 Plant uptake

Maize is an important crop in many countries and is known to be sensitive to a wide range of chemicals. Sweet corn was previously recommended by the US EPA as a test species and has been extensively used to study the uptake, accumulation and translocation of heavy metals (An, 2004). Metals contrast toxic organic compounds since they are non-degradable to non-toxic forms. However, metals can transform into inert forms and are thereby biologically unavailable, unless they are transformed into more active substances once again (Baird and Cann 2008). A large fraction of metals is bound to the soil which makes it unavailable for biological uptake or leakage to water. As mentioned above, the metal might become available again by desorption or by being dissolved. This means that, when looking at the environmental risk of a metal, the total concentration does not mean as much as one might assume (Berggren Kleja et al. 2006). It is important to have knowledge about soil conditions such as pH, clay content and DOC as they affect the metals speciation and thereby the behaviour (Essington, 2004). The speciation of metals in the water phase is important to estimate its bioavailability and toxicity (Berggren Kleja et al. 2006).

For substances such as lead(II), an effective adsorption in complex bound form is beneficial since it lowers bioavailability for plants. This is also concerns micronutrients such as copper(II) if the levels are too high, i.e. in Cu contaminated soils. The effect complexes have on solubility depends highly on their solubility and stability. Commonly, the bound metals mobility increases with the solubility of the complex (Eriksson et al. 2011).

Cadmium is relatively easily available in the soil (Eriksson et al. 2011). It does not have any biological function for plants but since cadmium(II) has similar chemical properties as zinc and calcium ions, plants take up Cd anyway. With higher amounts in the soil, subsequently, the plants will take up more. With decreasing soil pH, plants will increase the Cd uptake since the more cadmium(II) becomes available for ion exchange. However, compared to the macronutrients Ca^{2+} and Mg^{2+}, Cd^{2+} is relatively strongly bound and the mobility is relatively low unless the soil properties are extremely acidic (Baird and Cann 2008; Eriksson et al. 2011; Essington 2004).

3.2.4 Specifics on heavy metals

As mentioned earlier, Cd, Cr and Pb are three of the most environmentally hazardous heavy metals which is why focus will be on these three metals. In soils and natural waters, these heavy metals are present in the oxidized forms cadmium(II), chromium(II) and lead(II).

Cadmium (Cd)

Sources
The soil receives Cd from atmospheric deposition. Where Cd exists in soil minerals it is strongly associated with Zn since they have similar chemical properties. The most common Zn mineral containing Cd is sphalerite (ZnS) but other Zn minerals are also often rich in Cd. For this reason, most Cd is produced as a by-product of Zn smelting, which is why contaminations often occur in areas surrounding Zn smelters (Eriksson et al. 2011; Baird and Cann 2008).

A major use of Cd is as electrode material in rechargeable Ni-Cd batteries used in calculators and similar devices (Baird and Cann 2008). Cd has also been used in PVC-plastic, pigment in paint and in different alloys. Many areas of use have or are about to be phased out but disposal from incineration of waste material containing Cd such as plastics or paint is still an important source (Berggren Kleja et al. 2006; Baird and Cann 2008).

Agricultural activities provide important non-point sources of Cd. P-fertilizers are the most abundant source of Cd contamination because of the naturally relatively high concentration of Cd in the apatite used for the manufacture of phosphate fertilizers (Sajidu, 2008).

Occurrence in soil and water
The only common ion of Cd is Cd^{2+} (Baird and Cann 2008). Cd^{2+} binds to organic material in the soil and in a smaller share to Fe-oxides and carbonates at high pH. Cd^{2+} is also involved as a smaller fragment in many primary minerals, e.g. carbonates, and sulphides in reduced environments. In water, the dominating form is Cd^{2+} and different complexes with e.g. carbonate and DOC. Cadmium salts are rather soluble in water except the sulphide which has very low solubility (Berggren Kleja et al. 2006).

Important soil chemical processes
Cd^{2+} is complex bound to organic material, and can also bind to Fe-, Al- and Mn-oxides and precipitate with carbonates, especially at high pH. The surface complexes with Fe-oxides are fairly weak and Cd^{2+} desorbs easily when pH decreases. Cd^{2+} is easily precipitated as sulphides in reduced environments. This means that Cd is strongly bound in the soil at high pH and in anaerobic soils but is easily soluble at low pH and under aerobic conditions. (Berggren Kleja et al. 2006).

Toxicological effects
For the main part of humans, the greatest exposure to Cd is from our food supply. The majority of Cd in the diet commonly derives from potatoes, wheat, rice and other grains, since they are most consumed. Otherwise, seafood and intestine food have higher Cd levels than most foods (Baird and Cann 2008).

Cd is acutely toxic and the lethal dose is about 1 g. Humans are somewhat protected against chronic exposure at low levels due to the presence of *metallothionein* – a sulphur rich protein which regulates zinc metabolism. Due to the many sulfhydryl groups, it can complex bind almost all ingested Cd^{2+} which is then eliminated in the urine. However, when the capacity of the protein is exceeded, Cd is instead stored in mainly liver and kidneys. Cd is not biomagnified but accumulates in the body since its lifetime in the body is several decades, if not eliminated quickly. Chronic exposure eventually leads to an increased chance of kidney diseases (Baird and Cann 2008). High intake of Cd can also cause, for example, both fibrotic and emphysematous lung damage, promote cancer and has also major effects in bone. In a contaminated area in Japan, hundreds of people contracted a degenerative bone disease called *itai-itai,* translated to ouch-ouch, where the bone slowly becomes porous until it fractures and collapses. This happened because Cd^{2+} replaced Ca^{2+} in the bones due to the same charge and virtually similar size (Baird and Cann 2008; Berggren Kleja et al. 2006).

Copper (Cu)

Sources
Large quantities of Cu are used in the society in for example alloys, electrical cables, pluming and coins. Waste from electric and electronic equipment is the Cu containing waste that increases the most. Large amounts of Cu might locally come from mines and smelting. In urban areas, corrosion of copper roofs is an important source (Berggren Kleja et al. 2006; Chang 2010).

Occurrence in soil and water
Oxidation state: commonly (II) and sometimes (I) in strongly reducing environments with suitable ligands (Berggren Kleja et al. 2006).

Dominating form in water: Cu^{2+} and its complex with DOC, with the latter usually strongly dominating (Berggren Kleja et al. 2006).

Occurrence form in soil: Above all, strongly bound to organic material, but also strongly bound to Fe-, Al- and Mn-oxides. In reducing environments, Cu forms poorly soluble sulphides. In oxidizing environments, at high pH and high Cu-concentrations, malachite, $Cu_2(OH)_2CO_3$, may precipitate (Berggren Kleja et al. 2006).

Important soil chemical processes
Cu^{2+} is characterised by very strong complex formation to humus, which is also strong even at low pH (4). Comparing to lead(II), Cu^{2+} forms strong complexes to humus and weaker ones to oxide surfaces, which results in that the content of organic material in the soil in general decides how much Cu^{2+} which is bound. The transport of Cu in soil and water occurs mainly as dissolved humus complexes (Berggren Kleja et al. 2006).

Toxicological effects
Cu is essential for both plants and animals but high levels of Cu^{2+} is very toxic. Chronic exposure can lead to an accumulation in, and damage to, liver, brain, kidney and cornea. Cu^{2+}

can also cause damage to the immune system but is not carcinogenic (Berggren Kleja et al. 2006; Sajidu 2008).

Chromium (Cr)

Sources
Cr is extensively used for electroplating, corrosion protection and leather tanning, and is also a common additive in steel, which is why corrosion of Cr-containing materials is a source. Other sources are the use of ferrandromium scrap from steel plants and mine waste with chromite ore. Cr is a common water pollutant as a consequence of industrial emissions and also the second most abundant inorganic contaminant of groundwater under hazardous waste sites (Baird and Cann 2008; Berggren Kleja et al. 2006).

Occurrence in soil and water
Cr normally exist in the form of inorganic ions where the common oxidation states are +III and +VI. Chromium(III) occurs under reducing conditions and low pH in cationic form, and occurs practically exclusively in the soil. Under very aerobic conditions and high pH, Cr occurs in the +VI state which is always an anion and commonly the chromate ion, CrO_4^{2-} (Baird and Cann 2008; Berggren Kleja et al. 2006; Sajidu 2008; United States Enviromental Protection Agency 2000).

In soil, Cr^{3+} is bound to organic material and oxic mineral surfaces and precipitated with Fe-oxides, and chromate is weakly adsorbed to Fe- and Al-oxides (Berggren Kleja et al. 2006).

In water, chromium(III) occurs as the Cr^{3+} ion which has a low solubility in neutral water and it is often precipitated as its hydroxide. It can also occur as different chromium(III) complexes with e.g. DOC. Chromium(VI) usually occurs as the chromate ion which are highly soluble in water (Berggren Kleja et al. 2006; Baird and Cann 2008).

Important soil chemical processes
Cr(III) is strongly bound in the soil, even at low pH, through complex formation to organic material and on mineral surfaces and can also precipitate with Fe-oxides.

Cr(VI) can form week complexes with Fe- and Al-oxides at pH below 6 but is in general rather mobile in the soil since it is not strongly absorbed by many types of soil. It can be reduced to the less mobile trivalent form by the humic substances in soils that are rich in organic matter but this is an extremely slow process and if chromium(VI) is discharged into the environment, it will persist for a very long time (Berggren Kleja et al. 2006; Baird and Cann 2008; United States Enviromental Protection Agency 2000).

Toxicological effects
Cr is essential but at high concentrations, it can cause problems with trachea, cause lung cancer after long exposure, and also complex binding to DNA. The hexavalent Cr is more toxic, more soluble and more mobile than trivalent Cr and carcinogenic making it a more severe pollution. The chromate ion enters biological cells, seemingly because of its structural resemblance to the sulphate ion. Inside the cell, chromate can oxidize DNA and RNA bases (Baird and Cann 2008; Berggren Kleja et al. 2006).

Lead (Pb)

Sources

Important sources of Pb are mining, smelting, glass industry, military, accumulator industry, old lead based paint and earlier gasoline. The deposition of Pb has decreased greatly the last decades due to the out-phasing of leaded gasoline in the 1990s and decreased emissions from industries (Berggren Kleja et al. 2006). However, many countries still use leaded gasoline where the air is the major source of Pb ingested by humans (Baird and Cann 2008). Pb is also still used in many other products such as pigments, solder, stained glass, ammunition, jewellery, toys and also in some cosmetics and traditional medicines. Drinking water running through Pb-pipes or pipes joined with Pb-solder may contain lead (World Health Organization, 2014). Pb-glazed dishware is still a major source, especially in developing countries, as a source of dietary Pb. Lead arsenate is another former source of Pb in soil from the time it was used as a pesticide (Baird and Cann 2008). The spread from products to the environment is mainly from combustion of waste and leakage from waste dumps (Berggren Kleja et al. 2006). Un-recycled car batteries are the main source of Pb in municipal waste (Baird and Cann 2008).

Occurrence in soil and water

The stable ion of lead is lead(II) (Baird and Cann 2008). Pb^{2+} is strongly bound to organic material and Fe-, Al-, and Mn oxides. In a reducing environment, Pb forms poorly soluble sulphides and in an oxidizing environment with high pH and high Pb-concentrations, $PbCO_3$ may precipitate. In water, Pb occurs as Pb^{2+} and also its complex with DOC, which in general strongly dominates (Berggren Kleja et al. 2006).

Important soil chemical processes

Pb^{2+} binds very strongly to humus as well as oxide surfaces, even at low pH (4). The transport of lead(II) in soil and water largely occurs as dissolved humus complex, alternatively as colloids with iron oxides and humus (Berggren Kleja et al. 2006).

Regarding leaded gasoline, after the atom is liberated it ends up as PbO which exists as an aerosol in the atmosphere up to a couple of days. This means that it can travel far distances and enter the food chain at distant sites if it is deposited on vegetables or on fields used by grazing animals (Baird and Cann 2008).

Toxicological effects

Elemental Pb is not an environmental problem to most life forms. However, it does become a genuine concern when it dissolves to yield ionic species. Lead(II) is bioconcentrated by microorganisms but is not biomagnified in the food chain. The forms of lead(II) that have alkyl groups attached are highly toxic. The reason is because they are molecules and therefore soluble in animal tissue and can pass through biological membranes. The toxicity of the ion Pb^{2+} is much less since charged ions are less prone to pass membranes (Baird and Cann 2008).

The body absorbs Pb^{2+} better from water than food (Baird and Cann 2008). The main part of ingested lead(II) in humans is initially stored in the blood. When a certain level is reached, excess amounts will enter the soft tissue including organs and particularly the brain. Finally,

Pb^{2+} becomes deposited in the bone where it replaces calcium since Pb^{2+} is antagonistic to Ca^{2+} due to the similar size and metabolism (Baird and Cann 2008; Sajidu 2008). At high Pb^{2+} levels, inorganic Pb^{2+} is a general metabolic poison. The toxicity is proportional to the amounts of Pb in soft tissue and not to the levels in blood or bone. Pb can accumulate in the body since it remains in the bones for decades. When the bone dissolves due to age or other causes such as pregnancy, Pb is remobilized back into the blood where it can produce toxic effects (Baird and Cann 2008).

Another source of lead for children is ingested contaminated soil, accidently or willingly. It is possible that Pb contaminated soil, and also Pb containing paint stains, is ingested more than usual since lead compounds have a sweet taste. Pb contamination in soil also gives rise to lead dust which actually is the largest Pb source for children in U.S. inner cities. Children under the age of 7 are most at risk for lead(II), even at low levels, since they absorbs a greater percentage of dietary Pb and also because their brains are growing rapidly (Baird and Cann 2008). Undernourished children are even more at risk since their bodies absorb more Pb if other nutrients, such as Ca, are lacking (World Health Organization, 2014).

Exposure to lead is known to affect the central nervous system and impair learning ability and the intellectual development, where small children and foetuses are especially sensitive (Berggren Kleja et al. 2006). The main risk for children is the interference with the normal brain development and Pb appears to have deleterious effects on their behaviour, attentiveness and possibly also their IQ (Baird and Cann 2008). Neurological and behavioural effects of Pb are believed to be irreversible (World Health Organization, 2014). As mentioned earlier, Pb can cross the placenta and further be passed on to the foetus. Pb can also be transferred postnatal to the child via breast milk. Pregnant women exposed to excessive levels of lead can cause miscarriage, stillbirth, premature birth and low birth weight as well as other birth defects (Baird and Cann 2008; World Health Organization 2014). Pb can also cause anaemia, high blood pressure, kidney failure, impaired uptake of iodine, increased risk for cardiovascular diseases, immunotoxicity and toxicity to the reproductive organs but is not carcinogenic (Berggren Kleja et al. 2006; Sajidu 2008; World Health Organization 2014).

Zinc (Zn)

Sources
Large quantities of Zn are used in the modern society. The largest sources of Zn in urban areas are particles from car tyres and galvanized metal constructions (Berggren Kleja et al. 2006).

Occurrence in soil and water
Zinc(II) is mainly bound to organic material and to a smaller extent to Fe- and Mn-oxides at high pH. In strongly contaminated soils there is also precipitation with phosphate hydroxide. In water, Zn^{2+} forms relatively strong complexes with DOC, which normally is the dominating form at high pH (>6). At lower pH, Zn^{2+} usually dominates (Berggren Kleja et al. 2006).

Important soil chemical processes

At high pH (>6), Zn^{2+} occurs in general complex bound to the soils organic material. At low pH, Zn^{2+} occurs mainly adsorbed to organic material and clay particles. The solubility of Zn^{2+} strongly increases with decreasing pH (Berggren Kleja et al. 2006).

Toxicological effects

Zn is essential for plants and animals and has in general a very low toxicological effect on mammals (Berggren Kleja et al. 2006). Zn does however exhibit toxic properties and at high concentrations, it can affect and impair cellular functions (Sajidu, 2008).

3.3 Guideline values

Background levels are the sum of natural concentrations and anthropogenic diffuse pollution, such as airborne deposition. The levels vary between areas depending on natural processes and a result of human activities. SEPA considers an area contaminated if the levels are higher than the background levels. Reference samples from the area or local, regional and national charting can give information about the background levels in the area. Guideline values are a tool that can be used in a risk assessment. In a basic risk assessment, measured concentrations of a contaminant on site are compared with generic or site-specific guideline values. In the context of the remediation of contaminated sites, a guideline value is the concentration of a contaminant in soil under which the risk of harmful effects on human health, environment or natural resources is acceptable. However, it is not certain that negative effects arise because the concentrations exceed the guideline values (Swedish Environmental Protection Agency, 2009).

In Table 2, SEPA's Swedish generic guideline values are presented. They are based on normal conditions for the majority of contaminated sites in Sweden but cannot be applied for all sites. Where the generic values cannot be used, site-specific guideline values can be calculated instead, taking actual site conditions into account. The generic guideline values are derived for two different kinds of land use, sensitive and less sensitive. This affects the degree to what protection of the soil environment is required. The land use determines the expected activities on the site and further to what extent exposure will occur, e.g. when crops are grown and consumed, sensitive land use applies. The guideline values include considerations of; exposure by direct contact with the soil and indirect exposure via air, groundwater and plants. They also take protection of the soil environment, ground and surface water into account (Swedish Environmental Protection Agency, 2009).

Table 2 – Median elemental content of uncontaminated soils and generic guideline values for contaminated soils in sensitive land use including the limiting factor setting the value (Essington, 2004) (Swedish Environmental Protection Agency, 2009)

Substance	Median levels in soil (mg/kg soil)	Generic guideline values (mg/kg TS)	Limiting factor
Cd	0.35	0.5	Health, consumption of plants
Cr	70	80	Soil environment
Cu	30	80	Soil environment
Pb	35	50	Health, consumption of soil
Zn	90	250	Soil environment

3.3.1 Tolerable daily intake

The guideline value's acceptable level depends on which type of toxicity a substance shows. For substances not affecting the genetic material TDI values are primarily used. For most types of toxicity, it is considered to be a dose lower than at which no apparent negative effects normally emerge. For these chemicals, TDI can be calculated. A TDI value corresponds to the amount of a chemical a human can consume orally per kg body weight and day under a whole life time without negative effects (see Table 3) (Rosén et al. 2006). The dose of the substance is usually expressed as the mass of the chemical per unit body weight (usually mg/kg). This division is necessary since the toxicity of a given amount of a substance usually decreases as the size of the individual increases (Baird and Cann 2008).

Table 3 - Tolerable Daily Intake (Swedish Environmental Protection Agency, 2009)

Heavy metals	TDI (mg/kg bodyweight and day)
Cadmium (Cd)	0,0002
Copper (Cu)	0,5
Chromium total (Cr)	1,5
Lead (Pb)	0,0035
Zinc (Zn)	0,3

4. Materials and Methods

The following is a short description of how the sampling and analysing was performed, which is instead thoroughly described in Appendices 1 and 3.

4.1 Sampling sites

This study had three sampling sites: Zomba's official waste dump (WD), Chikanda waste water treatment plant (WWTP) and one reference site (Ref). At the WD, about 12 % of Zomba's generated waste was disposed in an open disposal where no waste was sorted. At the WWTP, all waste water connected to the sewage system arrived. The treatment plant was a cylinder filled with gravel with a bio filter in the bottom and a rotating arm distributing the water evenly over the gravel. However, this water distributor was broken during the whole study and information was given that the fields were frequently flooded with waste water. The reference site was fertilized with inorganic fertilizer.

4.2 Pilot study

A pilot study was performed before the main study to determine the standard variation in the samples to further calculate how many samples were needed. Another purpose was to get an idea of which metals were present in the soil. The final reason was to test the equipment and methods in order to be well prepared for the main study.

4.2.1 Sampling

The method is described in Appendix 1 – Sampling performance.

The pilot study consisted of five randomly placed soil surface samples at the WWTP where each sample consisted of twelve mixed samples where one aliquot was taken.

4.2.2 Analysing

The method is described in Appendix 3 – Analyses.

The soil samples were analysed for heavy metal concentration using AAS after a tri-acid digestion.

4.3 Main study

4.3.1 Sampling

The method is described in Appendix 1 – Sampling performance.

Nine soil surface samples and several different plants were sampled from the two possibly contaminated sites: waste dump and waste water treatment plant (WWTP). In the same way as the pilot study, each sample consisted of twelve mixed samples where one aliquot was taken. At the WWTP, water was also sampled, before and after treatment. At the waste dump, ash from the waste was collected. This was done to give an indication if those were the source of contamination. Five soil surface samples and some plants were sampled at the reference site due to assumptions of lower variation.

4.3.2 Analysing
The method described in Appendix 3 – Analyses

The total concentration of Cd, Cu, Fe and Zn in the soil was measured using AAS after a di-acid digestion. Following analyses were also performed on the soil samples: moisture content, texture, pH, EC, CEC, TOC, total nitrogen and phosphorous. The plants were extracted using a tri-acid mixture after drying in the oven over night and further analysed for metal concentration using AAS.

4.4 Control study
A selection of samples of soil, crops, water and ash were brought back to SLU, Sweden, for controlling the levels of Cd and also analyse for Cr and Pb. This was done using AAS.

4.5 Calculations and statistical analyses
In *Appendix 4 – Calculations*, all calculations are presented. Below, the calculations made for heavy metal content are briefly described.

4.5.1 Calculations
Before analysing the samples, a calibration curve was made for each metal. Following is the calibration curve and equation for Cd in the pilot study as an example.
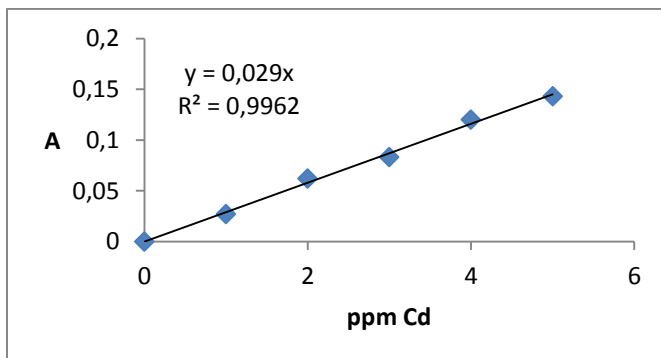
Figure 7 - Calibration curve for cadmium

The trend line's equation was used to calculate the metal concentration in the samples from the measured absorbance.

$$C_{Cd}\ (ppm) = \frac{A}{0.029}$$

Following equation was used to correct the measured concentration after sample weight and dilution, and to get the final result in mg/kg.

$$C_{Cd}(mg/kg) = \frac{C_{Cd}\ (ppm) * MCF * 0.1}{Sample\ weight} * 1000$$

27

4.5.2 Number of samples

As described in *Appendix 1 – Sampling performance*, a pilot study was performed to collect data to determine the minimal sample number needed in the main study for a confidence interval of 95 %. This was done using a *a priori*-test in the statistical software program G*Power with the settings: F-test, ANOVA: Fixed effects, omnibus, one-way. This was performed for each metal separately using the standard deviation and mean value gained from the pilot study.

4.5.3 Significant differences

To support the keeping or rejecting of the null hypothesis the software Minitab was used to see if there were any significant differences between the sites. The data was analysed with one-way ANOVA using the Tukey method. The confidence interval chosen was 95%.

5. Results

The grouping information gained by using ANOVA is presented under each part to see if there was any significant difference between the sites.

5.1 Pilot study

The results from the pilot study performed at WWTP are presented in Table 4. The concentration of Cd was very high with all values above the generic guideline values for contaminated soil. The mean value for Cu was not particularly high but had a large variation between the sampling points. Zn also had a large variation but no values above the guidelines. These results were obtained in the laboratory in Malawi and as indicated below, in section 5.2.2, the results for Cd are probably false, due to analytical problems. The data presented in Table 4 should therefore be interpreted with care regarding the absolute values.

Table 4 – Total metal concentration at each sampling point and mean values from the pilot study in mg/kg soil and guideline values (Swedish Environmental Protection Agency, 2009)

Sampling Point	Cd	Cu	Fe	Zn
		(mg/kg soil)		
1	10	69	17200	170
2	9	64	17600	210
3	5	63	17100	180
4	4	13	14700	130
5	9	5	15900	160
Mean	*8*	*43*	*16500*	*170*
Guideline values	*0.5*	*80*	*-*	*250*

Since no background levels were known for the area, the software program G*Power was used to calculate the minimal sample size needed for a confidence interval of 95 %. The standard deviation and mean values used in G*Power are presented in Table 5. The minimal sample size required was highest for Cu and therefore a sample number of 75 should have been used. To achieve an even spread and make sure enough samples were collected, 108 samples were chosen. The reference site was assumed to have a lower variation which is why only 60 samples were taken there. To reduce the number of analyses, composite sampling was done where twelve samples were taken at each sampling point and one aliquot was further taken for analyse. This resulted in 9 samples from WD and WWTP and 5 samples from Ref.

Table 5 - Standard deviation and estimated mean values used for G*Power for all analysed metals and following needed sample size (n)

	Cd	Cu	Fe	Zn
		(mg/kg soil)		
SD	3	31	1191	28
M1	7.5	42	16493	169
M2	7.5	42	16493	169
M3	4.8	11	8247	85
	n=45	*n=75*	*n=6*	*n=12*

5.2 Main study

5.2.1 Soil properties

All three sites soil properties are presented in Table 6. The WWTP and reference site were classified as sandy clay loams while the waste dump where classified as a clay loam due to higher silt content. Note the higher fraction particles (>1 mm) in the soil from the WD resulting in a larger fraction sorted away when sieving the sample.

There was a clear difference in pH between the sites where WWTP had a very low pH, WD a neutral pH and the reference site a pH in between these. The electrical conductivity was more than twice as high at WD and WWTP compared to the reference site. The WWTP had the highest nutrient status with both higher amounts of nitrogen and phosphorus. The nitrogen content was more than three times higher than the other sites and phosphorus was three times as high compared to WD and over five times as high compared to the reference site. To clarify, the reference site had the lowest nutrient status even though it was the only site fertilized. The carbon content was also twice as high at the WWTP compared to the other. There was not a large difference in CEC between the sites but the highest was also found at the WWTP and all sites had a higher CEC than expected.

Table 6 - Summarised soil properties for all three sites

	WWTP	WD	Ref
Type	Sandy clay loam	Clay loam	Sandy clay loam
Clay content	29 %	35 %	35 %
Silt content	19.4 %	27.4 %	19.4 %
Sand content	51.6 %	37.6 %	45.6 %
Fraction > 1 mm	11 %	37 %	15%
pH	3.71	7.06	5.90
EC (µS)	142	117	50.6
C (%)	10.9	5.21	5.04
N (mg N/100 g soil)	273	82.5	80.0
P (mg P/100 g soil)	1930	619	373
CEC (cmol$_c$/kg soil)	76.4	74.7	66.0
C/N	40	65	63

5.2.2 Heavy metal concentration

Unreliable data

Before presenting the results of metal concentrations in soil and plants it is important to emphasize the uncertainty of the obtained results. In Table 7, a comparison is demonstrated between the results analysed in Malawi and the once analysed at SLU in Sweden. As can be seen, there is a large difference between the two results and also a large variance between some of the samples analysed in Sweden. For this reason, further discussed in *Discussion* (chapter 6), the results from Malawi regarding Cd were not used. The results from Sweden were considered more trustworthy and were therefore used instead. However, since only a few samples were analysed in Sweden, these results are neither reliable nor were any statistical analyses made due to the insufficiency in number of samples.

Table 7 - Comparison of Cd concentration in soil analysed in Malawi versus in Sweden in mg/kg soil

	Cd (mg/kg soil)	
	Malawi	Sweden
WWTP SS2a	8	-
WWTP SS5a	5	28
WWTP SS8a	5	-
WD SS2a	10	2.3
WD SS5a	5	2.8
WD SS8a	10	1.0
Ref SS1a	3	-
Ref SS3a	8	-
Ref SS5a	10	-

Soil

The results from the analyses performed in Malawi are presented in Table 8. Figure 8 presents the mean values in a column chart to visualize the difference between the sites. Error bars are included to show the standard deviation between the sampling points.

Comparing the three sites, the mean value for Cu at WWTP is remarkably higher than at the other sites and a significant difference was found compared to the reference site. This mean value of 118 mg/kg soil is also a lot higher compared to the results from the pilot study (43 mg/kg soil) which took place at the same location. The mean value exceeds the guideline value but the large standard deviation demonstrates that the mean value might not be ideal in this case. If we would instead use the median value of 77 mg/kg soil, the site does not exceed the guidelines. A significant difference was found for Fe between WD and the reference site. All sites had Zn levels below the guidelines but both WWTP and WD had about three time's higher concentrations than the reference site which is why a significant difference was found for both sites.

Table 8 – Mean concentration of Cu, Fe and Zn in soil in mg/kg soil, statistical information and grouping information using Tukey method. Sites that do not share a letter are significantly different. These metals were analysed in Malawi (Swedish Environmental Protection Agency, 2009).

	n	Cu	Fe	Zn
Mean values (mg/kg soil)				
WWTP		118	11000	140
WD		12	9600	160
Ref		35	11000	56
Guideline values		*80*	*-*	*250*
Standard deviation				
WWTP		112	470	31
WD		12	1200	72
Ref		4.4	280	38
P-value		0.003	0.0	0.0
Grouping information				
WWTP	9	A	A	A
WD	9	B	B	A
Ref	5	B	A	B
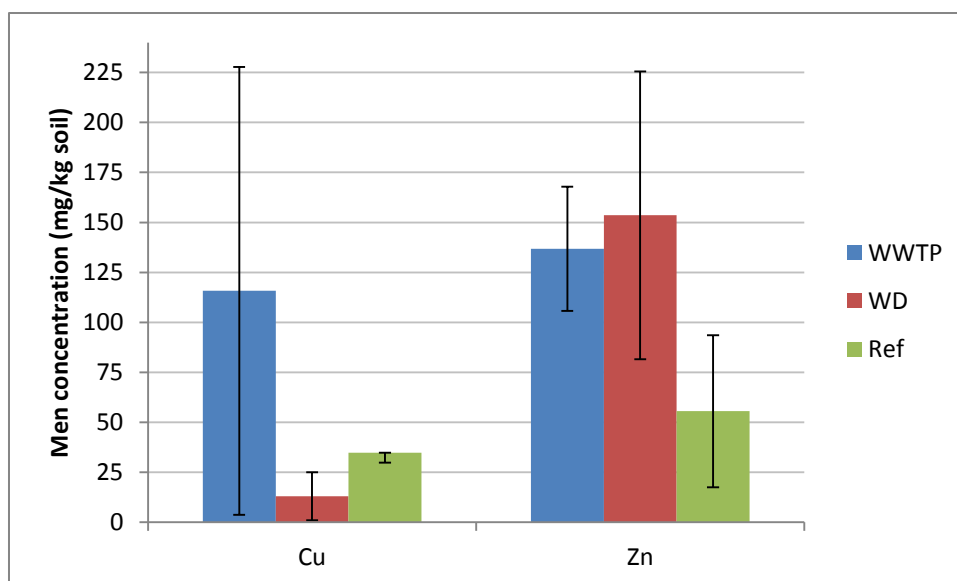
Figure 8 - Comparison of concentrations for Cu and Zn for all sites in mg/kg soil. This was analysed in Malawi. The error bars show the standard deviation for each metal at respective site.

The results from the analyses performed in Sweden are presented in Table 9 and Figure 9. Since only a few samples were analysed, no statistical calculations were performed. No Cd was found at the reference site but the mean values for the other two sites were above the guideline values. However, regarding WWTP, no Cd was detected in two of three samples while one sample is high above the guidelines with a Cd level of 28 mg/kg soil. Once again, note the high standard deviation and that the mean value might be misleading. At the WD, the Cd levels were more even with a mean value of 2.0 mg/kg soil. Cr was outstandingly higher at the WWTP compared to the other sites with a mean level of 50 mg/kg but does not exceed the guideline values. Regarding Pb, the reference site had the lowest levels while the WWTP had the highest with twice the amount, exceeding the guideline values. The mean value at WD is close to the guidelines and comparing the sample points, two out of three are above.

Table 9 – Concentration of Cd, Cr and Pb and mean values for each site analysed in Sweden in mg/kg soil

Sample	Cd	Cr	Pb
	(mg/kg soil)		
WWTP SS2a	-	57	62
WWTP SS5a	28	52	66
WWTP SS8a	-	39	74
Mean	*9.3*	*50*	*67*
WD SS2a	2.3	11	51
WD SS5a	2.8	3.1	52
WD SS8a	1.0	10	45
Mean	*2.0*	*8.3*	*49*
Ref SS1a	-	8.7	30
Ref SS3a	-	13	42
Ref SS5a	-	11	30
Mean	*-*	*11*	*34*
Guideline values	*0.5*	*80*	*50*
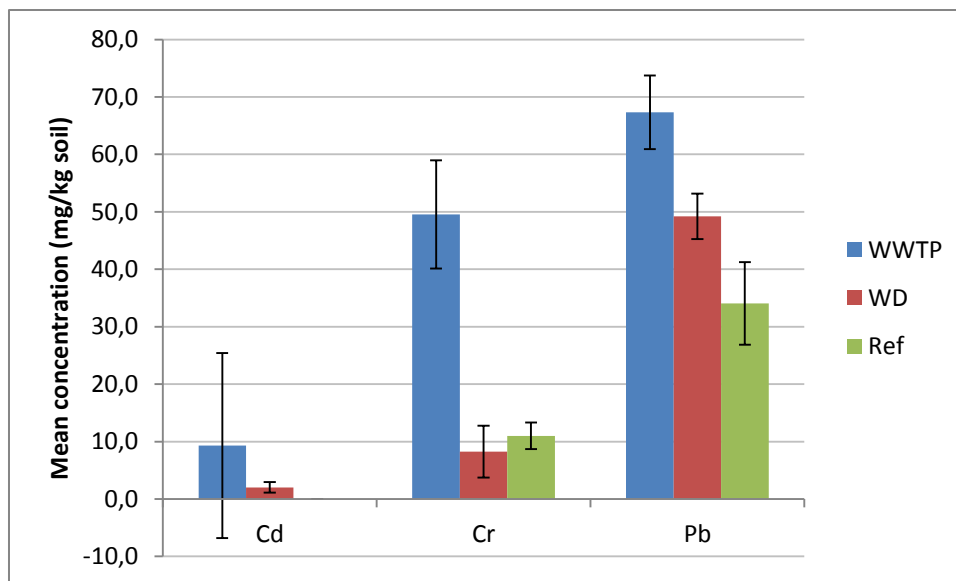
Figure 9 - Comparison of concentrations for Cd, Cr and Pb for all sites in mg/kg soil. This was analysed in Sweden. The error bars show the standard deviation for each metal at respective site.

Plants

Table 10 presents the results of metal concentration in maize analysed in Malawi. Cu is outstandingly high at WD with 88 mg/kg DM compared to 1 mg/kg DM at the reference site and a significant difference was found. However, this mean value is actually higher than the concentration in the soil. The standard deviation is also very high but as seen in Figure 10, the concentration is regardless higher than the other sites. No significant difference was found for Fe where the values were about the same. A significant difference was found for Zn at both study sites compared to the reference site with values about four times higher.

Table 10 - Mean values for metal concentration in maize in mg/kg DM, statistical information and grouping information for soil samples using Tukey method. Sites that do not share a letter are significantly different. This was analysed in Malawi.

	n	Cu	Fe	Zn
		(mg/kg DM)		
Mean values (mg/kg DM)				
WWTP		2	130	130
WD		88	120	150
Ref		1	140	34
Standard deviation				
WWTP		3	64	56
WD		57	93	100
Ref		3	78	20
P-value		0.00	-	0.02
Grouping information				
WWTP	9	B	A	A
WD	5	A	A	A
Ref	5	B	A	B

33
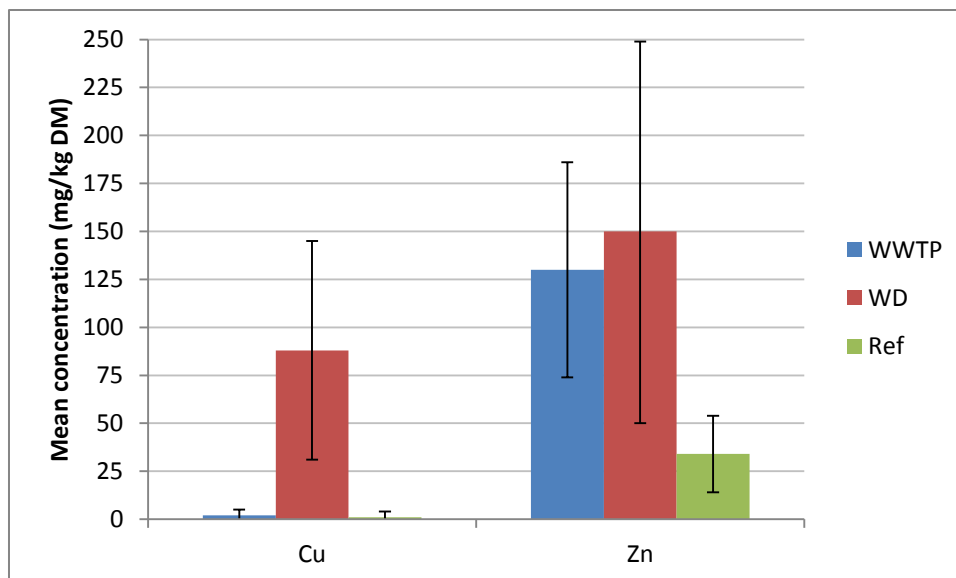
Figure 10 - Comparison between concentration of Zn and Cu in maize in mg/kg DM. This was analysed in Malawi.

The results from the analyses made in Sweden are presented in Table 11 and Figure 11. There was a large variation in Cd between the sites where the concentration in maize was highest at WWTP. In two out of three maize samples the levels are above 60 mg/kg while nowhere else are any values above 10 mg/kg. This might seem odd but note the asterisk clarifying that the third sample was from maize which was not ripe which, in turn, might indicate that this is not comparable to the other two and that Cd was actually very high at WWTP. Cr was found in two out of three samples at WD and in all maize at the reference site with very high levels in one. The sample with the highest Pb content was found at the WD, which also had the highest mean value but not far from the mean value at the reference site.

Table 11 - Mean values for metal concentration in maize in mg/kg DM. This was analysed in Sweden. *Maize 8 was not ripe and very small.

	Cd	Cr	Pb
	(mg/kg DM)		
WWTP			
Maize 2	60	-	26
Maize 5	62	-	23
Maize 8	7.2*	-	38
Mean	*43*	*-*	*29*
WD			
Maize 1	2.8	-	32
Maize 3	8.0	6.9	41
Maize 5	6.1	6.6	53
Mean	*5.7*	*4.5*	*42*
Ref			
Maize 1	6.4	4.9	26
Maize 4	1.7	6.9	49
Maize 5	-	24	42
Mean	*2.7*	*12*	*39*

34
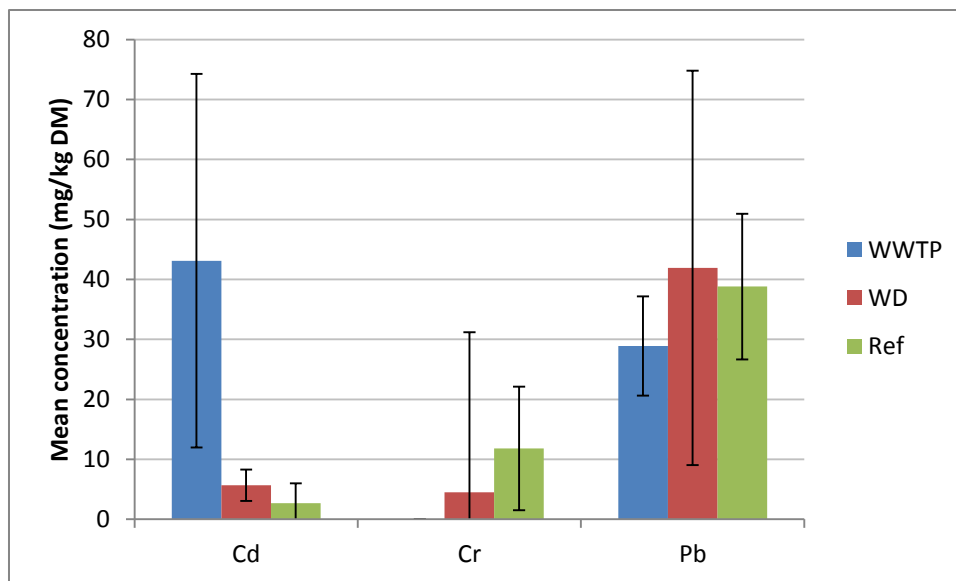
Figure 11 - Comparison between concentration of Cd, Cr and Pb in maize in mg/kg DM. This was analysed in Sweden.

The Zn levels in pumpkin leaves were about three times higher at the WWTP where a significant difference was found (Table 12). No significant difference was found for Cu or Fe due to the large standard deviation.

Table 12 - Mean values for metals in pumpkin leaves in mg/kg DM, statistical information and grouping information for soil samples using Tukey method. Sites that do not share a letter are significantly different. This was analysed in Malawi.

	n	Cu	Fe	Zn
Mean values				
Ref		1	1300	87
WD		-	220	88
WWTP		3	2400	300
Standard deviation				
Ref		3	1100	29
WD		0	25	15
WWTP		7	905	120
P-value		-	0.02	0.00
Grouping information				
Ref	5	A	A B	B
WD	2	A	B	B
WWTP	9	A	A	A

Eatable weed and pumpkin fruit was only found and collected at the WD and WWTP. As seen in Table 13, all metal levels were higher in pumpkins collected from the WWTP than the WD. There was less difference found in eatable weed except concerning Zn where the WWTP have more than four times as much Zn.

Table 13 - Mean values for pumpkin fruit and eatable weed collected from the waste dump and waste water treatment plant in mg/kg DM. This was analysed in Malawi.

	Cu	Fe	Zn
Pumpkin fruit			
WD	-	180	79
WWTP	10	260	120
Eatable weed			
WD	-	260	73
WWTP	-	360	400

The results for plants other than maize based on the analyses made in Sweden are given in Table 14. As for maize, no Cr was found at the WWTP. No large differences can be seen for Pb at either of the sites in pumpkin leaves but Pb is a bit higher at the WWTP in pumpkin fruit compared to WD. Cd in pumpkin leaves was lowest at the reference site and highest at the WD. In the pumpkin fruit, Cd was also higher at the WD compared to the WWTP. No pumpkin fruit was collected from the reference site.

Table 14 – Other plant samples analysed in Sweden in mg/kg DM

	Cr	Pb	Cd
		(mg/kg DM)	
WWTP			
Pumpkin leaf 3	-	30	6.7
Pumpkin fruit 6	-	36	7.2
WD			
Pumpkin leaf 1	-	34	8.4
Pumpkin fruit	3.7	23	9.3
Ref			
Pumpkin leaf 4	1.6	39	5.4

Ash

Table 15 presents all results of metal content in ash from the waste dump. Cu, Fe and Zn was analysed in Malawi for three ash samples while Cd, Cr and Pb for one ash sample (Ash 1) was analysed in Sweden. The Cu concentration is a lot higher compared to 12 mg/kg that was found in the soil. Fe is about twice as high compared to the soil and Zn has about the same concentration as in the soil. Cd differs a bit from 2.0 mg/kg in the soil, Cr is about twice as high and Pb is about the same.

Table 15 - Metal concentration in ash collected from waste dump in mg/kg ash. Cu, Fe and Zn were analysed in Malawi while Cd, Cr and Pb for Ash 1 was analysed in Sweden.

	Cu	Fe	Zn	Cd	Cr	Pb
Ash 1	88	1600	170	3.19	15.7	45.0
Ash 2	63	2100	110			
Ash 3	61	1300	230			
Mean	*71*	*1700*	*170*			

Water

The waste water treated at the WWTP was not used for drinking purposes but comparisons were still made with guideline values for drinking water to estimate the concentration in the waste water. There were no proposed guideline values for Fe and Zn but for the rest of the researched metals, guideline values are displayed below Table 16. Cu, Fe and Zn were analysed in Malawi while Cd, Cr and Pb was analysed in Sweden. Cu was below the guideline values even before treatment. Cd was detected with values above the guideline values except in Pond 1 where it was not detected at all. Pb before treatment was above the guideline values but was not detected in the water after treatment. Regarding Fe, Cu, Cd and Cr, there is no clear decrease of any of the metals before and after treatment through the biofilter.

Table 16 - Mean values in metal concentration from the water found at the WWTP in mg/l. Cu, Fe and Zn were analysed in Malawi while Cd, Cr and Pb were analysed in Sweden (World Health Organization 2011).

	Cu	Fe	Zn	Cd	Cr	Pb
Before treatment	0.5	0.6	0.79	0.0185	0.015	0.11
Pond 1	0.5	0.8	1.1	-	-	-
Pond 2	0.6	0.6	0.5	0.074	-	-
Outlet	0.5	1.3	0.3	0.079	0.016	-
Guideline values	*2*	*-*	*-*	*0.003*	*0.05*	*0.01*

5.3 Waste management

The final disposal of solid waste in Zomba, Malawi, is one open disposal site where all the collected waste from Zomba City is disposed. The waste is disposed in a pile close to the road during the rainy season when farmers are growing crops behind it. During the dry season, all waste is transported down to the field. There is no sorting of the waste and no rules regarding what can be deposited. No industries are leaving waste here but at the site everything from food leftovers to car batteries are dumped (Zomba City Assemble, 2015). Except this official waste dump, several public waste heaps were observed close to trading centres and villages. In some places, some kind of cement containers had been set up by the local government but observably, they were not emptied often or at all and people still threw waste all around it.

By observations of the waste it was clear that the main fraction was organic material at about >50-60 % where most of it was dry leftovers from maize. ~20 % was plastic, mainly plastic bags and the rest was made up of clothes, ceramics, glass and metal cans. Batteries were also observed, both in the waste pile and still remaining on the field.

5.4 Interviews with farmers

The field at the waste dump is owned by Zomba City Assemble who allowed a man to farm there, whom had no other land to cultivate on. The fields close to the waste water treatment plant was also own by the City Assemble but in this case, the land functioned as a privilege for the employees whom were assigned a piece of land each which was then rotated. Interviews were performed with the two farmers growing crops at the two study sites. They both grew maize as main crop and some pumpkins and other naturally growing plants. The farmer at the waste water treatment plant manages to get 75 kg maize/month for his family of 6 people. The farmer at the waste dump got 50 kg maize/month for his family of 5 people.

They both consume everything they grow on their own and some extra has to be bought for the farmer at the WWTP. The farmer on the waste water treatment plant spends 2 h/day for 2 months a year on the site while the farmer on the waste dump spends 5 h/day for 2 months a year.

Calculations for TDI values were made by assuming that the daily intake of maize is equally distributed in the families resulting in 0.41 kg/day from WWTP and 0.33 kg/day from WD. A mean value was calculated for each metal concentration in the maize. Wet weight for maize was calculated by: $WW = DW \times ((100-\%moisture)/100)$ from the average moisture percentage value 82 % earlier calculated for the analyses. This was further multiplied by the consumed mass maize to see the daily intake of heavy metals. The results are shown in Table 17.

Table 17 - Heavy metals consumed for the families growing crops at the two contaminated sites

	WWTP			WD		
	mg/ kg dry weight	mg/kg wet weight	Daily intake mg/day	mg/ kg dry weight	mg/kg wet weight	Daily intake mg/day
Cd	43	7.7	3.1	5.7	1.0	0.33
Cu	2.0	0.36	0.15	88	16	5.1
Cr	-	-	-	4.5	0.80	0.26
Pb	29	5.2	2.1	42	7.5	2.5
Zn	130	23	9.5	150	27	8.7

A comparison between the TDI to the daily intake of heavy metals through maize is made in Table 18. This is illustrated with two examples, one adult of 70 kg and a child of 10 kg to see how much metals can be consumed before negative health effects can arise. The maize consumed per day is assumed to be 0.37 kg based on an average between the farmers.

Here it is viewed that Cd and Pb exceeds TDI for all sites. Comparing this to a child of 10 kg body weight, the values are further exceeded. Copper is exceeded for children at the WD. Zn is also exceeded for children at all sites.

Table 18 - Tolerable Daily Intake per 70 and 10 kg body weight and comparison between all sites with the same average consumption. Cd, Pb and Cr are from analyses made in Sweden.

	Tolerable daily intake		Consumption		
	70 kg	10 kg	WWTP	WD	Ref
Cadmium (Cd)	0.014	0.002	2.8	0.37	0.18
Copper (Cu)	35	5	0.13	5.8	0.065
Chromium tot (Cr)	110	15	-	0.29	0.79
Lead (Pb)	0.25	0.035	1.9	2.8	2.6
Zinc (Zn)	21	3	8.5	9.8	2.2

6. Discussion

6.1 Waste management and environmental issues

Estimations show an increase in Malawi's population from 11.3 to 22.8 million people in 25 years which is beyond imaginable. To put this in relation, we can compare it to an industrialized country such as Sweden which has an expected increased from 8.9 to 10.3 million people in the same years (The World Bank, 2013). Worth mentioning is that Sweden is about four times the size of Malawi which results in a difference in population density of 21.6 pop/ km^2 for Sweden and 146.7 pop/ km^2 for Malawi (The Central Intelligence Agency, 2014). This rapidly increasing population and following population density will make the waste management more challenging with time. More people contribute to more waste and with urbanization and industrialization the composition of the waste will change from the larger fraction being organic material to more hazardous materials such as plastic, metals and electronics. Currently, about half of Malawi's population, and even more in Zomba, digs down their garbage at home and only 12 percent of Zomba city's waste is collected and transported to the official waste dump. What will happen when this changes and more waste is transported to this location, their only waste dump?

Following the waste hierarchy, a reduction in waste is priority one and this is seemingly achieved better in developing countries than in industrialized ones as a smaller amount of material and products are used in general. However, an observation made in Zomba was frequent sightings of plastic bags lying in ditches. These bags are used when buying groceries during which everything is packed in very small plastic bags. This is why waste management should be raised to a higher priority in Malawi: the amount of waste is lower than in developed countries due to lower consumption and possessing, not because people are trying to protect the environment. Waste is thrown everywhere and with an increase in population and urbanization, this will only get worse. Reuse of products and recycling of material is not only a way of reducing waste for disposal but also of importance for saving resources. Malawi is developing fast and products from the Western world are imported without the ability to take care of the resulting waste. An example is the beverage Red Bull which is imported and such aluminium cans were also frequently observed in ditches. The text on the can says it should be recycled but there is nowhere to put it for recycling. What seems to be the issue here is that the development of the market is faster than the infrastructure development. Companies such as Carlsberg and Coca-Cola have factories in Blantyre where bottles are refunded on their return, washed and reused. Maybe this is the only way beverages should be sold until a recycling system is initiated. Even if there are no possibilities to build recycling systems, there might be possibilities to export for recycling. For example, Africa's second largest smelting factory is located in Malawi's neighbour country Mozambique (Wikipedia, 2015). As mentioned in the section about waste management, one problem about recycling is the collection. However, this is partly already implemented with the glass bottles and also gives possibilities for waste pickers to earn money. Another positive aspect of reuse and recycling is all the jobs it creates. The majority of Malawi's population are farmers growing crops at very small areas. Maybe a better solution is for a larger part of the population to have other jobs, earning money and buying food from fewer farmers with larger fields. With more

39

jobs outside the agricultural sector, Malawi could also be more self-dependent rather than importing products that are currently made in other countries, e.g. China.

When speaking to a worker from Zomba City Assemble, they said that they burn parts of the waste dump to avoid plastic bags flying around. When asked about the ash flying around instead and the environmental impacts of that, it was clear that this was not considered as a problem. Every day in Zomba, you can see someone burning their waste in their backyard. Except this possessing a risk in fire spreading it is never healthy inhaling smoke, independent of its content. If waste is to be burned, it should be done in an incinerator, where at least the vast majority of hazardous particles and environmental pollutants can be contained. This is also a way of creating jobs and an incinerator even produces electricity which would be good for a country where electricity is not always guaranteed.

Since the majority of Malawi's population are farmers growing crops for their own consumption, it is easy to understand that the government will not have a working tax-paying system anytime soon. It is neither likely that the inhabitants are willing to pay for the waste management services when it is custom to just dig down the waste in the backyard. This could however be solved by encouraging the private sector to provide these services where they can make money from it, charging for services etc. A large part of the waste problem could be solved by just sorting the waste at a house hold level. It seems very unnecessary to mix food leftovers with plastic and other hazardous materials and put it in the same pit. A good and effective first step would be to just sort the organic material from the rest and only let that part end up in the fields. Composting can be encouraged with the incentive that it will increase the growth of crops and therefore yield. If we want to focus on improving the waste management as soon as possible, a landfill would be preferable to the present open dump. Since the generated waste in Zomba is still low, it does not necessarily have to be a large project. At the waste dump, the soil was very difficult to dig in, implying that the soil has very high clay content, later confirmed to be 35 %. This means that if a hole for a landfill is dug, a layer of clay will probably already be in the bottom, protecting from leakage. The most important part is of course that no one cultivates on top of the landfill but this will be impossible to do as long as the landfill is not filled and covered. However, even if this happens   it is still better than the current field covered with waste.

In a country as small as Malawi, it is hard to imagine the variety of weather throughout the country as well as the different seasons. Zomba was not very affected by the recent flooding due to the high elevation, but when traveling to Majete, large areas in the valleys were pointed out to have been flooded. However, we were informed that the flood had brought away large parts of the waste in Zomba and that this often occurs during the rainy season. This could be improved by building better containers for waste, if not a landfill. Another issue in developing countries in general is the lack of control systems. Developed countries such as in the EU have control systems forbidding products containing hazardous materials entering waste dumps. However, there is not much to do about the waste since there is no other alternative. Further, many developing countries also import sub quality products, banned from other countries which might be anything from plastics containing hazardous materials to fertilizers

containing cadmium. Due to this, it is even more important to study the environmental impact of waste and follow up contaminations.

Other environmental issues, such as deforestation, will not stand unaffected from the rapid population increase either. An increased lack of space for cultivation will probably increase deforestation together with an increased need for fuel. When passing the Shire River, it was obvious that eutrophication is a severe problem with aquatic plants covering almost the whole surface. More people, more waste and more unpredictable weather will only make this worse. When taking a closer look, they were actually harvesting the plants since they caused blockage in the turbines in the hydro power plant. Unfortunately the harvested biomass was not used for making biogas or similar but instead transported away and put in a pile, a very big pile, where the nutrients will probably run away again since the soil seemed sandy and had nothing growing on it. If this would be used for making biogas instead, not only would leakage be avoided, a new energy source should be implemented but also possibilities for cheaper fertilizers from the leftovers and further possibilities for jobs.

During the study in Zomba, it was observed that all places possible for growing were used for that purpose. As expected, food safety is not prioritised in a country when food security is still an issue, where contaminated food is, of course, a better option than no food at all. Still, what is alarming is the ignorance of the problem. The population density and following lack of space for farming is the main reason for growing crops at contaminated sites and when arriving in Zomba thought to be the only reason. When talking to farmers and even people working at the university it was seemingly obvious that farmers saw no problem in growing crops at contaminated sites. Moreover, this was even considered to be positive since the yield was better from the nutrients leaking from the waste. The general opinion among the inhabitants seems to be that waste is "free fertilizer". This is not necessarily only negative since it serves it purpose of bringing nutrients back to the soil but unfortunately it can also bring hazardous substances as well. However, this was obviously not known or at least not considered to be a problem at all. The government in Malawi should try and make food safety a larger priority than it is. By informing the population about the risks with contaminated sites, at least people will have the opportunity to make an informed choice. Also, if fertilizers were cheaper and easier to obtain, people would not need to use contaminated sites and waste as a source of nutrients.

6.2 Results
Unfortunately, Malawi did not have any guideline values for contaminated soil which is why SEPA's generic guideline values were used instead. Due to a lack of geological data, no background levels were known and it is therefore possible that some levels naturally occur in higher concentrations. These guideline values are generic and should therefore only be used for estimating a possible contamination and not to classify the sites as contaminated. Due to large differences in hydrogeological conditions etc. site specific guideline values are necessary for further risk assessments. It is of course neither possible to determine all kinds of risks based only on comparisons made with guideline values but it can serve as a good indication thereof. To further predict the risks and what will happen in the future, modelling would be a possible next step. The study was planned to include SEPA's "Conceptual model

for contaminant release, transport and exposure" but due to insufficient data for parameters, this was not possible. Another reason is that the farmers did not spend as much time in the fields as expected, lowering their exposure of inhalation or ingestion of soil. However, some heavy metals can be dangerous via direct contact to the contaminated soil even in small amounts and the farmers were not using protective clothes, not even shoes. In addition to the guidelines, a reference site was also used to compare the results. There are no guarantees that the chosen site is a suitable reference site due to little information about its history but it is assumed to have a lower risk of contamination.

The water at the WWTP was said not to be used for drinking water. However, even if no one was drinking the water at the site there is no guarantee that water is not collected further down the stream. Also, it was observed that children were playing both at the constructed bio-filters (which was broken during the whole stay) and in the ditches where accidental consumption is highly possible. For these reasons, WHO's drinking water quality guidelines was used but mainly to give an estimation of the concentrations found.

Unfortunately, not enough samples were brought back to Sweden to statistically verify significant differences between the sites as was done for the analyses made in Malawi. Without significant differences it was not possible to decide on keeping or rejecting the null hypothesis. It is therefore important to remember that the results of Cd, Cr and Pb are not significant and should only be considered as indications of excessive levels. Also as mentioned earlier, even the results of Cu, Fe and Zn analysed in Malawi are uncertain.

Unreliable data - Comparison with earlier studies

Prabpai et al. (2009) conducted a study to research the effects of residues from a municipal solid waste landfill on maize yield and heavy metal content (Table 19). The landfill was filled about 10-15 years ago and was now excavated and used for this study. A hybrid sweet corn was cultivated on four different soil-residue compositions (with residues added at 20, 40, 60 and 80% v/v) and one control with no residues. The results showed no significantly different metal content in maize grain except for Cd, Ni and Zn compared to the control. Cd and Zn in maize grain were also strongly positively correlated with the concentrations in the soil where the concentration was at highest in the 80 % treatment which was significantly higher than the control. However, all heavy metal content was within regulated limits for human consumption (Prabpai et al. 2009).

Carbonell et al. (2011) also researched the effects of municipal solid waste compost on soil properties and uptake but also the distribution in the maize (Table 19). The results showed an increase in Cu, Pb and Zn in the soil but no significant differences were found in maize compared to the control. The biomass was also considerably enhanced. The results regarding distribution indicate that the maize root system acts as a barrier for Cr and Pb which means that metal uptake and translocation is lower in aerial plant parts (Carbonell et al. 2011).

Table 19 – Heavy metal content in maize and soil from two earlier studies (Prabpai et al. 2009; Carbonell et al. 2011)

Metal	Prabpai		Carbonell	
	Concentration in maize grain	Concentration in soil mixed with 80 % residue	Concentration in maize shoot	Concentration in MSW compost
Cd	0.018	1.69	0.07	0.21
Cr	0.06	23.8	<0.01	21.38
Cu	5.3	82.1	1.12	16.14
Pb	0.07	83.8	0.16	35.61
Zn	41	369.6	15.12	66.43

This comparison was made to be able to validate the gained results. Of course different analytical methods and soil conditions might result in large differences but we can still compare the general differences between the concentrations in each site´s soil to the concentration in maize. There are also differences in the waste composition and amount, e.g. the landfill in Prabpai et al. (2009) was old and large parts of the waste was fully degraded while Zomba´s WD was filled with new waste continually on the topsoil.

At all sites in Malawi, the concentration of Cd was higher in maize than in the soil which was not the case in the earlier studies. The concentration of 43 mg/kg in maize at the WWTP is clearly incorrect compared to the previous studies: Carbonell et al. (2011) had 0.07 mg/kg and Prabpai et al. (2009) had 0.018 mg/kg. WWTP had the highest concentration of Cr in soil but no Cr was found in maize at all. This is not unreasonably since Cr is strongly bound in the soil and both earlier studies only found very low levels in the maize. However, the concentration in soil at Ref and WD are lower than the earlier studies and still high concentrations were found in maize. This seems highly unlikely to occur. The concentration Cu in maize at WD is actually a lot higher than the concentration in the soil. This is probably not true but the WWTP and Ref follow the same pattern as the earlier studies indicating that these values might at least be true. Prabpai et al. (2009) had high levels of Pb in the soil, higher than all study sites, but still only 0.07 mg/kg in maize. The study sites concentration of 29-42 mg/kg indicates that this study´s result is probably wrong. Prabpai et al. (2009) also had the highest Zn concentration in the soil but still the maize only had one ninth the concentration. At the study sites, the concentrations of Zn are almost the same as in the soil which is probably not the case. Concluding, the results cannot be trusted except possibly Cu at the WWTP and Ref. However, the same method was used for all sites so even if the values are too high, the differences between the sites might still be usable and the discussion will focus on that (Prabpai et al. 2009; Carbonell et al. 2011).

Soil properties

The method used for extraction of nitrogen, CEC etc. made it difficult to compare results with other studies using different analytical methods. However, the results were compared with each other to see if there were positive aspects on cultivation close to WWTP or WD. The difference in soil properties was mainly pH and nutrient status. The WWTP had the highest nutrient status, highest carbon content and lowest pH. The higher nutrient status was unexpected since the soil was unfertilized except for the overflows of waste water. The reference site was fertilized but had the lowest nutrient status. At WWTP there were areas

where nothing was growing or at least the maize were a lot smaller. This might be due to the low pH.

Cadmium

As mentioned in *Results*, the results from Malawi were not used due to the improbable high concentrations way above the guideline value. Instead, samples were brought back to Sweden to control the accuracy. One value at WWTP turned out to be higher than all other results and was more than 50 times higher than the guideline values. However, since no Cd at all was found in the other two samples, it is probably an analytical error but might of course also be a "hot spot". Further discussed regarding analyses, it is assumed that the analyses made in Sweden are more reliable and those mean values will be the ones further discussed. It is still important to remember that neither these values can be fully trusted. WD had a mean value of 2.0 mg/kg soil which exceeds the guideline value of 0.5 mg/kg. There was suspicions that Cd contaminated fertilizers were used at the reference site but no Cd was detected at the reference site. This indicates that the excessive levels at WD origin from the waste, further confirmed by the Cd found in ash. This is not unlikely since Cd is found in products such as PVC-plastics, paint, batteries and different alloys. Regarding maize, there were small differences. At the WWTP, two of the samples had values over 60 mg/kg dry matter while all the other maize samples had below 10 mg/kg. This could either be explained by the two mentioned samples being some kind of error but another explanation is that the values are accurate and that the third value for WWTP of 7 mg/kg is misleading. This is based on the fact that Maize 8 from WWTP was very small and unlike the others not ripe at all. Cd levels above the guideline value of 0.003 mg/l was found in the water both before treatment, after treatment and even out into the stream with no clear decline in concentration. This indicates that the Cd contamination comes from the treatment plant. It does not seem unlikely that the maize at the WWTP had the highest levels since the mean values were higher in the soil and the fact that the pH was very low, increasing the Cd uptake since it becomes more available. Actually, the results support the correlation with lower soil pH and higher Cd concentration in maize, and the other way around, for all three sites. If this is the case, recommendations are to lime the soil to increase the pH to reduce the Cd uptake. Further, this would probably also increase the yields, since the pH at the moment is very low, especially at the WWTP.

Chromium

No sites had Cr levels above the guidelines. Cr was outstandingly higher at the WWTP with a mean level of almost 50 mg/kg soil compared to 11 and 8 mg/kg for WD and Ref, respectively. The guideline values are for total Cr and no guaranties are that chromium(VI) is not present. However, this is unlikely due to low pH and reducing conditions in the soil. The reason for the higher amount of Cr at the WWTP might be because Cr can be used for corrosion protection in pipes. The Cr found in ash was about twice as high than the soil at the WD. Cr was found in the water collected from the WWTP but no levels were over the guideline values.

Copper

Cu is remarkably higher at the WWTP with 118 mg/kg soil, exceeding the guideline value of 80 mg/kg soil, where a significant difference was found. It is however important to keep in

mind the high standard deviation. Low levels were found in the soil at the WD but the maize had more than twice as high levels compared to the other two sites. The higher amount copper in the soil at the WWTP might be explained by that Cu^{2+} forms strong complexes to humus meaning that the organic material content in the soil in general decides how much Cu^{2+} is bound. This theory is supported by the fact that the TOC was twice as high at the WWTP compared to the others. This might also be the reason for why Cu^{2+} is not as easily taken up by the plants at the WWTP as it is at the WD. In urban areas, where the WWTP is located, corrosion of copper roofs is an important source. This might explain why the levels where higher here since there was no houses close to the WD, only one house close to the field at the reference house but several houses close to the WWTP. Unfortunately, there is no information about the roof material. Cu was found in the water sampled at the WWTP but below the guidelines for drinking water of 2 mg/l. Since the values were so low, it is unlikely that this is contributing to the contamination. However, since the levels were about the same throughout the treatment it is possible that the Cu is accumulating.

Lead

Pb was analysed in the pilot study where all levels exceeded the guideline values. The absorbance was 0.002-0.004 for all sampling points, resulting in 200 mg/kg soil for all due to significant figures. These values were not used since they are clearly inaccurate. The AAS lamp did not work in the main study and Pb was instead analysed in Sweden. The reference site had the lowest levels while the WWTP had the highest with twice the amount, exceeding the guideline value of 50 mg/kg soil. The WD had a level of 49 mg/kg which is on the limit of the guideline values. Pb was found in the ash in a somewhat higher concentration than the soil, indicating it might be the source of lead to the areas. In spite of the WWTP having the highest levels in soil, this site has the lowest levels in maize. This might be explained by Pb^{2+} binding very strongly to humus as well as oxide surfaces, even at low pH. The WWTP had a very low pH of 3.7 but also twice as much carbon as the other sites.

Lead was expected to be highest at the waste dump since leakage from waste dumps are one of the main sources. Further, the WD was located close to the road where it could possibly have been contaminated from leaded gasoline. However, this was removed in the 90s and before that the activity of cars in Malawi was very low. Pb is used in many industries, however no industries were located anywhere near the area, although lead can travel far distances. Instead, the source for the high levels at the WWTP was most likely the waste water. The Pb levels in the water at the WWTP before treatment had levels way above the guideline values. However, no Pb was found after treatment but as mentioned earlier, the WWTP frequently floods the area and was currently broken with water leaking in all directions which is probably what was causing the contamination.

Zinc

The Zn concentration in soil were all below the guideline values but a significant difference was found for both sites compared to the reference site which had less than half the concentration. The same was a fact for maize where a significant difference was found for the reference site's lower concentration. Large quantities of Zn are used in the society, which is

why it was expected in the waste. Due to zinc's low toxicity, the guideline values are set high and for now Zn should not cause any harm.

Objectives and hypothesis

The main objective of this study was to evaluate if the two study sites were contaminated with heavy metals and if they significantly differed from the chosen reference site. If the null hypothesis was rejected, the study sites had a significantly higher concentration of heavy metals compared to the reference site. As mentioned, Cd, Cr and Pb analysed in Sweden did not have a sufficient amount of samples to be able to perform statistical analyses. Also, keep in mind that the values gained are unreasonably high and that this comparison might be misleading or even completely incorrect.

The grouping information gained from Tukey´s test shows that the null hypothesis is rejected for Zn at both sites regarding both soil and maize. It is also rejected for Cu at WWTP regarding soil and Cu at WD regarding maize. The significant level was <0.05 and all of these had P-values below this level meaning that with a certainty of 95 %, there is a significant difference.

Tolerable daily intake

The daily intake of the heavy metals analysed was based on the interviewed farmer's daily average consumption of 0.37 kg maize. This was also based on assuming that the maize is distributed even in the families, which is not guaranteed. The calculations for TDI values were based on assuming that an adult weighs 70 kg and a child 10 kg. However, a child weighing 10 kg will probably not consume the same amount of food as an adult. What is also important to keep in mind is that women usually weigh less, which makes them more vulnerable and especially if they are pregnant. If anything, pregnant women should not consume contaminated crops since it might be transferred to the foetus. Keep in mind that the some of these values are not significant and cannot be trusted but can still be seen as an indication of excessive levels.

As presented in the results, all sites had Cd and Pb levels exceeding the TDI in the maize. For children, Cu was exceeded at WD and Zn at all sites. As mentioned under toxicological effects of cadmium in *Theory* (chapter 3)*,* the protein regulating zinc metabolism reduces the effects of chronic exposure of chromium at low levels. However, since the levels are so high above TDI and since zinc was also fairly high in the maize, it is possible that the protein capacity is exceeded. This might then result in kidney diseases, lung damage and bone degradation for the farmers, not to forget that cadmium is carcinogenic. The intake of lead for children was 80 times higher than the TDI at the WD which is very frightening since children are most at risk due to them absorbing a higher percentage and also because their brains are growing rapidly. Undernourished children are even more at risk since their bodies absorb more Pb if other nutrients, such as Ca, are lacking. It is therefore very likely that these lead contaminated crops might interfere with their normal brain development, impairing learning ability and intellectual development. It is important to remember that these neurological and behavioural effects are probably irreversible. It is also important to remember that lead can cross the placenta and cause severe harm to both the foetus and the mother. The lead was also

very high for adults, about ten times higher than TDI, which can cause for example anaemia, high blood pressure and kidney failure. Zn is essential for humans and has a very low toxicological effect but it does exhibit toxic properties at high concentration and can impair cellular functions. Cr was not exceeded for any site but this TDI value is based on total Cr and not Cr(VI). However, as mentioned, hexavalent chromium is unlikely at this low pH and reducing conditions.

6.3 Sources of error

The first liabilities observed at Chancellor College were all the broken equipment: everything from analytical instruments to broken beakers and pipettes. A lack of completely cleaned materials might also have affected the results by contaminating the samples. However, for the main part of the laboratory work, new beakers etc. were used to avoid this. As mentioned, the MP-AES instrument planned to be used for analyses was broken during our stay. Instead, an old AAS (Buck Scientific Model 200A) was used where several lamps were broken or overused. This might be one reason for the unreliable results, especially for cadmium. However, the calibration curves prepared all showed correct linear responses ($R^2 > 0.98$). Possible explanation might instead be different kinds of interferences such as matrix interferences or background absorption due to a lower flame temperature which is probably even more likely due to the old instrument (Essington, 2004). It is not possible to draw any conclusions but the instrument should be further tested to see if it is reliable. The study was planned to contain a pilot study where all possible metals were analysed and based on that make a qualified decision about which metals to study. Instead, the metals analysed were the ones possible to analyse with the AAS which made this the largest limitation of the study.

The other main reason for the unreliable data is the limitation given by the analytical method. There is always a detection limit when performing these kind of analyses and therefore also when using AAS. The detection limit depends on the element of interest, the compositional properties of the samples solution and the instruments set-up variables (Essington, 2004). According to Shahin Norbakhsh, assisting with the analyses made at SLU, AAS is of best use for concentrations measured in mg/L which is also mentioned in Essington 2004. When the concentrations go below or close to this concentration, the AAS will give a result of zero even if the sample is not free from that specific metal. Also, this gives big room for uncertainties where small variation gives a large difference after calculations to the final results. Jon-Petter Gustafsson at the Department of Soil and Environment at SLU further explained that AAS is not ideal for analysing Pb and Cd due to the low concentrations. For these reasons, the measured concentrations are highly unreliable. Due to suspicions about very high Cd concentrations, some samples were brought back to Sweden for control analyses where it was confirmed that the values were very different which can be explained by the values being close to the detection limit. The AAS at Chancellor College gave about the same absorbance for Cd for all samples (~0.4-0.6) but when calculating and taking the dilution into account, the concentration of Cd becomes twice as high in the plants which seem to be a legit explanation as to why the plant samples had twice as high Cd content than the soil. To prevent this uncertainty, there are two ways to go: a change in analytical method to one with a lower detection limit or increase the concentrations in the samples. By using higher concentrations,

i.e. more soil in the samples, or a lower dilution, i.e. another extraction method, there will be less deviation between the samples and more reliable results. When the low levels of Cd were observed at SLU, an effort was made to use the AAS's graphite oven but unfortunately, it was also broken.

As mentioned in the methods, the extraction method was changed from tri-acid digestion to di-acid digestion regarding the soil. This change was made due to a lack of hydrofluoric acid. The di-acid digestion is known as pseudo digestion or partial digestion since not all is digested but this was not considered to be a problem since the main interest was what is easily and biologically available for plants. However, this might result in lower concentrations of the metals than what is actually in the soil. Also, one mistake made was not to use the same acids for the standard solutions, this is important for further analyses.

6.4 Future actions

Obviously, the first precaution should be to avoid cultivating at contaminated sites. In Malawi, this is not as easy as it sounds where contaminated food is better than no food at all. If better land would be distributed, people would not have to farm at contaminated soil. At least, people should be aware of the risks they are exposed to and possibly be taught counter measures. The second action should be to avoid having one family consuming all contaminated crops. Maybe a better solution would be to evenly distribute the contaminated crops between several families where children and at least pregnant women are spared. Since consumption of some toxic metals exceeded TDI, health examinations should be considered for the families consuming crops from the contaminated sites and protective clothes should be distributed to the farmers. The easy improvements mentioned could for example be a landfill instead of the open dump, which would reduce the environmental impact. This would also result in a smaller area needed for the waste and at least before it is covered with soil, impossible to cultivate on. This should of course be done at a location where it would have as little impact as possible. Sorting of waste at house hold level would also be beneficial and might encourage, through composting, to at least sort food waste from other kinds of waste.

As mentioned, the sites cannot be classified as contaminated based on these results. To further be able to perform a detailed risk assessment, to see if the sites are really contaminated or not, the state of the soils including background levels of metals should be investigated and specific guideline values should be set. This reports background information and results can be used for further improved studies. Following up on presented research, recommendations are to analyse for additional toxic heavy metals, not presented in this thesis, and to analyse more samples for significant results regarding the metals analysed. In this thesis, only heavy metals were considered. In future risk assessments, other contaminants such as pathogens should also be investigated, especially at the WWTP. Additional scientific research that should be made is to develop guideline values for contaminated soil in Malawi since this can differ between countries. Further, other locations should also be investigated where cultivations occur on waste dumps or other possible contaminated sites. Finally, it is recommended that further studies use more modern and appropriate analytical equipment than what is currently available at Chancellor College and that standardized methods are prepared and followed.

7. Conclusions

Comparing the gained results to SEPA's generic guideline values for sensitive land use, the waste water treatment plant had excessive levels of copper, cadmium and lead, and at the waste dump cadmium was exceeded. Lead was also exceeded at the waste dump in two out of three samples but not as a mean value. It is however important to emphasize the uncertainty of the results. Cu had a very high standard deviation and at WWTP, Cd was only found in one out of three samples and at a very high concentration. Regarding Cd and Pb, the analytical method used (AAS) was not ideal since the levels were close to the detection limit. Compared to the earlier studies presented, all gained results showed higher concentrations in maize compared to what was found in the soil except for perhaps Cu at the WWTP and Ref.

Regarding TDI, it was shown that the heavy metal consumption was exceeded for Cd and Pb at all sites and in addition Zn for children. Cu was also exceeded for children at the waste dump. However, no conclusions can really be drawn with these results and even if there are indications of excessive levels, the results should be interpreted with caution. It is also important to understand that even if the concentrations are above the generic guidelines this does not mean that the sites are contaminated but gives an indication that the levels might be excessive.

Even if the gained values are inaccurate, the same method was used for all samples indicating that the differences between the sites might still be true. Comparing the study sites, the null hypothesis was rejected for Zn at both sites regarding both soil and maize. It was also rejected for Cu at WWTP regarding soil and Cu at WD regarding maize. This is why further risk assessments are still recommended. The most important conclusion drawn from this study is that the method needs to be changed in further research. A higher accuracy is acquired with more reliable instruments and combined with certified methods would increase possibilities for corrects comparisons with other studies.

Despite the inaccuracy of the results, waste management should be made a higher priority since the contaminations will only increase with growing population size and industrialization. Cultivation on contaminated sites should be avoided if possible and people should at least be aware of the risks and consequences it can have on their and their children's health. With informed choices, people might be able to reduce the affects, e.g. avoiding hot spots or increasing the soil's pH by liming. The open dump should gradually be improved to a sanitary landfill where all waste is collected until a recycling system or other better alternative is initiated. It is important to remember the risks for future contaminations if nothing is improved. It is also possible that other contaminants not analysed in this study are present.

Literature

An, Y.-J., 2004. Soil ecotoxicity assessment using cadmium sensitive plants. *Environmental Pollution,* p. 21–26.

Baird, C. & Cann, M., 2008. *Environmental Chemistry.* s.l.:W.H. Freeman and Company.

Berggren Kleja, D. et al., 2006. *Metallers mobilitet i mark,* Stockholm: Naturvårdsverket.

Burnley, S. J., 2007. A review of municipal solid waste composition in the United Kingdom. *Journal of Waste Management 27,* pp. 1274-1285.

Carbonell, G. et al., 2011. Effects of municipal solid waste compost and mineral fertilizer amendments on soil properties and heavy metals distribution in maize plants (Zea mays L.). *Chemosphere 85,* p. 1614–1623.

Chang, R., 2010. *Chemistry.* New York: McGraw-Hill.

Chonghaile, C. N., 2015. *The Guardian.* [Online]
Available at: http://www.theguardian.com/global-development/2015/feb/10/malawi-floods-devastation-far-worse-than-first-thought
[Accessed 27 April 2015].

Codex Alimentarius Commission, 2003. *Codex Alimentarius.* [Online]
Available at: ftp://ftp.fao.org/codex/Publications/Booklets/Hygiene/FoodHygiene_2003e.pdf
[Accessed 15 March 2015].

Elding, L. I., n.d. *Nationalencyklopedin - Komplexbildning.* [Online]
Available at: http://www.ne.se/uppslagsverk/encyklopedi/l%C3%A5ng/komplexbildning
[Accessed 3 June 2015].

Ellis, F. & Manda, E., 2012. Seasonal Food Crises and Policy Responses: A Narrative Account of Three Food Security Crises in Malawi. *World Development,* Volume 40, p. 1407–1417.

Eriksson, J., Dahlin, S., Nilsson, I. & Simonsson, M., 2011. *Marklära.* 1:1 ed. Lund: Studentlitteratur.

Essington, M. E., 2004. *Soil and Water Chemistry: An integrative approach.* Boca Raton, Florida: CRC Press LLC.

Food and Agriculture Organization of the United Nations, 2006. *Malawi.* [Online]
Available at: http://www.fao.org/nr/water/aquastat/countries_regions/mwi/index.stm
[Accessed 6 February 2015].

Google, 2015. *Google Maps.* [Online]
Available at: https://www.google.com/maps/place/Zomba,+Malawi/@-15.3950316,35.3239397,13z/data=!4m2!3m1!1s0x18d904a4e69c5955:0x3f17a7caed60f7de!5

m1!1e4
[Accessed 26 February 2015].

Guerrero, L. A., Maas, G. & Hogland, W., 2013. Solid waste management challenges for cities in developing countries. *Waste Management,* p. 220–232.

Kampa, M. & Castanas, E., 2007. Human health effects of air pollution. *Environmental Pollution 151,* pp. 362-367.

Magrath, J. & Sukali, E., 2009. *The winds of change: Climate change, poverty and the environment in Malawi,* Lilongwe: Oxfam International.

Malawi Orphan Care Project, 2015. *Malawi: The Warm Heart of Africa.* [Online]
Available at: http://malawiorphancareproject.org/about-malawi/
[Accessed 6 February 2015].

Minghua, Z. et al., 2009. Municipal solid waste management in Pudong New Area, China. *Journal of Waste Management 29,* p. 1227–1233.

Naseri, M., Vazirzadeh, A., Kazemi, R. & Zaheri, F., 2014. Concentration of some heavy metals in rice types available in Shiraz market and human health risk assessment. *Food Chemistry,* p. 243–248.

National Statistical Office, 2012. *Integrated Household Survey 2010-2011,* Zomba: National Statistical Office.

Pare, S., Persson, I., Guel, B. & Lundberg, D., 2013. Trivalent Chromium removal from Aqueous solution using Raw Natural Mixed Clay from BURKINA FASO. *International Research Journal of Environment Sciences,* pp. 30-37.

Prabpai, S. et al., 2009. Effects of residues from municipal solid waste landfill on corn yield and heavy metal content. *Waste Management 29,* p. 2316–2320.

Rosén, L. et al., 2006. *Riskvärdering vid val av återgärdsstrategi,* s.l.: Naturvårdsverket.

Rundquist, F.-M. A., n.d. *Nationalencyklopedin -.* [Online]
Available at: http://www.ne.se/uppslagsverk/encyklopedi/l%C3%A5ng/malawi
[Accessed 2 June 2015].

Sajidu, S. M. I., 2008. *Characterisation and interaction of mixed alkaline clays and Moringa seeds with heavy metals in contaminated water,* Malawi: University of Malawi.

Schübeler, P., 1996. *Conceptual Framework for Municipal Solid Waste Management in Low-Income Countries,* St. Gallen: Swiss Centre for Development Cooperation in Technology and Management.

Sharholy, M., Ahmad, K., Vaishya, R. & Gupta, R., 2006. Municipal solid waste characteristics and management in Allahabad, India. *Waste Management 27,* p. 490–496.

Sujauddin, M., Huda, S. & Rafiqul Hoque, A., 2008. Household solid waste characteristics and management in Chittagong, Bangladesh. *Journal of Waste Management 28,* pp. 1688-1695.

Swedish Environmental Protection Agency, 2009. *Riktvärden för förorenad mark - Modellbeskrivning och vägledning,* s.l.: Naturvårdsverket.

Swedish Environmental Protection Agency, 2012. *From waste management to resource efficiency,* Bromma: Swedish Environmental Protection Agency.

Swedish Environmental Protection Agency, 2012. *From waste management to resource efficiency - Sweden's Waste Plan 2012–2017,* s.l.: Swedish Environmental Protection Agency.

Swedish Institute for International Affairs, 2011. *Malawi - Befolkning & språk.* [Online]
Available at: https://www.landguiden.se/Lander/Afrika/Malawi/Befolkning-Sprak
[Accessed 6 February 2015].

The Central Intelligence Agency, 2014. *Africa: Malawi.* [Online]
Available at: https://www.cia.gov/library/publications/the-world-factbook/geos/mi.html
[Accessed 9 February 2015].

The Central Intelligence Agency, 2014. *The World Factobook - Sweden.* [Online]
Available at: https://www.cia.gov/library/publications/the-world-factbook/geos/sw.html
[Accessed 6 March 2015].

The World Bank Group, 2013. *Population, total.* [Online]
Available at:
http://data.worldbank.org/indicator/SP.POP.TOTL/countries/MW?page=6&display=default
[Accessed 7 March 2015].

The World Bank, 2013. *World Development Indicators.* [Online]
Available at: http://wdi.worldbank.org/table/2.1
[Accessed 6 March 2015].

United Nations Development Programme, 2014. *Table 1: Human Development Index and its components.* [Online]
Available at: http://hdr.undp.org/en/content/table-1-human-development-index-and-its-components
[Accessed 6 February 2015].

United Nations Human Settlements Programme, 2010. *Solid Waste Management - In the world's cities.* London: Earthscan.

United States Enviromental Protection Agency, 2000. *In Situ Treatment of Soil and Groundwater Contaminated with Chromium,* Washington, DC: United States Enviromental Protection Agency.

Wikipedia, 2015. *Mozal.* [Online]
Available at: http://en.wikipedia.org/wiki/Mozal
[Accessed 18 May 2015].

World Food Programme, 2014. *Malawi - Food security.* [Online]
Available at: http://www.wfp.org/countries/malawi/food-security
[Accessed 5 March 2015].

World Food Programme, 2015. *Malawi - Overview.* [Online]
Available at: http://www.wfp.org/countries/malawi/overview
[Accessed 5 March 2015].

World Health Organization, 2011. *Guidelines for Drinking-water Quality,* Malta: World
Health Organization.

World Health Organization, 2014. *Food safety.* [Online]
Available at: http://www.who.int/mediacentre/factsheets/fs399/en/
[Accessed 1 March 2015].

World Health Organization, 2014. *Lead poisoning and health.* [Online]
Available at: http://www.who.int/mediacentre/factsheets/fs379/en/
[Accessed 12 May 2015].

Zomba City Assemble, 2015. *Interview.* Zomba: s.n.

Appendices 1-4

Author: Sofie Orvestedt*

Table of content

Appendix 1 – Sampling performance

Background

A sampling strategy containing a detailed description of how the sampling was to be performed was first made. It contained descriptions and situational planning such as the area of sampling, locations for the sampling points and how the samples should be taken and handled.

The aim of was to by good planning perform sampling of high quality with the right equipment and methodology to avoid influence on the quality of the collected data (Swedish geotechnical society, 2013).

This strategy was throughout the study revised due to limitations. This is the final document describing in detail how the sampling was performed.

Objectives

The first objective with this study was to evaluate the concentrations of heavy metals in the surface soil and edible plants two sites of arable lands, one site close to a waste water treatment plant and one on a waste dump. The second objective was to evaluate possible positive influence from nutrient leaching from the waste water treatment plant/the waste dump to the arable land (Norrman et al. 2009).

Prior knowledge

No known earlier studies with a similar objective had been performed on either of the study sites.

Limitations

The contamination was assumed to be present in the whole chosen area and no subdividing of the sites was made. The equipment did not allow deep soil samples without destruction of valuable crops therefore the depth was limited to 0-20 cm for the majority of the soil samples.

Sampling scale

In order to take samples representing a larger soil volume, twelve samples from every sample point was mixed and one aliquot was further taken for analysis, Figure 1. This is called composite sampling and reduces the possibility for small variations in local concentration to affect the final results (Norrman et al. 2009).

Composite sampling is not recommended for volatile substances. In this study the only volatile substance of interest was mercury, but the concentrations of mercury were assumed not to be high (Norrman et al. 2009).
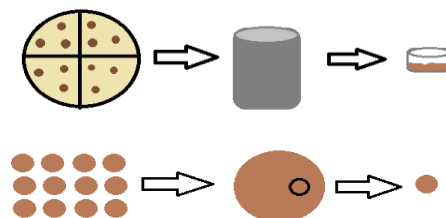

Figure 1 - An illustration of the composite samples from 12 individual samples to 1 composite sample and one aliquot for further analysing.

Approach

This study was designed with a probability-based approach to hypothesis testing. This means that the number of samples was calculated beforehand to ensure the chosen certainty in the results. To do this, a number of estimations were needed to be done (Norrman et al. 2009):

- Choice of statistical parameter (usually mean value).
- Estimation of statistical distribution of data. Keep in mind that data from contaminated areas usually do not have a normal distribution.
- Estimation of coefficient of variability. This can be done by performing a pilot study or by experiences from former studies.
- Decision of desired certainty.
- Choice of sampling pattern.
- Determination of needed number of samples.

The decided statistical certainty gives the risk of wrongly rejecting or not rejecting the null hypothesis, H_0. This can lead to two kinds of errors, called type I and type II (see Figure 2). If the null hypothesis is set as a hypothesis of zero change, meaning that there is no difference between the study site and a reference site, a type I-error would lead to that a clean area is declared as contaminated. In the same situation, a type II-error would result in that a contaminated area is declared clean. The risk for committing a type I error is given as α, and is commonly set as 0.05 or lower. For type II-errors the risk is given as β, and is commonly set as 0.2 or lower. The levels of α and β has to be adjusted according to the severity of the consequences from committing errors (Grandin, 2012).

	H_0 is true	H_0 is false
Reject H_0	Type I-error	Correct
Don't reject H_0	Correct	Type II-error

Figure 2 - Type I and type II errors

Pilot study

The sampling began with a pilot study to determine the standard variation in the samples. Based on these samples, calculations were performed in G*Power to decide how many samples were needed for an acceptable confidence interval. Limitations of costs or other resources can further reduce the number of samples but this was not a problem during the study.

The pilot study was planned to consist of 10 randomly placed soil surface samples within each location but this was delimited to one site – the waste water treatment plant. This delimitation was due to a lack of time. These samples were only analysed for heavy metals to estimate the standard deviation.

Documentation

It is important to thoroughly document samples and sample points, but also to document conditions and observations at the location and its surroundings. This was documented and is presented in *Appendix 2 – Field protocol* and examples of documentations that should be made are:

– Topography, geology and hydrological conditions
– Photographic documentations
– Weather
– Land use and other activities in the vicinity
– Field observations, e.g. smell and visual impressions indicating contaminations (Swedish geotechnical society, 2013)

Materials and methods

Soil samples

Most metals are bound to a certain extent in soils, mainly through surface reactions involving soil organic matter or iron and aluminium oxides, but it can also be through precipitation reactions. To what extent metals are bound depends on pH, redox conditions, DOC, concentration of competing ions etc. It is also important to consider the speciation of metals in the water phase since this affects bioavailability and toxicity. Heavy metals cooperate with the biological system in the soil (microbes and roots) and the soil particles in physiochemical reactions (e.g. adsorption). As a result of this, some metals stays in the upper soil layers due to adsorption of soil particles, root uptake and microorganisms or precipitates where the concentration of dissolved metals are larger than their solubility (e.g. at the soil surface at evaporation) (Berggren Kleja et al. 2006).

Analyse for: Moisture, texture, pH, electrical conductivity, TOC, DOC, available N, CaCO3, total P and K, P-AL, K-AL, CEC and total and dissolved heavy metals

Method:
Preparations

– Location of sampling point
– Naming of sampling point
– Making sure that all equipment was available and clean
– Making sure that all safety equipment was available
– Marking of all sampling vessels and making sure it was clear if there were several sampling vessels for the same sampling point and level

Documentation

- The sampling was documented in a sampling protocol
- Notations of soil type, smell and visual impressions etc. were made.
- Deviations were documented in the sampling protocol
- The location of the sampling point were noted

Note

- Avoid to smell the samples
- Document control samples or other quality controls

Cleaning of sampling equipment

- Mechanical cleaning was made between each sampling level
- Cleaning between sampling points were made with water due to limitations of washing-up liquid and since the risk of cross contamination was considered to be small.

Packing, transport and storage

- The samples were put in marked sampling vessels and sealed
- The samples were delivered and analysed as soon as possible

Note

- Pack the samples as soon as possible and store the sample so that vaporization is minimized
- Control how the samples should be transported and stored

(Swedish geotechnical society, 2013)

Soil profile
At the waste water treatment plant, a soil profile description was performed following FAO's guidelines for soil description (FAO, 1990). The purpose was to get a good overview of the soil's composition and to get samples from deeper layers (Swedish geotechnical society, 2013).

Materials:
- Shovel, knife
- Tape measure
- Water
- A flat piece of wood for rolling clay
- Sample vessels: plastic jars and buckets
- Safety equipment: gloves, boots, face mask

Method:
Sampling

- A hole was dug of approximately 0.5 m depth
- The shaft wall was cleared before sampling
- Samples were taken from each soil layer and mixed into one sample representing the arable soil

Note

- – It is generally not good to take samples of volatile substances from sampling holes
- – The soil was put back in the same way it was dug up, i.e. the soil layer should be as they were.

Soil surface

To be able to quantify the amount of heavy metals in the soil surface and to map heavy metal concentration, the samples were taken in a systematic grid pattern. The distance between the sample points was adjusted with consideration of the total site area and available time and resources. The number of samples taken at each site needed to be a sufficient amount to ensure that the conclusions from the study can be taken with a sufficiently low risk for type I and type II errors.

Materials:
- – Soil survey drill called "Trekantenborr" (see Figure 3)
- – Buckets
- – Tape measurements
- – Sample vessels: plastic jars and buckets
- – GPS
- – Sticks to mark out sample points

Method:
Sampling

- – The soil survey drill was put down in the soil to take out 12 samples in the same way as Figure 4 illustrates.
- – The soil from the drill was emptied in a bucket and mixed with all the soil taken from the sampling circle before one single sample was taken from the bucket (the aliquot) (Instutionen för mark och miljö, 2013).
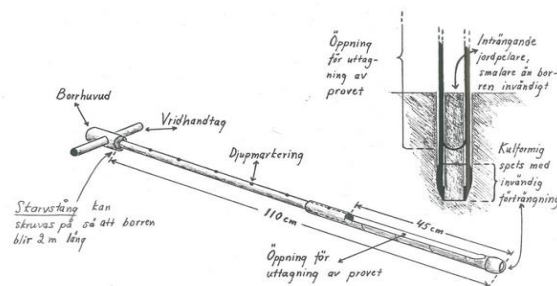- – The sampling circles were placed in a grid evenly distributed (Figure 5).

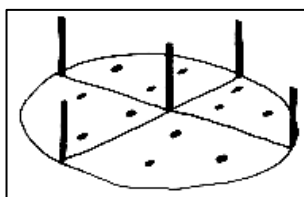**Figure 3 - Soil survey drill "Trekantenborr"**

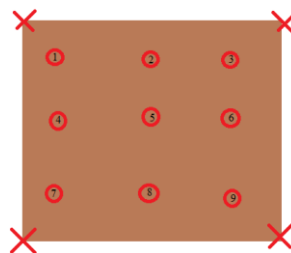**Figure 4 - Illustration of the sample circle and how the surface soil samples were taken**

Figure 5 - Sampling grid without fixed distance

Crop samples

Heavy metals can enter plants directly via rain and dust and also via uptake in the root system. If a plant is contaminated with heavy metals, the respiration and growth might be reduced. This leads to an interference with the photosynthetic processes and inhibits fundamental enzymatic reactions if accumulated at high concentrations. However, as long as these toxic metals are present in the soil at a low concentration, plants continue to grow regularly even though accumulating these heavy metals (Galal and Shehata 2014). Not only is the yield affected, crops growing in contaminated areas cause a serious health risk to consumers (Sarala Thambavani and Prathipa 2012).

Analyse for: Total heavy metal concentration

Materials:
- Buckets
- Sample vessels: plastic bags
- Safety equipment: gloves and boots

Method:
- Plant samples were planned to be taken from the same sampling circle as the soil but adjustments had to be made due to how the maize was growing. It was instead taken as close to the soil sampling circle as possible.
- Only eatable plants as maize and pumpkin leaves were sampled

Water samples

Metals in surface water can form complexes with ligands in the water, adsorb to soil particles in the water or on the solid materials surrounding it (Allison and Allison 2005). Water samples were planned to be taken from surrounding surface water and ground water if found when doing the soil profile description, however, only surface water was found.

Analyse for: Total heavy metal concentration

Surface water

Fast changes in the waters chemical composition might occur in water courses, e.g. after precipitation. It is therefore difficult to take manual samples and get a representative picture about changes in water quality (Swedish geotechnical society, 2013). The samples were taken to be as representative as possible, which is why the samples were taken from the shore in the same way as water for drinking, cleaning or irrigation would be taken.

Materials:
- Sample vessels: plastic bottles with lids
- Safety equipment: gloves, boots and waders

Method:
Preparations

- Location and naming of sampling point
- Making sure that all equipment was available and clean
- Marking of all sampling vessels and making sure these were distinct if there were several sampling vessels for the same sampling point

Sampling

- − Plastic gloves were put on (preferably disposable and free from talc)
- − The bottle was brought down vertically in the water with the opening first so that the water surface was not included in the sample.

Note

- − When noticeable film of surface water, the opening might be covered until the bottle is submerged.
- − The concentration in surface waters is often very low and the risk of contamination from other sources such as hands and outside of bottles is therefore large. Do not use metal constructions.
- − Take samples both upstream and downstream
- − Avoid wading out in the water course or in other ways stir up the sediments. Use a boat or other ways to reach the sampling point if the distance is too far.

Cleaning of sampling equipment

- − The sampling was performed by hand directly in the vessels which is why there was no equipment to clean.

Packing, transport and storage

- − The vessels were sealed well
- − The samples were deliver and analysed as soon as possible

Note

- − Pack the samples as soon as possible and store the sample so that vaporization is minimized
- − Control how the samples should be transported and stored. In general, water samples are transported and stored dark and cold.

(Swedish geotechnical society, 2013)

Appendix 2a – Site map

Below is a map composed from Google showing where the study sites are located in Zomba (see Figure 6). The coordinates collected from the GPS device used in Zomba were converted from Universal Transverse Mercator (UTM) to Geographic (latitude, longitude) coordinate system in the converter *AWSM tools* (awsm-tools.com, 2015). The grid zone for Malawi is 36L which was also shown in the coordinates. The datum (ellipsoid) used was WGS84 since it is the one generally used to model the Earth in the UTM coordinate system. This can result in the current UTM northing the point 200+ meters of the old (Wikipedia, 2015). This was also observed when placing the coordinates at the map. This is shown in the map where the stars show the coordinates and the red dots show an approximation of the actual location based on a more zoomed in map.
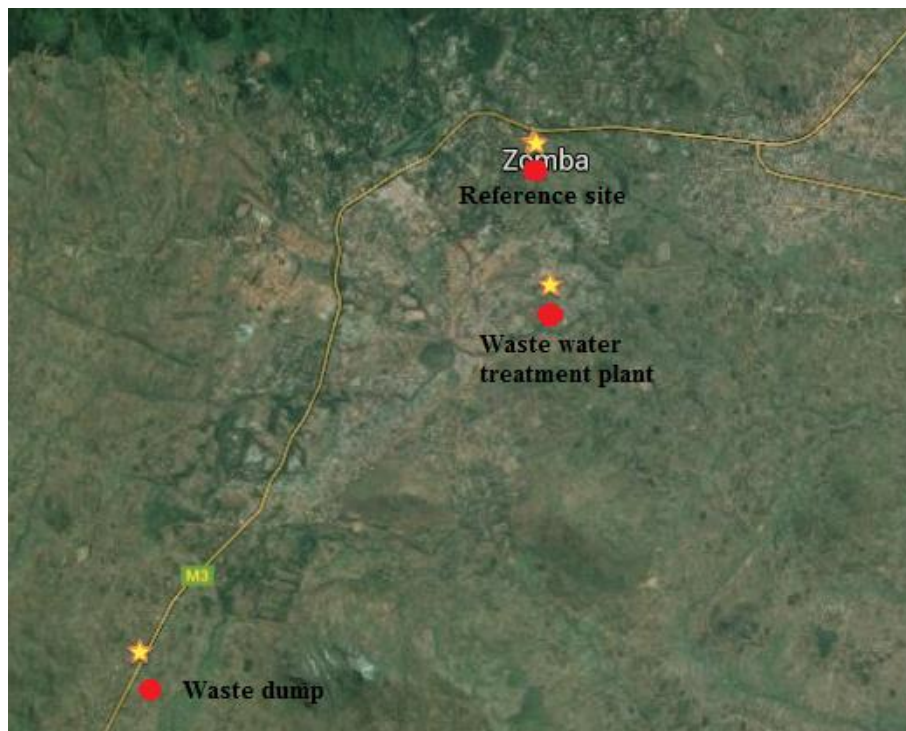

Figure 6 - A google map over Zomba showing the sampling locations. The stars show the coordinates and the red dots shows the estimated location (Google, 2015)

Appendix 2b – Field protocol: Pilot study

Name of location:	Coordinates:
Chikanda Waste water treatment plant	36L0750493; UTM8296619
Date:	Sampling executed by:
26/02/2015	Sabina Braun and Sofie Orvestedt

Medium	Name	Coordinates	Elevation	Sample volume	Instrument used
Surface soil	PS SS1	36L0750493; UTM8296619	879 m	100 ml aliquot for analyse from 1200 ml composite sample	Soil survey drill – "Trekantenborr", bucket, brush, tape measure, GPS, gloves, sticks for marking and sample vessels in plastic with lids
	PS SS2	36L0750490; UTM8296620	877 m		
	PS SS3	36L0750485; UTM8296619	875 m		
	PS SS4	36L0750491; UTM8296618	877 m		
	PS SS5	36L0750487; UTM8296614	875 m		

Deviations:
Instead of taking 10 samples as planned only 5 were taken due to the small size of the field. Instead, it was decided that the aliquot will be divided into two replicates for analysing. Random numbers that had been prepared were adjusted since the area was too small.

Other information:
The field was located not far away from a hill (see Figure 7) and with a GPS, the elevation was measured. The weather was very hot and slightly cloudy. There had been no rain this day but the day before. This site was located close to a waste water treatment plant where the water was further led through two ponds before reaching a river. Corn was grown on the field with some pumpkins.

Figure 7 - The sampling site at the waste water treatment plant

Appendix 2c – Field protocol: WWTP

Name of location: Chikanda Waste water treatment plant	Coordinates: 36L0750484; UTM8296616
Date: 9/3/2015	Sampling executed by: Sabina Braun and Sofie Orvestedt

| Medium	Name	Coordinates	Elevation	Sample	Instrument used
Surface soil	WWTP SS1	36L0750484; UTM8296616	877 m	100 ml aliquot for analyse from 1200 ml composite sample	Soil survey drill – "Trekantenborr", bucket, brush, tape measure, GPS, gloves, sticks for marking and sample vessels in plastic with lids
	WWTP SS2	36L0750488; UTM8296617	871 m		
	WWTP SS3	36L0750501; UTM8296618	872 m		
	WWTP SS4	36L0750486; UTM8296613	873 m		
	WWTP SS5	36L0750493; UTM8296614	873 m		
	WWTP SS6	36L0750499; UTM8296614	873 m		
	WWTP SS7	36L0750489; UTM8296615	882 m		
	WWTP SS8	36L0750492; UTM8296609	879 m		
	WWTP SS9	36L0750502; UTM8296610	878 m		
Soil profile	WWTP SP	36L0750492; UTM8296609	879 m	100 ml	Shovel, knife, sample vessels in plastic with lid
Crops	WWTP P1	36L0750484; UTM8296616	877 m	One corn and pumpkin leafs	Plastic bags and bucket
	WWTP P2	36L0750488; UTM8296617	871 m	One corn and pumpkin leafs	
	WWTP P3	36L0750501; UTM8296618	872 m	One corn and pumpkin leafs	
	WWTP P4	36L0750486; UTM8296613	873 m	One corn and pumpkin leafs	
	WWTP P5	36L0750493; UTM8296614	873 m	One corn and pumpkin leafs	
	WWTP P6	36L0750499; UTM8296614	873 m	One corn, pumpkin leafs and one pumpkin	
	WWTP P7	36L0750489; UTM8296615	882 m	One corn, pumpkin leafs and one pumpkin	
	WWTP P8	36L0750492; UTM8296609	879 m	One corn and pumpkin leafs	
	WWTP P9	36L0750502; UTM8296610	878 m	One corn and pumpkin leafs	
	WWTP P0	-	-	Other eatable leafs	
Water	WWTP Bf1	-	-	30 ml untreated water taken before the bio-filter treatment	Sampling vessels in plastic with lids, boots, gloves
	WWTP Bf1	-	-		
	WWTP Bf2	-	-		
	WWTP Bf2	-	-		
	WWTP WB1	-	-	30 ml water from the first pond after treatment	
	WWTP WB2	-	-		
	WWTP WB3	-	-	30 ml water from the second pond after treatment	
	WWTP WB4	-	-		
	WWTP WB5	-	-	30 ml water from the outlet into the river	
	WWTP WB6	-	-		

Deviation:
The sampling was performed in a grid as planned but followed the furrows to simplify the sampling and affect the field as little as possible. The plants collected were picked as close to the soil sampling site as possible.

Other information:
Figure 8a shows a Google map over the area where the red ring points out the sampling site. The sampling from the water bodies was taken two from the first pond, two from the second and two from the outlet to the river (see Figure 8b). Four samples of untreated water before entering the treatment plant were also taken.

Figure 8a - A google map showing the waste water treatment plant area and a red ring showing the sampling site (Google, 2015)
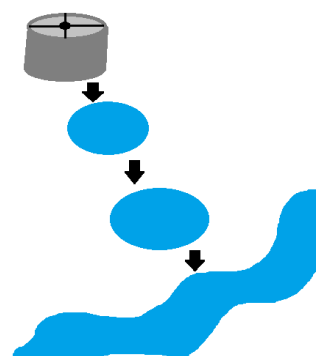
Figure 8b - An illustration of how the waste water goes through two ponds before reaching the river

The weather was very hot with some clouds. The field had a big variation in crop growth with areas that were almost bare (see Figure 9a and 9b).

Figure 9a - The sampling site, 8*8 m of unfertilized soil in this field

Figure 9b - The other side of the sampling site showing a big variation in crop growth

Appendix 2d – Field protocol: Waste dump

Name of location:	Coordinates:
Waste dump	36L0746115; UTM8292815
Date:	Sampling executed by:
11/3/2015	Sabina Braun and Sofie Orvestedt

Medium	Name	Coordinates	Elevation	Sample volume	Instrument used
Surface soil	WD SS1	36L0746115; UTM8292815	981 m	100 ml aliquot for analyse from 1200 ml composite sample	Soil survey drill – "Trekantenborr", bucket, brush, tape measure, GPS, gloves, sticks for marking and sample vessels in plastic with lids
	WD SS2	36L0746115; UTM8292808	980 m		
	WD SS3	36L0746120; UTM8292808	981 m		
	WD SS4	36L0746117; UTM8292816	976 m		
	WD SS5	36L0746118; UTM8292811	985 m		
	WD SS6	36L0746119; UTM8292808	978 m		
	WD SS7	36L0746118; UTM8292817	983 m		
	WD SS8	36L0746119; UTM8292818	983 m		
	WD SS9	36L0746122; UTM8292809	979 m		
Crops	WD M1	-	-	One corn	Plastic bags, marker and bucket
	WD M2	-	-	One corn	
	WD M3	-	-	One corn	
	WD M4	-	-	One corn	
	WD M5	-	-	One corn	
	WD PL1	-	-	Pumpkin leafs	
	WD PL2	-	-	Pumpkin leafs	
	WD P	-	-	One pumpkin	
	WD P0	-	-	Other eatable leafs	
Ash	Ash 1	-	-	100 ml	Sample vessels in plastic with lids, gloves, boots and face masks
	Ash 2	-	-	100 ml	
	Ash 3	-	-	100 ml	

Deviation:
The sampling was performed in a grid as planned but followed the furrows to simplify the sampling and affect the field as little as possible.

No water was found which is why no water samples were taken.

The field was rather big which is why an area of 8*8 m was chosen for sampling. This was also performed in a part where it was possible to move with the equipment and perform the sampling. The maize was not ripe here though which is why the farmer owning the land was sent off to collect some maize and leaves that were. This was only done about 10-20 m away.

Other information:
The field was located down a small but steep hill from the waste dump (see Figure 10a and 10b). However, in the dry season, this field is also used as a waste dump and garbage is moved to this location. There were traces of garbage in the soil, mainly glass but batteries were also seen.

The weather was hot and sunny. The field had an odour of garbage.

Figure 10a - The sampling site in a depression below the waste dump

Figure 10b - Zomba city's waste dump, located just above the field

Appendix 2e – Field protocol: Ref

Name of location:	Coordinates:
Reference site	36L0750324; UTM8298125
Date:	Sampling executed by:
11/3/2015	Sabina Braun and Sofie Orvestedt

Medium	Name	Coordinates	Elevation	Sample volume	Instrument used
Surface soil	RF SS1	36L0750324; UTM8298125	-	100 ml aliquot for analyse from 1200 ml composite sample	Soil survey drill – "Trekantenborr", bucket, brush, tape measure, GPS, gloves, sticks for marking and sample vessels in plastic with lids
	RF SS2	36L0750324; UTM8298127	920 m		
	RF SS3	36L0750349; UTM8298097	-		
	RF SS4	36L0750349; UTM8298104	918 m		
	RF SS5	36L0750356; UTM8298102	914 m		
Crops	RF P1	36L0750324; UTM8298125	-	One corn and pumpkin leafs	Plastic bags, marker and bucket
	RF P2	36L0750324; UTM8298127	920 m	One corn and pumpkin leafs	
	RF P3	36L0750349; UTM8298097	-	One corn and pumpkin leafs	
	RF P4	36L0750349; UTM8298104	918 m	One corn and pumpkin leafs	
	RF P5	36L0750356; UTM8298102	914 m	One corn and pumpkin leafs	

Deviation:
Since the reference site was assumed to have a lower variation, only five samples of soil were taken. Instead of sampling in a grid, random samples were made to cover a larger area, both for soil and crops.
No water was found which is why no water samples were taken.

Other information:
The weather was hot and sunny. The field (see Figure 11) was fertilized.

Figure 11 - The sampling site

Appendix 3 – Analyse performance

Background
This is a detailed description of how the analyses were performed and why. This was written before the analyses and was revised throughout the study due to emerging limitations. The aim of these analytical methods was that they were supposed to be possible to repeat with the available material at the Chancellor College. In an attempt to accomplish this aim, *A manual on analytical techniques* from the Department of Chemistry was used for most of the methods presented in this appendix. When another source was used, this is presented under respective method.

Limitations
Some analyses could not be performed at Chancellor College due to a lack of material which is why it was sent to another lab. This is presented under each analysis method.

Material and methods

Soil

Preparation of sample
Before any analyses were performed the soil samples were air dried, grinded and sieved to a particle size less than 1 mm. The sorted fractions were weighted and the proportion calculated.

Moisture content (M)
The results of soil analyses were calculated on the basis of oven dried sample weight. Therefore, the moisture analysis was executed before any other analysis. The result from the other analyses on the basis of the air-dry weight was multiplied by a moisture correction factor (mcf).

Procedure
- Some glass beakers was placed in an oven at a temperature around 110 °C for at least two hours.
- Then the beakers were cooled to room temperature in a desiccator and weighted.
- Around 5 g of soil sample was placed in each beaker. The exact weight was noted.
- The beakers with samples were placed in the oven at 110°C over night.
- Then the beakers and samples cooled down in a desiccator and weighted again.

Texture
The particle size distribution of a soil expresses the proportions of the various size classes (clay < 0.002 mm, silt 0.002-0.02 mm and sand 0.02-2.0 mm particle size), commonly represented by weight percentages of the total soil. The texture analysis was not possible to perform at Chancellor College which is why they were sent to a lab at the Forest department in Zomba. They used the hydrometer method to determine the proportions which is based on Stokes's law which states that the rate of fall of particles in a suspension is directly proportional to their size.

pH
pH of the soil was measured potentiometrically in 1:2 soil – water suspensions

Apparatus
pH meter, mechanical shaker

Procedure
- Approximately 10 g of air dried, 1 mm sieved sample was weighted into a 100 mL flask and 20 mL distilled water was added. The flask was then shaken for one hour.
- The pH meter was calibrated using pH buffer and after that, pH of the suspensions was measured.

Electrical Conductivity

The measurement of EC gives the concentration of soluble salts in the soil solution at any particular temperature. EC was measured in 1:2 soil-water suspensions with the help of a conductivity meter.

Procedure

The EC meter was calibrated using standard KCl solution and EC was determined of the suspension used in the pH determination.

CEC determination

The following procedure was not taken from "A manual on analytical techniques" but Samson Mkali Idruss Sajidu's dissertation "Characterisation and interaction of mixed alkaline clays and Moringa seeds with heavy metals in contaminated water".

Apparatus
- E-flasks
- Centrifuge tubes
- Centrifuge
- AAS

Reagents
- 26.89 g $CuCl_2$ (0.2 mole) was dissolved in 200 mL distilled water.
- 30.05 g ethylenediamine (33.39 mL, 0.5 mole) was dissolved in 500 mL distilled water.
- 50 mL of the $CuCl_2$ solution was added to 102 mL of the ethylenediamine solution
- This was diluted to 1 litre.
- The final solution had 0.05 M $[Cu(EDA2)]^{2+}$

Procedure
- 0.3-0.4 g of soil sample was weighted into a centrifuge tube. The exact weight was noted.
- 4.0 mL of the complex solution was diluted to 25 mL with distilled water and added to the soil sample.
- This was shaken for 30 minutes and centrifuged.
- The concentration of copper(II) was analysed in the supernatant by AAS. (Sajidu, 2008)

Total Organic Carbon (Walkely and Black 1934)

Equipment and Apparatus
- Analytical balance, resolution $\pm$ 0.01 g and weighing vessel
- 250-mL wide mouth graduated Erlenmeyer flask
- Fume hood
- Titration stand and burette
- Stirring plate with light and stirring rods

- *1N Potassium dichromate:* 49.04 g $K_2Cr_2O_7$ was dissolved in approximately 500 ml distilled water and made up the volume of one litre.
- Concentrated Sulphuric acid (H_2SO_4)
- Concentrated Orthophosphoric acid (H_3PO_4)
- *0.5N Ferrous ammonium sulphate:* 196 g Ferrous ammonium sulphate was dissolved in distilled water, 20 ml of concentrated H_2SO_4 was added and the volume made up to one litre.
- *Diphenylamine indicator:* 0.5 g of diphenylamine was dissolved in a mixture of 20 ml distilled water and 80 ml concentrated H_2SO_4.

Procedure
- 1 g soil was weighted into a 500 ml conical flask (Borosil/corning).
- 10 ml of 1 N $K_2Cr_2O_7$ and 20 ml of concentrated H_2SO_4 was added.
- The flask was swirled carefully and allowed to stand for 30 minutes.
- 200 ml distilled water and 10 ml H_3PO_4 was slowly added.
- 1 ml of diphenylamine indicator was added and titrated against 0.5 N Ferrous ammonium sulphate solution until a green colour started appearing indicating the end point.
- A blank was run simultaneously.

Total Nitrogen (Kjeldalh method)

Due to a lack of time and experience, this analysis was performed by a laboratory worker at the Forestry Department. The Kjeldalh method was used which only measures organic and ammoniacal form where nitrate is excluded.

Sample Preparation for Elemental Analysis

For the release of mineral elements from soil and sediments, wet oxidation of sample is carried out. Wet oxidation employs oxidizing acids like HNO_3-$HClO_4$-HF triacid mixture or HNO_3-$HClO_4$ diacid mixture. Use of $HClO_4$ avoids the volatilization loss of potassium and provides a clear solution while hydrofluoric acid (HF) helps removing silica. The diacid oxidation method is easier, less time-consuming and convenient but it is not a total digestion as soil does not dissolve completely, particularly silicate minerals, therefore, di-acid digestion is known as pseudo digestion or partial digestion.

The pilot study were performed using tri-acid, but due to the hazards of handling HF-acid and lack of proper equipment the main study were performed with di-acid oxidation.

$HClO_4$-HF Digestion (Tri-acid oxidation)
- Around 1.0 g of sample, two replicates per sample point, was weight into clean 250 ml E-flasks. Exact weights were noted.
- Two ml mL of $HClO_4$ (70%) and 12 mL of HF (40%) was added and the mixture was heated to near dryness.
- Then 8 mL of HF was added and the mixture heated to dryness.
- Now add two mL of $HClO_4$ and about 5 mL of distilled water and heat to incipient.
- The remaining residue was dissolved in 8 mL of hydrochloric acid and 20 mL of water.
- The mixture was filtrated
- Using distilled water the filtrate was diluted to 100 mL.
- The concentrations of concerned metals were determined by AAS.

HNO3/HClO4 Digestion (Di-acid oxidation)
- Around 1.0 g of sample, two replicates per sample point, was weight into clean 250 ml E-flasks. Exact weight was noted.
- 3 mL HNO_3 was added and the mixture heated to 145 °C for one hour.
- Then 4 ml of $HClO_4$ was added and the mixture heated to 240°C for one further hour.
- The mixture was cooled and filtered then diluted with distilled water to 50 mL volume.
- The concentrations of concerned metals were determined by AAS.

Water

Procedure
- 1 ml Nitric acid was added to liberate all metals of interest
- The water was filtered through filter paper
- The water was analysed for metals in AAS

Plants

Processing the plant sample:
1. The samples were only cleaned with water to replicate how they would be cleaned before eating, i.e. removal of soil etc.
2. The samples were placed on paper in room temperature to dry of excessive water from cleaning and to easier be able to remove the eatable part of the maize.
3. Final drying at 100-110 °C to obtain a constant weight upon which to base the analysis.
4. Mechanical grinding to produce a material suitable for analysis.

Tri-acid digestion
Tri-acid mixture: Mix AR grade conc. HNO_3, H_2SO_4 and $HClO_4$ in 10:1:4 ratio and cool.

Procedure
- Approximately 1.0 g of dried and processed plant sample was transported to a 250 mL conical flask.
- 5 mL of conc. H_2SO_4 was added
- A glass funnel was kept on the flask which was placed in a water bath and heated at 100 °C for about 30 minutes
- After cooling 5 mL of tri-acid mixture was added
- It was heated at 180-200 °C on hot plate until the dense white fumes evolved and transparent white contents were left
- After cooling about 50 mL of double distilled water was added and filtered into 100 mL volumetric flask, giving 3-4 washings. Finally the volume was made up to 100 mL.
- The filtrate was then analysed in AAS.

Appendix 4 - Calculations

Moisture in soil
Equation 1

$$M = \frac{(B - C) \times 100\%}{(C - A)}$$

Equation 2

$$mcf = \frac{100 + M(\%)}{100}$$

Where

M = Moisture content (%)

A = Empty Beaker weight

B = Sample + Beaker weight

C = Final weight

Metals
The concentration of metals was determined by AAS. Before analysis of the samples a calibration curve for each metal was made from solutions with a metal concentration of 1, 2, 3, 4 and 5 ppm (see figure 12). The equation from the trend line was then used to calculate the metal concentration in the samples from the measured absorbance (A). Equation 3 was used to correct the measured concentration for sample weight and dilution, and to get the final result in mg/kg.

Equation 3

$$C_{Cd}\ (ppm) = \frac{A}{0.029}$$

Equation 4

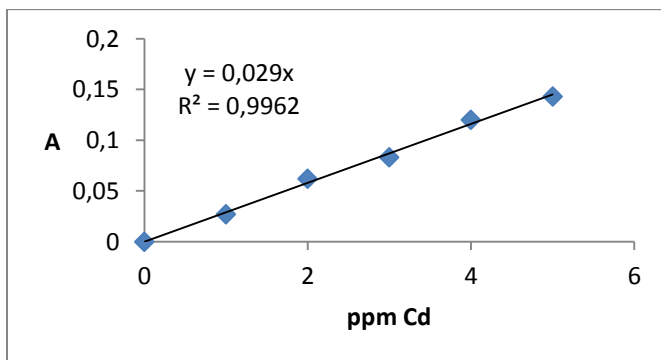$$C_{Cd}(mg/kg) = \frac{C_{Cd}\ (ppm) * MCF * 0.1}{Sample\ weight} * 1000$$

Figure 12 - Calibration curve for Cd

Phosphorus

The acid digests of soil samples was mixed with vanadate-molybdate reagent and the concentration of P analysed with spectrophotometry and the soils P-content calculated with equation 5.

Equation 5

$$P\ (\mu g/g) = \frac{R * 50}{10} * \frac{100}{Sample\ weight\ (g)}$$

Where:

R = reading of spectrophotometer P mg/l.
10 = volume of acid digest used for colour development.
50 = Volume make up for colour development.
100 = Volume make up after acid digestion.
g = Sample wt. (g) for acid digestion.

Organic carbon

OC was analysed with the Wakley-Black method. The C % was calculated using Equation 6.

Equation 6

$$OC\ \% = \frac{10 * (B - S) * 0.39 * mcf}{B * W}$$

Where:

B= ml ferrous ammonium sulphate solution used for blank
S= ml ferrous ammonium sulphate solution used for sample
mcf= moisture correction factor
w= sample weight (g)
0.39= conversion factor for a supposed 70 % oxidation of carbon

CEC

For determination of CEC, a known concentration of Cu^{2+} was added. The samples were shaken, and the concentration of Cu in the supernatant was analysed. The difference in moles from before and after the mixing with the soil corresponds with half of the total charge in the soil. The moles of charge per gram soil were calculated according to equation 7.

Equation 7

$$Charge\ (moles/g\ soil = \left(\frac{\left(Moles/L_{Cu\ before} - Moles/L_{Cu\ after} \right) * 0.025\ L}{Sample\ Weight\ (g)} \right) * 2$$

Literature

Allison, J. D. & Allison, T. L., 2005. *Partition coefficients for metals in surface water, soil and waste,* Washinton: U.S. Environmental Protection Agency.

awsm-tools.com, 2015. *awsm-tools.com.* [Online]
Available at: http://awsm-tools.com/geo/utm-to-geographic
[Accessed 4 June 2015].

Berggren Kleja, D. et al., 2006. *Metallers mobilitet i mark,* Stockholm: Naturvårdsverket.

FAO, 1990. *Guidelines for soil description.* Rome: Food and agriculture organization of the United Nations.

Galal, T. M. & Shehata, H. S., 2014. Bioaccumulation and translocation of heavy metals by Plantago major L. grown in contaminated soils under the effect of traffic pollution. *Ecological Indicators,* p. 244–251.

Google, 2015. *Google Maps.* [Online]
Available at: https://www.google.se/maps/place/Nandolo,+Zomba,+Malawi/@-15.4006727,35.3424488,22763m/data=!3m1!1e3!4m2!3m1!1s0x18d904c05d8c2371:0xa5cff4daa0259f8a!6m1!1e1
[Accessed 4 June 2015].

Google, 2015. *Google Maps.* [Online]
Available at: https://www.google.se/maps/@-15.3983767,35.3329914,550m/data=!3m1!1e3
[Accessed 4 June 2015].

Grandin, U., 2012. *Dataanalys och hypotesprövning för statistikanvändare,* s.l.: Swedish environmental protection agency.

Instutionen för mark och miljö, 2013. *Yttäckande miljöövervakning av åkermark och gröda - Provtagningsinstruktioner.* Uppsala: s.n.

Norrman, J. et al., 2009. *Provtagningsstrategier för förorenad jord,* Stockholm: Naturvårdsverket.

Sajidu, S. M. I., 2008. *Characterisation and interaction of mixed alkaline clays and Moringa seeds with heavy metals in contaminated water,* Malawi: University of Malawi.

Sarala Thambavani, D. & Prathipa, V., 2012. A study of heavy metal contamination in the urban soil of Dindigul town, Tamil Nadu. *An Asian Journal of Soil Science,* pp. 150-158.

Swedish geotechnical society, 2013. *Fälthandbok - Undersökningar av förorenade områden,* Stockholm: Swedish geotechnical society.

Wikipedia, 2015. *Universal Transverse Mercator coordinate system.* [Online]
Available at: http://en.wikipedia.org/wiki/Universal_Transverse_Mercator_coordinate_system
[Accessed 4 June 2015].