Sveriges lantbruksuniversitet
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The impact of waste handling on small-scale farming in Malawi

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Master's Thesis in Soil Science
Agriculture Programme – Soil and Plant Sciences

Examensarbeten, Institutionen för mark och miljö, SLU
2015:06

Uppsala 2015

SLU, Swedish University of Agricultural Sciences
Faculty of Natural Resources and Agricultural Sciences
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EX0430, Independent project/degree project in Soil Science - Master´s thesis, 30 credits, Advanced level, A2E
Agriculture Programme – Soil and Plant Sciences 270 credits (Agronomprogrammet – inriktning mark/växt 270 hp)

Series title: Examensarbeten, Institutionen för mark och miljö, SLU
2015:06

Uppsala 2015

Keywords: soil management, poverty, land use, fertilisers, agriculture, food security

Online publication: http://stud.epsilon.slu.se

Cover: Maize cultivated on waste dump in Malawi, 2015, photo by author

Abstract

This study assess the impact of human waste and household garbage on the concentrations of heavy metals in arable land on two sites located close either to a waste collecting point (WD) or waste water treatment plant (WWTP). Malawi suffers from poverty, low food security and problems with access to land. The aim was to find out if the assessed areas are contaminated with heavy metals and to evaluate the results and the land use in a historical, social and political context. Another objective is to evaluate the possible positive effects the waste can give in form of plant nutrients against the potential harmful effect that comes from heavy metal contamination.

Soil and plant samples were collected from the three sites, and the concentration of Cd, Zn, Cu and Fe was measured with atomic absorption spectrophotometry (AAS) at the University of Malawi. After evaluation of the results, some samples were brought to Sweden for a second AAS-analysis for Cd, Pb and Cr. Unfortunately the results for Cd were considered unreliable and were therefore not used in the assessment. The concentration of metals in the soil was then compared with the general guideline values calculated by the Swedish Agency for Environmental Projection. In the comparison WD and WWTP both showed concentrations of Pb exceeding the general guideline value. The concentration of Pb found was much higher than expected, and the results need to be treated with care. The sites had both a higher soil concentration of N and P compared with a reference site.

The study was limited by time constraints and hampered by broken equipment. However, the results can be used for planning a more detailed risk assessment of the areas. Future actions suggested in this study are: a more detailed risk assessment of metal pollution and hygienic aspects, updated information about background levels of metals in soil, control of Cd-content in imported fertilisers and an overall focus on ensuring access to agricultural land and input as well as secure places for depositing waste.

Popular science summary

Malawi has only been independent since 1964, and was previously a British protectorate. During the first 30 years of independence, Dr Hastings Kamuzu Banda, was the country's leader . The politics during both the British leadership and the Banda regime are still visible in the agricultural sector. During that time the agricultural focus was on national self-sufficiency in maize, combined with export of cash crops such as tobacco, sugar, tea and coffee. During colonial time the best land was seized by the British for production of lucrative cash crops, and after independence that pattern of land distribution continued, but with the local “elite” in charge instead. Small-scale farmers have historically been excluded from the trade with export crops, and have instead been locked into production of maize. Access to land and agricultural input, such as fertiliser and improved seeds, is a problem currently addressed by the government. To increase access to fertilisers the Malawi Farm Input Subsidy Program (FISP) was implemented in 2005. The program aims to give small-scale farmers vouchers for fertiliser and seed to help them escape poverty.

When travelling around in Malawi, the first thing one notice is that all unoccupied areas are cultivated, even if there only is room for a few plants. Maize is everywhere. This can be seen as a good use of available land, but what happens when the only land available might be contaminated? With arable land covering 49 % of the land area, and an estimated 82 % of the total land considered suitable for agricultural production, one might think that this problem will never occur. However, with a fast growing population, already exceeding 16 million, Malawi is one of the most densely populated countries in the world, and about 85 % of the population is engaged in agricultural activities. The average household plot size is only 1.4 hectare, and most households are net-buyers of maize, the staple food. A growing population will need either more intense agriculture or more agricultural land, but at the same time more space and resources will be needed for housing, waste management etc.

This study investigated the concentration of heavy metals at two agricultural sites in Zomba, Malawi. One of the sites is on a waste dump (WD), and one is close to a waste water treatment plant (WWTP). No inorganic fertilizer was used on either site. The results show that the concentrations of the toxic metal lead are above Swedish general guideline values. On the flip side, the concentrations of the essential plant nutrients nitrogen and phosphorus were higher than the concentrations at a reference site where inorganic fertilisers have been used. In conclusion, the concentration of metals is higher than recommended, but the sites give good yields without use of expensive inorganic fertilisers. Hopefully the areas will be the focus of a more specific risk assessment to help local farmers and government make a qualified decision about future land use.

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1. Introduction

Malawi is a small sub-Saharan country with a large population. Small scale farming is common, especially in the rural areas, and issues with food security have been painfully prevalent in recent starving events. The climate in Malawi has episodes of both floods and draughts, which affect the agriculture and the population very negatively. Just before this study was performed Malawi experienced a serious episode of flooding, affecting over one million people (Al Jazeera, 2015). This catastrophe also led to great losses of yield and its full impacts are yet to be estimated.

Agriculture is an important part of the economy (31 % of GDP), and a majority of the population is engaged in agricultural activities (FAO 2013). The average plot size is small and low access to land has been addressed as an important issue (CEPA 2013). With a rapidly growing population, Malawi faces enormous challenges in the future, especially considering that the country is one of the poorest nations in the world. Utilisation of available land is therefore important for the development of the country. This project studies the effect of poor waste management on heavy metal contamination of arable land close to waste collecting areas. All sampling and analysing was performed in cooperation with Sofie Orvestedt. In her thesis from 2015 she is discussing the results from an environmental point of view, meanwhile this thesis focus on the agricultural, economic and political aspects and causes of this possible contamination.

During the 19th century the Europeans ‘discovered’ and colonized Africa. The first Malawi election was held in 1961, three years before the actual independence in 1964. In this election the Malawi Congress Party (MCP) won the majority of the votes and in 1963 Dr Hastings Kamuzu Banda was declared president (Grauers, Fischer, & Odén 1997). Dr Banda was later made life-president of Malawi. Although Banda did not rule Malawi for his full life, he remained president for the first thirty years after independence. Under his regime agriculture was the main focus for governmental investments in an attempt to increase the country’s economic growth. The focus on the agricultural export sector was a logical choice since Malawi is scarce of other valuable resources, such as minerals. He also kept the agricultural orientation created by the colonial leaders and worked for an increased production of the same export crops. Big estate owners got favourable loans and were over all favoured over small-scale farmers who could not export their crops. (Grauers *et al* 1997). In 1992 Banda started to get seriously pressured by the international and local community who wanted a system-change. In 1993 the Malawian people were given the chance to vote for either a return of the multi-party political system, or the retention of the present one-party rule. The support for a multi-party system was overwhelming, and a general election was held in 1994. Commonly this is considered the first multi-party election of Malawi, although this is not true according to Muula & Chanika (2004) who highlights the fact that four parties contested in the election 1961, before independence. Regardless of if it was the first of its kind or not, the election in 1994 was the end of President Bandas rule, as he found himself defeated by Mr. Bakili Muluzi, representing the United Democratic Front (UDF) (Muula & Chanika 2004). Muluzi was then followed by Dr Bingu Mutharika (2004-2012), Joyce Banda (2012-2014) and the current president Peter Mutharika.

2. Objectives

This study has two specific and one general objective:

First: To find out if the areas close to the waste water treatment plant in Zomba and the waste dump located just outside Zomba are contaminated with heavy metals.

Second: To determine the phosphorus and nitrogen status in the soils at the waste treatment plant and the waste dump, and compare them with a reference soil where inorganic fertilisers currently are used.

Third: To discuss the political, economic and social forces that make people grow food on areas with suspected contamination.

2.1 Hypotheses

Null hypothesis: There is no difference between the reference site and WD/WWTP regarding:

a) Concentration of Fe, Zn, Cu, Cd, Pb and Cr in soil
b) Concentration of Fe, Zn, Cu, Cd, Pb and Cr in plants
c) Nutrient status

2.2 Limitations

This project was designed to be easy to repeat under local conditions. As a consequence the methods of analysis were chosen for simplicity and low price, and not for being up-to-date or the most accurate. The study was also limited by the short time available in field and the wet weather conditions during February and March. The soil samples were limited by our equipment which only allowed us to take samples from the top soil, 0-20 cm, without any damage to crops. For analyses the plan was to use microwave plasma - atomic emission spectrometry (MP-AES) but unfortunately the machine was broken during my time in Malawi. Instead all metal analyses were performed using atomic absorption spectrophotometry (AAS), and were therefore limited to the available lamps (Fe, Cd, Zn and Cu). A second AAS analysis of some samples was performed in Sweden, where Cr and Pb concentrations were analysed.

Another important aspect to consider is that the laboratory, the equipment, chemicals and glassware at the University of Malawi have a lower quality compared to a high-income country. The short time period also made it hard to form professional relations with the employees and the flow of information was sometimes insufficient.

3. Background and theory

This section contains information about Malawi's agricultural and political history regarding food security, and a brief theory about how metals are introduced to and transported in the soil-plant system.

3.1 Food security

Ensuring food security is high on the political agenda in Malawi, both currently and historically. Food security is defined as "when a person has permanent physical and economic access to sufficient, safe and nutritious food to meet his or hers dietary needs and food preferences for an active and healthy life" (IHS3 2010/11). Factors contributing to low food security are, among others, low access to agricultural production inputs and small average plot size (Figure 1). In Malawi those and other factors combined leads to a declining maize production and unstable food prices (Sahley *et al* 2005). Food security is also intimately connected with poverty.

Now, around 50 years after independence, Malawi's agricultural and industrial situation remains too under-developed to ensure sufficient food security or help the country out of poverty. During the last fifteen years Malawi's population has gone from 11.3 to 16.4 million people (The World Bank 2015), and about half of the population is considered to be poor (IHS3 2010/11:207). Despite past political efforts to ensure food security the Global Food Security Index 2014 ranks Malawi as number 94 out of 109 countries. According to the third integrated household survey (IHS3 2010/11) only a little more than half of the population can be assumed to have a high food secure status and one third suffers from very low food security.

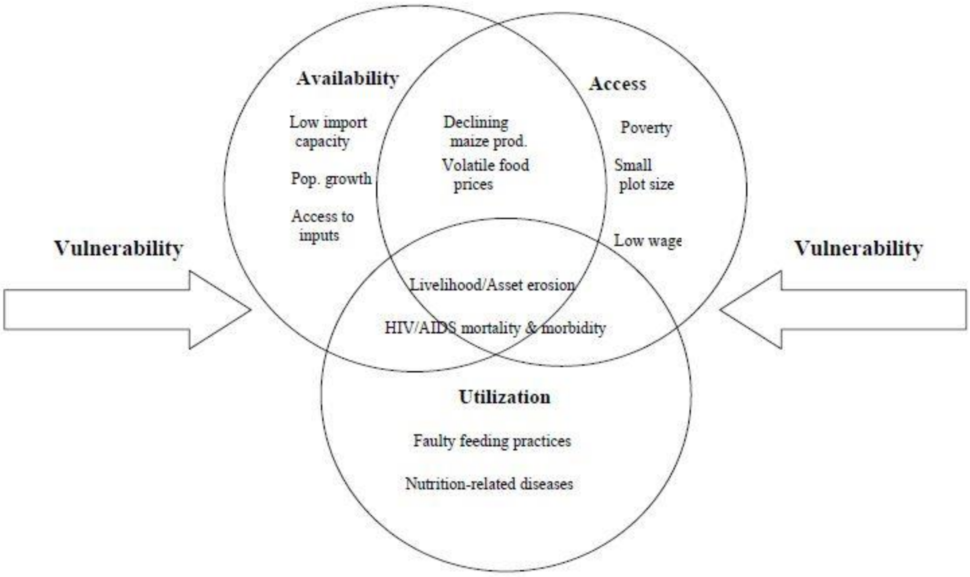

Figure 1 - Factors affecting food insecurity (Sahley *et al* 2005)

3.1.1 Access to land

On the 14th of May 1891 Malawi was made a British protectorate called Nyasaland (Muula & Chanika 2004). During this period the foundation of the current export-orientated agricultural system was built (Sahley *et al* 2005). Malawi was ruled indirectly by use of tribal authorities who implemented colonial policy on the local level. This colonial land policy introduced English property concepts to appropriate land for the European settlers and some of the best agricultural land was ceased for production of export crops such as tobacco and tea (Sahley *et al* 2005). Natives rights to land were redefined as “occupation rights” to prevent establishment of land rights equivalent to the freehold or the concessions held by the settlers (Malawi National Land Policy 2002). The Land Ordinance of 1951 defined land as private, public or customary. However, the customary land was considered a type of private land leading to a situation where natives became tenants of their own land (Malawi National Land Policy 2002). After independence the Land Act in 1965 was passed but did not change the status and insecurity of customary land rights (Malawi National Land Policy 2002). Small scale farming mostly took place on customary land, meaning that it falls under the law of the actual ethnic group (Takane 2007). Private land ownership mostly applies for the big estates and requires a freehold title, leasehold title, or a Certificate of Claim granted by the early colonial governors (Takane 2007). Public lands include national parks, forest reserves and conservation areas and is owned or held in trust by the government or local authorities as well as the areas former known as customary land (CEPA 2013;Takane 2007).

In 2002 the government of Malawi passed the National Land Policy. It was an initial step to revise the legal framework governing land rights and has eight objectives (USAID 2010):

1. To promote tenure reforms that guarantee security, confidence and fairness in all land transactions
2. To guarantee secure tenure and access without discrimination or gender bias
3. To curb land encroachment, unapproved development, land speculation and racketeering.
4. To promote decentralized and transparent land administration.
5. To extend planning strategies for land use to all urban and rural areas.
6. To establish a modern land registration system for delivering land services to all.
7. To enhance conservation and community management of local resources
8. To promote research and capacity-building in land surveying and land management

In the National Land Policy of 2002 the government also addressed eleven problems associated with land. The most relevant in this context are residual effects of colonial land policy, high population to land ratio, worsening land pressure, land scarcity in spite of idle lands and mismanagement of land development (Malawi National Land Policy 2002). All these issues can be considered to be connected with the situation addressed in this study. A Land Bill and a Customary Land Bill were passed in 2013. The purpose was to implement some of the recommendations from the Malawi National Land Law from 2002 (CEPA 2014). The Land Bill of 2013 also excluded the customary land and makes it a part of the public land, which have been criticised as reinforcing the alienation of the customary land (CEPA 2013).

Today, the agricultural land cover 49 percent of the total land area, but an estimated 82 percent of the total area is suitable for cultivation (USAID 2010). About 85 percent of the households are engaged in agricultural activities and of those 84 percent are involved in crop production. The agriculture is dominated by poor farmers cultivating small areas and the average cultivated area per household is 1.4 ha (IHS3 2010/11). According to USAID (2010) approximately 30,000 farms can be considered to be large-scale estates with 10-500 hectares, but 84 percent of the agricultural land are either farmed by small holders or is considered by the government to be available to small-holding farming. The majority of the small scale farmers, who in total are about 2 million people, cultivate less than one hectare of rain fed land and 11 percent are almost land-less (USAID 2010). The most common ways to access land is by inheritance (52 %), marriage (18%) or allocation by traditional authorities (20 %). Other ways is by purchase (1 %), leases or government land programs. Both patrilineal and matrilineal systems of rights to land through marriage or inheritance are prevalent in Malawi. In the southern and centre region, land is handed down the female line, and in the northern region land is handed down the male line. This means that if one person moves to the spouse’s village and the marriage then is ended due to divorce or death, they often lose the right to the land. (USAID 2010)

3.1.2 Political actions and agricultural development

In 1998 the Malawian Starter Pack was launched. The program aimed to introduce new farming technologies and increase food security for all small holders using free starter packs containing improved maize seeds, legumes and fertiliser sufficient to cultivate 0.1 ha. The program reached 2.8 million people between 1998 and 2000. After 2000 the program was scaled down to the Targeted Input Program (2000-2002), mostly due to pressure from donors. The programme was to be scaled down in steps following introduction of other interventions under the Malawi National Safety Net Strategy. The recipients of the packages were now chosen according to a vulnerability criteria derived as part of the Safety Net. In 2000-2001 1.5 million people received starter packs, and in 2001-2002 one million people were reached. (Harrigan 2008)

In 2001/02 Malawi suffered a big food crisis. The event was connected with a national scandal when the strategic grain reserve was sold off just before the crisis occurred, and followed by investigation of seven high-ranked people on charges of criminal recklessness and negligent acts (Sahley *et al* 2005). After this food crisis the Targeted Input Program (TIP) was scaled up to the Extended Targeted Input Program (ETIP), lasting from 2002 to 2004 (Harrigan 2008). The Starter Pack, TIP and ETIP landed in a total cost of 91.1 million USD where 34.2 million was funded by the Government of Malawi (Harrigan 2008).

During Malawi's third president Dr Bingu Mutharika's time in office the country suffered two major starving events, 04-05 and 07-09. After the first one, in 2005/06, the government launched the still ongoing Farm Input Subsidy Program (FISP). The objectives are to improve smallholder productivity, reduce vulnerability to food insecurity and hunger and to promote self-sufficiency of food and development of the private sector input markets (SOAS 2008). To do this the strategy was to distribute vouchers for fertiliser for maize, fertiliser for tobacco and improved maize seeds to farmers nationwide (Dorward & Chirwa 2011). Later the program included legume seeds, cotton seeds and chemicals, tea and coffee fertilisers and chemicals for storing of maize (Dorward & Chirwa 2011). With the goal to reach all small-scale farmers in the country the big challenges for this program have been logistic and organizational problems (Dorward & Chirwa 2011).

During the last century global use of fertilisers, pesticides, tractors, irrigation systems and other technology has boomed, leading to an increase in global food production. However, the development of the agricultural sector is not evenly distributed between countries or even continents. In Malawi the usage of modern technology is low. Most of the field work is done by hand and the agriculture is mainly rain-fed. Only 2 percent of the farmers use irrigation (USAID 2010) leading to a crop production system with low resilience for droughts. Access to organic and inorganic fertilisers is a key factor to ensure high long term soil fertility, especially if the production is dominated by one type of crop.

3.1.3 Diversity of crops

The Malawian saying "Chimanga ndi moyo" means "maize is life", and maize is indeed an important staple food in Malawi. Maize of either local or hybrid sort covers 67 percent of the arable land (IHS3 2010/11) and makes up half of the average caloric intake (FAO 2013). Although being the most wide spread crop cultivated in Malawi, maize is only the third biggest agricultural commodity sorted by metric tonnes. Both cassava and potato was produced in higher quantities than maize in 2012 (FAOSTAT 2012). However, the production of maize in Malawi has increased during the last decades but most households have not acquired self-sufficiency. In 2008/2009 around 60 percent of all households were net buyers of maize (Holden & Lunduka 2013)

The high focus on maize can be traced to the political actions taken during the Banda regime. During that time self-sufficiency of maize became the main tool to ensure acceptable food security for the population. Before the mid-80’s talking about food shortages was considered to be taboo, and at times even considered subversion (Chilowa 1998). This one-sided focus on maize combined with other political factors led to a situation where Malawi was able to export maize to other African countries in the mid-80’s, but at the same time experienced some of the highest child mortalities in the world (Sahley *et al* 2005).

In 1971 the Agricultural Development Marketing Corporation (ADMARC) was created from the colonial Farmer’s Marketing Board (Christansen & Stackhouse 1989). This parastatal corporation had monopoly on purchase of tobacco and cotton, but the monopoly seems to have expanded to other agricultural products as well (Chilowa 1998). ADMARC were also responsible for the setting of maize prices, often under market price. This functioned as a tax for the small-scale farmers and kept the maize prize low for consumers (Sahley *et al* 2005). A majority of the poor farmers were locked into maize production and had to sell for low prices, meanwhile ADMARC used the profit to finance big estates producing export crops (Sahley et al 2005). Until a policy change in 1990 smallholders were not allowed to grow and market tobacco at all (USAID). ADMARC also had responsibility for the strategic grain reserve from the start in 1981 until 1999 when the National Food Reserve Agency was formed (Chilowa 1998; Harrigan 2003). To prevent food crises the National Food Reserve Agency (NFRA) still holds a strategic grain reserve and therefore plays an important role determining the maize price (Ellis & Manda 2012).

A number of previously mentioned subsidise programs have been financed by the government and external donors, aiming to give the country a higher resilience against food crises and to reduce poverty. The more specific purpose of these programs was to break the vicious circle where poor maize yields gives the farmers small opportunities to invest in agricultural inputs such as fertilisers or better seeds, leading to continually small yields (Dorward & Chirwa 2011). The most recent one is FISP, described above. One study show that FISP lead to a simplification of the crop production by a lower allocation of land for other crops (Chibwana, Fisher, & Shively 2012). The focus on maize was also one part of the critique of the Starter Pack program (Harrigan 2008). It is widely known that dependency of one crop gives a production with low resilience for both extreme weather situations and long-term changes of conditions such as the climate. The production is also more sensitive for other production threats, such as pests or diseases. Dependency of maize in Malawi had been described as “maize poverty trap”, where people are unable to increase the production and have a constant high risk of food shortage (Harrigan 2008). However the focus on maize has been justified as a cost effective way to obtain food security since the country’s land-locked situation and poor infrastructure gives high partial import costs (Harrigan 2008).

3.2 Mobility of metals in the soil-plant system

The soil environment is a complex system consisting of solid particles, water, air and various organisms (Eriksson *et al* 2011). In this system metals can be bound, released and/or transported between the soil, water and organisms in a number of processes. One fraction of the metal is bound to the soil material, another forms complexes with other dissolved compounds and the third are free in the solution and therefore accessible for biological uptake or leaching. If the concentration is sufficient there might also be some precipitation of the metal. Just a small fraction of the total concentration will be in the soil solution and there have the ability to spread to ground and surface water (Berggren Kleja *et al* 2006). The size of the different fractions are affected by the conditions in the soil, such as pH, concentration of DOC, clay content etc. The same metal can be present in various forms in the same fraction, so called species, which all have unique properties (Essington 2004:208). The different fractions and the speciation of the metal means that the total concentration of metals measured in the soil paints a false picture of the risk the contamination poses to surrounding organisms and systems (Berggren Kleja *et al* 2006). Therefore, it’s important to have knowledge about the properties of the site and the metal of interest before any risk assessment is performed.

3.2.1 Dissolved complexes and free ions

Metals in the soil solution can exist as dissolved complexes or free ions. This fraction is important, since the soil solution is the main phase in which substances transport in the soil (Essington 2004). Since water is polar, and thus have one negatively and one positively charged end, both cations and anions can exist free in water. The ion will create weak bounds with water molecules and therefore form a layer of water surrounding the ion. This process is called hydration (Berggren Kleja *et al* 2006). Metal cations can also undergo hydrolysis when they react with the oxygen in the water molecules, breaks the hydrogen-oxygen bond, and form new ionic species, a hydroxide or oxide. This process will change the metals behaviour in the soil environment (Essington 2004).

Many metal cations can form complexes with other ligands than water. The link can be directly between the metal and the ligand inside the hydration sphere, called an inner-sphere complex, or it can be an attachment outside the hydration sphere, called ion-pairs (Essington 2004).

The transport of solutes through the soil is affected by three mechanisms; convection, dispersion and diffusion. *Convection* is the transport of solutes with the movement of the soil solution. This transport is affected by *dispersion,* the mechanism that makes the flow of water and solutes in the soil go faster in bigger pores and in the middle of pores and slower in smaller pores and close to pore walls. *Diffusion* is the movement of solutes driven by concentration gradients, when an ion or compound moves from an area with higher concentration to an area with lower. (Messing 2010)

3.2.2 Adsorption and precipitation

Retention of metal transport in soil is mostly due to *adsorption* on the surfaces of clay minerals, oxides or organic matter or *precipitation* into secondary minerals (Berggren Kleja et al 2006). Adsorption is defined as a surface process that results in the accumulation of a dissolved substance (an adsorbate) at the interface of a solid (the adsorbent) and the solution phase (Essington 2004). Precipitation is the process when a compound increases in volume in a three-dimensional growth (Essington 2004). Together these processes will be referred to as *sorption*. These mechanisms are reversible, so the metals will eventually be released to the soil solution in a later stage if the conditions change (Berggren Kleja *et al* 2006).

Adsorption consist of a number of different mechanisms, were the most important ones are ion exchange and formation of surface complex (Berggren Kleja *et al* 2006). Those two mechanisms are both highly dependent on the pH value in the soil, since the pH affects the surface charge on the soil particles. Charge on the mineral surfaces in soil is pH-dependent. The pH-dependent charges results from a protonation and deprotonation of hydroxyl groups on the mineral surface and can be positive, negative or neutral depending on conditions. This is called a *functional group.* Those groups are commonly found on phyllosilicates, metal oxides, hydroxides and oxyhydroxides (Essington 2004). Formation of surface complex happens when an ion or molecule in the soil solution reacts with a surface functional group. This can be both as an inner-sphere and an outer-sphere complex. Ion exchange is the name for the process when ions that have formed electrostatic bonds with surface functional groups, so called outer-sphere complexes, is displaced by ions from the soil solution (Essington 2004).

Another important factor for the retention of metals in the soil is the content of organic matter. Soil organic matter (SOM) is divided into two groups, humic and non-humic substances. All organic substances that are recognizable as belonging to biochemical classes are considered non-humic. The rest of the SOM, the humic substances, are divided into humic acid, fulvic acid and humin. Metal ions have the ability to bind strongly with the organic matter in the soil, especially fulvic and humic acids. (Essington 2004)

Metals can also be precipitated as a secondary mineral, together with other ions in the soil solution. This process is in equilibrium and is affected by the present conditions, such as the concentration of different ions and molecules and the soil pH (Essington 2004; Eriksson *et al* 2011). Precipitation can only take place if the metal ion is present in sufficiently high concentration (Berggren Kleja *et al* 2006).

3.2.3 Plant uptake

Plants take up nutrients by passive or active transport of ions from the soil solution into the root cells (Fogelfors 2001). In this process metals present in the soil can be taken up and accumulate in the plant. For plant uptake to occur, the metal needs to be present in an available form. This can either be as free ions or complexes in the soil solution or adsorbed to soil particles and therefore available for ion exchange (Fogelfors 2001). The ability to take up metals and to allocate them in the different parts varies between plant species (Mattina *et al*

2003). Heavy metal contamination can have a hampering effect on the yield of crops. For example, a study performed by Bhogal *et al* (2003) shows that cereals and legumes fertilized with sewage sludge containing Cd, Cu and Cr gave lower yields then a control with no sludge applied.

Plants can also affect movement of elements in the soil in two important ways. One is by creating a mass flow of soil solution to the roots by suction, driven by the transpiration. This is an effect of the plants uptake of water. The other way is by the creation of a concentration gradient by uptake of elements. This lead to diffusion of elements from the soil solution to areas close to the root surface, where the concentration is lower. (Fogelfors 2001; Messing 2010)

3.3.4 Guideline values

In risk assessments for contaminated areas guideline values are often used to determine if the area pose as a health risk or not. The Swedish Environmental Protection Agency (SEPA) has developed a model for calculation of general guideline values for a number of different contaminants. Another option is to use area-specific guideline values, for a more specialised risk assessment. These guideline values can be calculated using an excel-model developed by SEPA, and the properties for the concerned site. If general guideline values are used it is important to make sure that the values are meant to be used for the actual target of projection and land usage (SEPA 2009). The values presented in Table 1 are the general guideline values for sensitive land use.

	Cd	**Pb**	**Cr**	**Zn**	**Cu**
General guideline value	0.5 mg/kg soil	50 mg/kg soil	80 mg/kg soil	250 mg/kg soil	80 mg/kg soil
Target of protection	Ingestion of plants	Ingestion of soil	Soil environment	Soil environment	Soil environment

Table 1 - General guideline values for sensitive land use (mg/kg dry soil), and the target of protection (SEPA 2009)

3.3 Sources and effects of metal contamination

The metals analysed in this study are the essential zinc (Zn), copper (Cu), chromium (Cr) and iron (Fe), and the non-essential cadmium (Cd) and lead (Pb). Of these metals cadmium, chromium and lead are the most toxic ones, and Cd and Pb are also without a biological function for animals and plants (Eriksson et al 2011). A study of metal concentration in soils performed by Sillanpää & Jansson in 1992 showed that Malawi have a low concentration of both Cd and Pb, compared to the rest of the world

Soil can be Cd-contaminated from both natural and anthropogenic processes. Natural processes can, for example, be weathering of minerals, volcanic activity or sea spray. Anthropogenic contamination mostly originates from mining of zinc, combustion of fossil fuel, waste, sewage sludge or spreading of contaminated fertilisers (Roberts 2014). It’s calculated that approximitly 30,000 tonnes of Cd is realesed into the atmotphere each year

(ATSDR 2005). The pollution of Cd in our envirionment is considered to be a serious concern since Cd is among the most toxic trace elements, for both animals and plants (Dias *et al* 2013).

Contamination of Pb mostly comes from weathering of primary or secondary minerals or from atmospheric deposition (Eriksson *et al* 2011). Lead was formerly used as an anti-knock agency in gasoline and leaded gasoline was a major source of contamination (Thomas *et al* 1999). Pb form strong bonds with organic material and the concentration in the soil solution is therefore usually low (Eriksson *el al* 2011).

Chromium in soil can exist as both Cr(III) and Cr(VI). Cr(VI) is the most toxic one, but it is uncommon in soil. Cr(III) is more common, but low solubility in neutral water makes it less of a threat to the soil environment and prevents plant uptake (Eriksson *et al* 2011). Since Cr is used in many different industries such as leather processing, hide tanning, metal plating and previously wood preservation the metal is widely spread in the environment (Shanker *et al* 2005).

3.3.1 Effects on plants

Some metals are essential for the growth and development of higher plants. Lack of those metals will inhibit growth and lower the yield. Other metals, such as Cd and Pb are not. Even if some metals have a higher toxicity than other, all of them can be harmful for plants if present in sufficient concentration in the soil. Three of the metals assessed in this study, cadmium, lead and chromium, are more toxic then the others. The toxic effects on plants of these three metals will be described in this part.

Cd is relatively easily available in the soil, compared to other metals. Between 10-40 % of the total Cd can be assumed to be available for ion exchange (Eriksson *et al* 2011). The amount of Cd available for ion exchange increases with lower pH-values. In extremely acidic conditions Cd can be transported in the soil, but under normal circumstances the mobility is low (Eriksson et al 2011). Plant uptake of Cd is regulated by its concentration and bioavailability in the soil, which is affected by pH, content of organic matter, temperature and presence of other elements (Dias *et al* 2013). The toxic effects of Cd can cause abnormalities and inhibition of growth in higher plants by inducing chlorosis, necrotic lesions, wilting, and disturbances in mineral nutrition and carbohydrate metabolism (Tran & Popova 2013; Dias *et al* 2013). Studies have shown that both long-term and short-term exposure to Cd inhibit photosynthesis in many plants by disturbing the biosynthesis of chlorophyll and carotenoids (Tran & Popova 2013). It’s also shown that Cd^{2+} ions affect the function of chloroplasts by targeting two key enzymes for CO_2-fixation, ribulose-1,5-bisphosphate carboxylase (RuBisCO) and phosphoenolpyruvate carboxylase (PEPCase) (Tran & Popova 2013). Cd might also interfere with the cell division and chloroplast replication in the leaf and has been shown to induce chlorosis in oilseed rape by decreasing the number of chloroplasts in the cells (Baryla *et al* 2001). Another harmful effect is that Cd can cause oxidative stress in plants by interfering with the antioxidant defence system leading to an increase in reactive oxygen species in the plant cells (Tran & Popova). Uptake and use of other, essential, elements and water may also be hindered by exposure to Cd (Tran & Popova 2013). All this factors combined leads to a decrease in production of biomass.

The toxic effects from Pb inhibit growth of both roots and aerial parts of the plant, and can also cause chlorosis on leaves. Inside the plant cell Pb can affect the enzyme activity, hormonal status, electron transport and water potential. It can also alter the permeability of the cell membrane. The photosynthesis can also be gravely affected by Pb contamination, since the metal disturbs the Calvin-cycle, the synthesis of chlorophyll, the electron transport and the opening of stomata cells. (Sharma & Dubey 2005)

Plant uptake of Cr happens through pathways for uptake of Fe, S and P. Both Cr(III) and Cr(VI) are highly toxic for the plant, and high uptake leads to disturbances in development and growth. High concentration of Cr in the soil also inhibits seed germination. Contamination of Cr can reduce the biomass production and reduce the yield by up to 50 %. (Shanker *et al.* 2005)

3.3.2 Metal contamination and human health

Contamination of heavy metals in food, water and environment are a widely known threat to the global human health. Copper, zinc, iron and chromium(III) are all essential elements for human life, but can have toxic effect in high doses. Cadmium and lead are both non-essential metals which can have toxic effects on the human body. This section will give a short overview of the possible health effects from exposure, and some limit values for human consumption of the metals assessed in this study.

The tolerable upper intake of copper for adults is recommended by the Scientific Committee on Food (SFC) as 5 mg/day for adults, but lower for children and for women during pregnancy and lactation. A too high intake if copper can lead to acute poisoning, or heart and neurological diseases. The US guideline for recommended intake of copper is 0.9 mg/day for adult males and females. (SCF 2003a)

Zinc is an important part of many enzymes, and in humans zinc is essential for growth, development, healing of wounds, testicular maturation and other important functions. The European Population Reference Intake (PRI) for zinc is 9.5 mg/day for females and 7.0 mg/day for males. Excess intake of zinc can lead to negative health consequences. Therefore the Tolerable Upper Intake Level is set as 25 mg zinc per day for adults, and lower for children. (SCF 2003b)

Iron is essential for humans to produce haemoglobin, an enzyme that transports oxygen through the body. Healthy adults run a very low risk for negative effects of excessive intake of iron. However, a one-time high dose (over 60 mg/kg body weight) can lead to organ failure and even death. The Tolerable Upper Intake is 45 mg/day for adults and children over 13 and 40 mg/day for children under 13. However, lack of iron is more common than excess intake. (NIH 2015)

Chromium can exist as both Cr(III), more commonly found from natural sources, and as the more toxic Cr(VI) which mostly have its source from anthropogenic activities. Cr(III) is essential for metabolism, but high exposure of Cr(III) can have negative effects. The tolerable daily intake for Cr(III) is set by European Food Safety Authority as 0.3 µg/kg body weight. No such limit exist for Cr(VI), since tests indicates that exposure of it can cause cancer (EFSA 2015).

Lead has been showed to have neurodevelopmental effects on developing foetus, children and adults (EFSA 2010). In 2010 the Panel on Contaminants in the Food Chain (CONTAM Panel) at European Food Safety Authority gave a scientific opinion that the tolerable weekly intake for lead set as 25 µg/kg body weight is not appropriate, since evidence shows that there exist no threshold for damaging lead-induced effects (EFSA 2010).

Cadmium has a tolerable weekly intake (TWI) of 2.5 µg/kg body weight, and the limit is set to protect children, vegetarians and people living in contaminated areas. The major source of exposure of cadmium is tobacco smoking and foodstuff. To high exposure leads to damage of kidneys and bones. (EFSA 2013)

3.4 Results from similar studies

To use waste compost as fertiliser is a wide spread-practise, and the possible consequences for soil quality have therefore been investigated in a number of different studies. The practise of cultivating food directly at a waste dump is however not as common, but the similarity is close enough to use this studies for background knowledge and comparison.

Hargreaves, Adl and Warman (2008) made a review of a large number of studies about the use of composted municipal waste (CMW) in agriculture. Their conclusion was that CMW can safely be used in agriculture, but only if the quality of the compost is controlled. It is important that the compost is mature and have a low metal content. For this purpose source separation is a necessary practice. The soil concentration of lead, zinc and copper was shown to increase from use of CMW. There are also studies that have shown an increase of the soil concentration of Cd and Cr.

For reference, the concentration of metals in plants and soil found in some other studies of contaminated areas are summarised in table 2. The studies were chosen with the criteria that it should include at least one of the plants analysed in this study, and that the plants should have been grown in soil contaminated by anthropogenic activity. In the study by *Mattina et al.* (2003) the analysis for Pb and Zn were performed with Inductively Coupled Plasma Emission Spectroscopy (ICP OES) and the analysis for Cd with graphite furnace AAS. The aim of the study was to investigate the concurrent plant uptake of heavy metals and persistent organic pollutants from soil. The site used for the study was agricultural soil treated with the pesticide Chlordane. Carbonell *et al.* (2011) analysed metal content in maize fertilized with both municipal waste compost and inorganic fertilisers (NPK). To determine the metal concentration they used flame AAS and graphite furnace AAS. This study found very low concentration of metals in the maize grain.

Table 2 – Metal concentration in soil and plants found in other studies on soils contaminated by anthropogenic activity.

Study	Plant	Metal	Concentration in plant (mg/kg)	Concentration in soil (mg/kg)
Mattina *el al.* 2003	Pumpkin leaves	Pb	<10	188
		Zn	74	63
		Cd	0.15	0.31
Carbonell *et al.* 2011	Maize (shoot)	Pb	1.16	35.61
		Cd	0.07	0.21
		Cu	1.12	14.01
		Cr	<0.01	21.38

4. Methods

This section shortly describes the sampling sites and the methods used for sampling and analysis. A full description can be found in in Appendix 1 and 2. All sampling and all analyses were made together with Sofie Orvestedt.

4.1 Site descriptions

This section contains a short description of the sampled sites. All areas were cultivated with maize and pumpkin.

4.1.1 Waste dump (WD)

This site is located around three miles northwest of Zomba Centre. At this area most of the household waste collected in Zomba is stored. No sorting is performed, but occasional burning of waste happens. During the wet season crop production takes place in the waste from the last dry season, and the new waste is stored in piles (Figure 2b). After harvest, in the dry season, the accumulated waste is spread over the whole area (Figure 2a). During the sampling plastic, glass and batteries was found in the field and the piles of waste nearby was mainly composed of organic waste and plastic bags, but also contained glass, broken china and metal cans.

Figure 2a - The sampling site, located in a depression below the main waste pile. Picture taken by Sofie Orvestedt

Figure 2b –The biggest waste pile, located just above the sampling area. Picture taken by Sofie Orvestedt

4.1.2 Waste water treatment plant (WWTP)

The sampled area is located close to the Zomba waste water treatment plan (Figure 3). The treatment plant consists of one infiltration bed (bio filter) and two ponds. During all our visits the rotating ramp over the infiltration bed was broken.

Figure 3 - A map of the area around the treatment plant. The circled area is cultivated. Source: Google Maps

4.1.3 Reference site

The reference site is located close to the Zomba University, and is cultivated by a member of their staff. This area is assumed to have a low risk of contamination, and is fertilized with an inorganic fertilizer containing nitrogen, phosphorus and sulphur. A picture of the site can be found in Figure 4.

Figure 4 - The reference site. Picture taken by Sofie Orvestedt

4.2 Sampling and analysing

Before the start of the main study a small-scale pilot study was performed. This was for three reasons:

I. To get a picture of the metals present in the soil.
II. To calculate the standard variation and mean values for the concentrations of metals.
III. To test the sampling plan, the equipment and the analysis method for metals on a smaller scale.

The original plan was to take 10 soil samples from each of the three sites, according to the method described in Appendix 1. Unfortunately bad weather conditions limited the time in the field, so only one site, WWTP, was sampled. Due to the small area of the site only 5 randomly placed soil samples were taken. In the pilot study moisture and metal concentration in the soil was analysed using AAS. The samples were prepared for analysis with tri-acid digestion, using HCl, HF and $HClO_{4,}$ following the method in Appendix 2.

The minimum number of soil samples to be collected in the main study was then determined using *a priori*-testing with the statistical software G*Power and data from the pilot study. G*Power was set as: F-test, ANOVA: Fixed effects, omnibus, one-way. The significant level was set to 95 %. The *a priori*-test were performed for all metals individually using the metals standard deviation and mean value from the pilot study. Two of the groups were assumed to have the same mean value as in the pilot study, and one (reference) was assumed to have half of the measured value. The used means and standard variations are shown in Table 2. The sample size in the main study was then set as the biggest total sample size calculated, which gave a minimum of 75 samples from all sites together to achieve selected level of certainty.

In the main study soil, maize, pumpkin leaves, pumpkin fruit, ash and water was collected from the sites. The number of samples collected is presented in Table 3. On the reference site and on WWTP the plant samples were taken from the same spot as the soil, but on WD the crop was too small for sampling. Therefore plant samples from the WD was collected on nearby fields, as close to the sampling place as possible. On each of the sample points 12 soil samples was collected with the soil drill and mixed together to produce one composite sample (for more details see Appendix 1). This procedure was to reduce the impact from eventual hotspots and natural variation.

The plant samples were dried in an oven overnight and then digested using heat and tri-acid mixture, made of AR grade conc. HNO_3, H_2SO_4 and $HClO_4$, following the method in Appendix 2. Water content was calculated on randomly selected plants of all tested sorts and parts. The concentration of Cd, Cu, Fe and Zn in all samples was measured using atomic absorption spectrometry (AAS) at University of Malawi. Three soil, three maize and one pumpkin leave sample from each site were brought to the Swedish University of Agricultural Science for a second analysis for Cd, Cr and Pb with AAS. One sample of ash, two of pumpkin fruit and five water samples were also analysed a second time. All samples were prepared at University of Malawi. The soil samples was prepared by digestion in two steps, using HNO_3 and $HClO_4$, following the di-acid digestion method described in Appendix 2. Two replicates from each sample point were prepared.

The soil content of organic carbon, total nitrogen and total phosphorous were analysed at University of Malawi. The Walkley-Black method was used for carbon, the Kjeldahl method (performed by laboratory assistants) for nitrogen and vanadate-molybdate reagent and spectrophotometry was used for measuring phosphorus. Due to limited time, only some of the soil samples were analysed for C, N and P. More detailed descriptions are given in Appendix 2 where the methods for measuring other soil properties as cation exchange capacity (CEC), pH and electric conductivity also are presented. Analysis of soil texture was performed by employees at another department.

Table 3 – Input values in mg/kg soil and calculated sample size (n) needed to be able to find significant difference between sites, for Cd, Pb, Cd, Zn and Fe.

	Cu	**Pb**	**Cd**	**Zn**	**Fe**
StDev	31	25	3	28	1191
Mean 1	42	196	7,5	169	16493
Mean 2	42	196	7,5	169	16493
Mean 3	11	98	4,75	85	8247
	n=75	*n=9*	*n=45*	*n=12*	*n=6*

Table 4 – Number and type of samples collected at each site during the main study. The soil samples are displayed as number of sampling spots*number of subsamples from each spot.

	Soil	Maize	Pumpkin leaves	Pumpkin fruit	Ash	Water
Ref	5*12	5	5	0	-	-
WD	9*12	5	2	1	3	-
WWTP	9*12	9	9	2	-	6

4.3 Atomic adsorption spectrophotometry (AAS)

All metal analyses in this study were performed using flame atomic adsorption spectrophotometry (AAS). Due to technical problems three different machines were used. Iron, copper, zinc and cadmium were analysed at University of Malawi. Chromium were analysed at SLU, the department for chemistry and biotechnology, and lead and cadmium (second analysis) at SLU in the students laboratory (MEKÖL).

The basic theory of AAS is to measure the quantity of an element in a sample by measuring the radiation adsorbed by it. Light with a known wavelength in the visible or ultra violet spectra passes through the sample, and some of it is adsorbed by the element and emitted at a higher energy level. The emission comes from electrons moving from one energy level to another within the atom, and in this process emitting a photon. Since all elements have a unique configuration of electrons in the outer shell, all elements absorbs energy at different wavelengths. A detector in the machine measures what wavelength that are transmitted from the sample, and compares it with the original wavelengths sent through it. By using Lambert-

Beers Law, saying that the absorption is directly proportional with the concentration, the concentration of the element can be calculated. Most often the calculation is done using a calibration curve created from samples with a known concentration. (García & Báez 2012)

The basic parts of an AAS-machine are illustrated in Figure 5. The wavelength selector, also called monochromator, is important for the selectivity of the AAS. A sample may contain a number of different elements, and the wavelength selector sort out the wavelength absorbed by the element of interest and excludes the rest of the radiation. The detector then translates the intensity of the light to a proportionally strong electrical signal which then is processed in the signal processor which translates it to the output value. Most often the radiation source is a lamp containing the element of interest, and does therefore only emit light of the wavelength that the element can absorb. In this case the wavelength selector sorts away all wavelengths but the one chosen for the analysis. (García & Báez 2012)

When measuring concentrations with flame AAS a number of different interferences can occur. Some examples of this are that formation of ions can cause lower absorption, or that other elements or particles creates the opposite effect when they also absorbs the used wavelength. These interferences can give a result that is lower or higher than the true concentration in the sample. To prevent this from happening it is important to make sure that the flame is hot enough to completely atomize the sample. (García & Báez 2012)

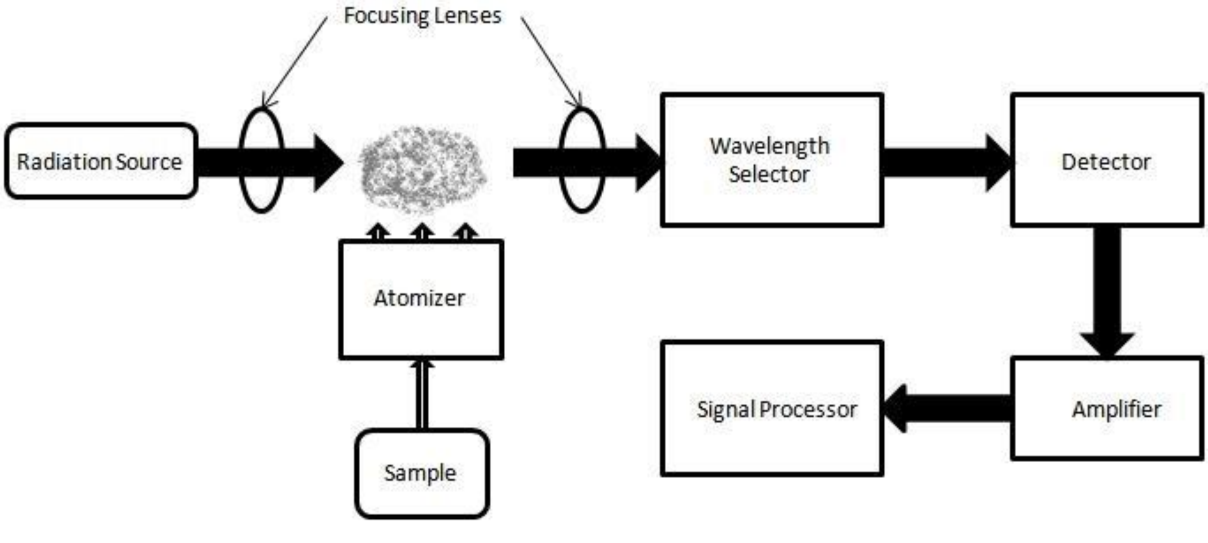

Figure 5 – The basic parts of an atomic absorption spectrophotometer. The figure is a part of the public domain, taken from Wikimedia Commons and created by the user K05en01.

4.4 Statistics

In this study an ANOVA (Analysis of variance) was used to determine if the three sites are significantly different from each other. Tukey’s test was used at a confidence level of 95 %. This statistical test was performed in the program MiniTab. Tukey’s test is the least conservative of all commonly used ANOVA-test. This means that the difference between the sites needed to give a significant difference is lower for Tukey’s test then for other ANOVA-tests (Grandin 2012). The number of samples needed and the *ad hoc* statistical power, the probability of a correct rejection of the null-hypothesis, was determined using the program G*Power. All the data from statistical tests are presented under “Results”.

5. Results

5.1 Pilot study

The mean values and the standard variation were used to determine a suitable sample size for the main study, as described above. The metal concentrations at all sampling points are summarised in Table 5.

Table 5 – Total Cu, Pb, Cd, Zn and Fe concentration at sample points and mean values for each metal in pilot study

Sampling point	Cu	Pb	Cd	Zn	Fe
	mg/kg soil				
1	69	183	11	166	17195
2	64	166	9	209	17592
3	63	209	5	180	17100
4	13	190	4	133	14693
5	5	231	9	158	15887
Mean	*43*	*196*	*8*	*169*	*16494*

5.2 Soil properties

In table 6 the soil type, clay, silt and sand content, size of fraction >1 mm, pH, EC, CEC, C %, P %, N % and C/N quota are presented for all sites. Two of the sites, the reference and WWTP, are classified as sandy clay loams and WD is classified as a clay loam. The carbon content at the WWTP is twice as high (~11 %) as at the other sites. The pH varied between the sites, were the lowest values were found at WWTP (3.71) and highest at WD (7.06). Analysis showed that WWTP were richest in both nitrogen and phosphorous. Lowest nutrient status was found at the reference site, despite present use of inorganic fertiliser. The calculated CEC is higher than expected .This can be due to a high amount of organic carbon, high clay content or measuring errors. Note that the titration-based methods used for C and N are very inexact compared with modern methods for analysis.

Table 6 - Soil properties for the reference site, WD and WWTP.

	Ref	**WD**	**WWTP**
Type	Sandy clay loam	Clay loam	Sandy clay loam
Clay content	35 %	35 %	29 %
Silt content	19.4 %	27.4 %	19.4 %
Sand content	45.6 %	37.6 %	51.6 %
Fraction > 1 mm	15%	37 %	11 %
pH	5.90	7.06	3.71
EC (µS)	50.6	117	142
CEC ($cmol_c*kg^{-1}$ *soil)*	66.0	74.7	76.4
C %	5.04	5.21	10.9
P (mg P $100\ g^{-1}$ *soil)*	373	619	1930
N (mg N$100\ g^{-1}$ *soil)*	80	83	273
C/N	63	65	40

5.3 Metal contamination

5.3.1 Unreliable data

The first and second AAS-analysis gave very different results regarding the concentration of Cd. Not one single plant or soil sample showed the same concentration in both analyses, and most of the plant dry matter showed a concentration higher than in the soil on the site. On account of this variance, which can be seen in Table 7 and 8, the results for Cd will not be included in any statistical analysis or used as base for discussion about possible risks.

Table 7 – Concentration of Cd in 9 of the soil samples, measured at University of Malawi and the Swedish University of Agricultural Science. Note the big difference between the two analyses.

Name	Malawi	SLU
Ref	*mg/kg soil*	*mg/kg soil*
1a	3	0
3a	8	0
5a	13	0
WWTP		
2a	8	0
5a	5	28
8a	5	0
WD		
2a	10	2
5a	5	3
8a	13	1

Table 8 – Cd concentrations in plant dry matter for samples analysed at both University of Malawi and the Swedish University of Agricultural science. Note the big difference between the two analyses, and that most of the concentrations in the plants are higher than the soil concentration.

Name	Malawi	SLU
Ref	mg/kg DM	mg/kg DM
Maize 1	15	6
Maize 4	20	2
Pumpkin leaves 4	20	5
WWTP		
Maize 2	10	60
Maize 5	10	62
Maize 8	15	7
Pumpkin leaves 3	15	7
Pumpkin fruit 6	24	7
WD		
Maize 1	19	3
Maize 3	15	8
Maize 5	29	6
Pumpkin leaves 1	20	8
Pumpkin fruit	18	9

5.3.2 Soil

The mean concentration of Pb, Cr, Cu, Zn and Fe are presented in Figure 4 and 5. In these diagrams the standard deviation is included as error bars. In Table 9 P-values, mean values and standard deviation for the metal concentration at each site are given. Data for Fe, Zn and Cu comes from results retrieved in AAS analysis at the University of Malawi and data for Cr and Pb from the analysis at SLU. The concentration of Pb was above the general Swedish guideline values at two points on WD and three points on WWTP. Cr did not exceed the guideline values at any test point.

An ANOVA analysis was performed for the metals that were analysed at University of Malawi (Fe, Zn and Cu). This was to determine if there were any significant differences between the sites (Table 9). The number of analyses for Cr and Pb was not sufficient for ANOVA analysis. Of the statistically analysed metals, Zn was the only one where both WD and WWTP differ significant from the reference, but not from each other. No site had a mean concentration of Zn above the guideline value. For iron WD, but not WWTP, differs from the reference site. The opposite situation is true for Cu, were WWTP but not WD differ from the reference. The concentration of Cu at WWTP is above the guideline value, but the standard variation is large. The median value for Cu-concentration at WWTP is 75 mg Cu/kg soil and only 7 of the 17 analysed samples were above the guideline value of 80 mg Cu/kg soil. This means that the use of the mean value in the risk assessment might not be optimal in this case. Since only three samples from each site were analysed for Pb and Cr, no ANOVA could be done for them.

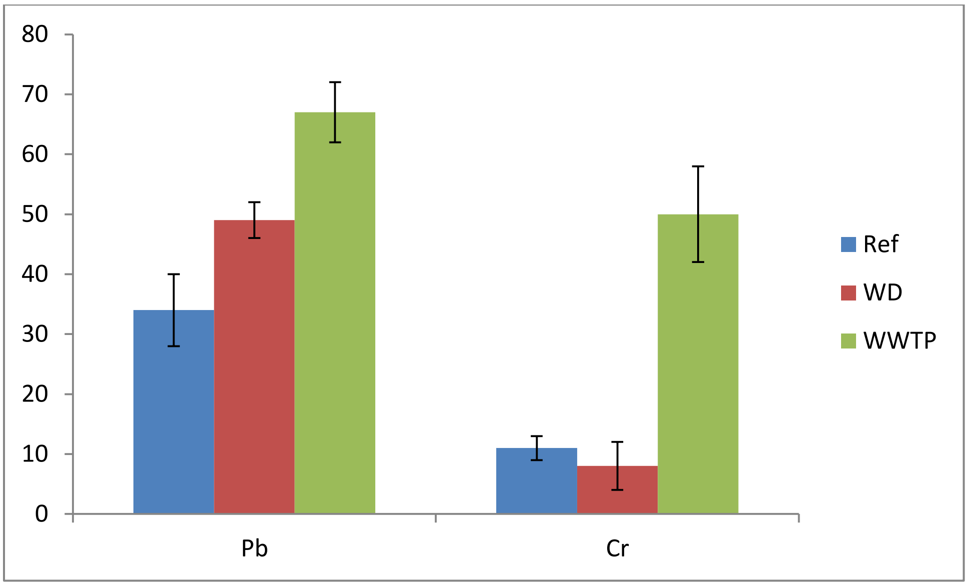

Figure 3- Mean concentrations for Pb and Cr from the analysis performed at SLU. Error bars show the standard variation.

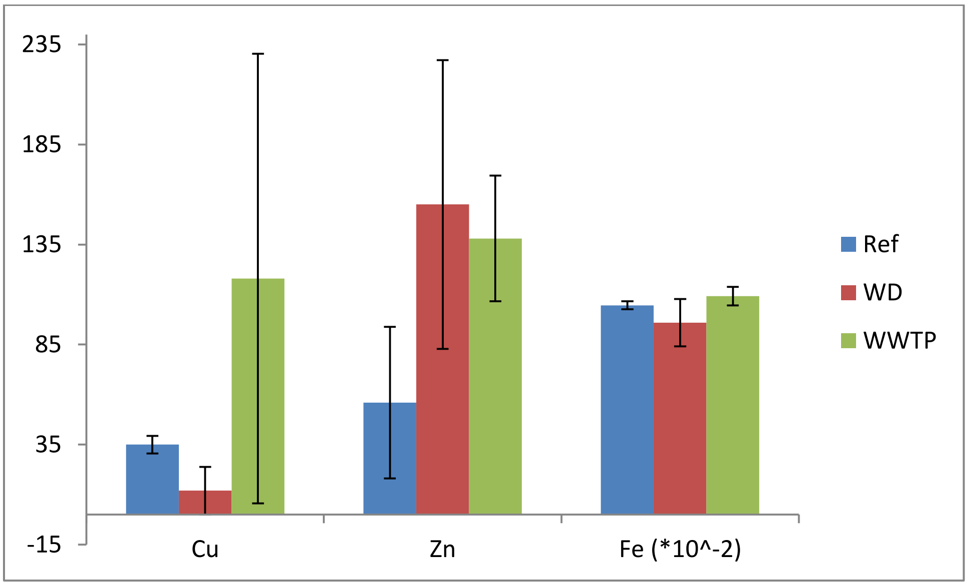

Figure 4 - Mean concentrations for Cu, Zn and Fe. The results for Fe are divided by a factor of 100, since the values are so much higher than the values for the other metals. Error bars show the standard variation.

Table 9 - Statistical information for soil samples. Asterisk marks values above the Swedish general guideline values.

	Pb	Cr	Cu	Zn	Fe
Number of samples analysed					
P-value	-	-	0.003	0.0	0.0
Statistical power	-	-	1.0	1.0	1.0
Mean value					
Ref			35	56	10461
WD			12	155	9591
WWTP			118*	138	10917
StDev					
Ref			4.4	37.9	284
WD			11.9	72.2	1182
WWTP			112.3	31.4	466

Table 10 – Concentration of Cr and Pb for all samples analysed at the Swedish University of Agricultural Science. Asterisk marks values above the Swedish general guideline values.

Name	Cr	Pb
Ref	mg/kg soil	mg/kg soil
ss1a	9	30
ss3a	13	42
ss5a	11	30
WWTP		
ss2a	57	62*
ss5a	52	66*
ss8a	39	74*
WD		
ss2a	11	51*
ss5a	3	52*
ss8a	10	45

Table 11 – Grouping information for soil samples using Tukey's test. Sites that do not share a letter are significantly different. The analysed data comes from the AAS-analysis performed in Malawi.

	N	Fe	Zn	Cu
Ref	5	A	B	B
WD	9	B	A	B
WWTP	9	A	A	A

5.3.3 Plants

In Table 11 the mean concentration of all metals in pumpkin leaves, pumpkin fruit, maize and soil are presented. The soil concentration is included for easy compilation. Tables 12 and 13 contain the results from the ANOVA analysis performed on the metals analysed at University of Malawi. For maize, there is a significant difference between the reference site and WD regarding Zn and Cu, but not Fe. For pumpkin leaves there are no significant differences between the reference and WD. Between the reference site and WWTP there is a significant difference in the concentration of Zn in both maize and pumpkin leaves, but none for Fe and Cu. Tables 14 and 15 gives the P-values, mean values and standard deviation for the maize and pumpkin samples respectively.

The Pb content in the plants is very high. Compared with the study performed by Mattina *et al.* (2003) were the concentration in the soil was 188 mg/kg soil and the concentration in pumpkin leaves <10 mg/kg dry matter, this result seems unlikely. The results from Carbonell *et al.* (2011), who had a soil concentration of 35 mg Pb/kg and negligible concentration of lead in maize grain, also confirms that these results might not be correct. Another unexpectedly high concentration is Fe in all plants. The iron content in fresh maize given from the National Food Agency in Sweden is 5 mg Fe/kg. The pumpkin leaves can be compared with iron-rich food such as fresh spinach (20 mg Fe/kg) and raw pork (12 mg Fe/kg). These values, also taken from the National Food Agency in Sweden, indicate that these results may be wrong. The plants content of Zn is high as well, but in Mattina *et al.* (2003) the Zn concentration in pumpkin leaves were higher than the soil concentration so this concentration might be accurate. If it is, the Tolerable Upper Limit on 25 mg Zn/day may be exceeded by the residents in the area.

For Cu the result for maize at the waste dump (87 mg/kg) is much higher than the soil concentration (12 mg/kg). Since both pumpkin leaves and fruit at WD shows zero content of Cu this result might be considered unreliable. Regarding Cr the highest soil concentration was found at WWTP, but the plants from that site showed no detectable amount of Cr. In Carbonell *et al.* (2011) the concentration of Cr in maize shoot and grain were very low (<0.01 mg/kg in shoots) even though the soil concentration was around 23 mg/kg. This result combined with the fact that Cr has low solubility in the soil solution makes the results for the reference site and WD unreliable.

Table 12 – Mean values for metal concentration in plant dry matter. Analysis for Cr and Pb performed at SLU and for Fe, Zn and Cu at the University of Malawi. Mean concentration in soil included for comparison.

	Ref	**WD**	**WWTP**
	mg/kg	mg/kg	mg/kg
Pb			
Pumpkin leaves*	39	34	30
Pumpkin fruit*	-	23	36
Maize	39	42	29
Soil	34	49	67
Cr			
Pumpkin leaves*	1.5	0	0
Pumpkin fruit*	-	4	0
Maize	12	4	0
Soil	11	8	50
Fe			
Pumpkin leaves	1286	217	2371
Pumpkin fruit	-	180	261
Maize	140	124	133
Soil	10461	9591	10917
Zn			
Pumpkin leaves	86	88	304
Pumpkin fruit	-	79	120
Maize	33	147	132
Soil	56	155	138
Cu			
Pumpkin leaves	1	0	3
Pumpkin fruit	-	0	10
Maize	1	87	2
Soil	35	12	118

Table 13 – Grouping information for maize samples using Tukey's test. Sites that do not share a letter are significantly different. The analysed data comes from the AAS-analysis performed in Malawi.

	N	Fe	Zn	Cu
Ref	5	A	B	B
WD	5	A	A	A
WWTP	9	A	A	B

Table 14 – Grouping information for pumpkin leaves using Tukey's test. Sites that do not share a letter are significantly different. The analysed data comes from the AAS-analysis performed in Malawi.

	N	Fe	Zn	Cu
Ref	5	A B	B	A
WD	2	B	B	A
WWTP	9	A	A	A

Table 15 – P-value, statistical power and standard deviation for maize samples

	Fe	Zn	Cu
P-value	-	0.02	0.00
Statistical power	0.05	0.7	1.0
StDev			
Ref	78	20	3
WD	93	102	57
WWTP	64	56	3

Table 16 – P-value, statistical power and standard deviation for pumpkin leaves samples

	Fe	Zn	Cu
P-value	0.02	0.00	-
Statistical power	0.8	0.9	0.2
StDev			
Ref	1115	29	3
WD	25	15	0
WWTP	905	124	7

5.3.4 Ash and water

Samples from the water at the waste water treatment plant and the ash from burning of waste at the waste dump were analysed. The concentration of zinc in all water samples are higher than WHO (2003) refers to as the normal level for surface water, 10 µg/L. In tap water the concentration can be as high or higher than in these samples, due to corrosion in pipes (WHO 2003). Pb was only found in the sample of untreated water, and in low concentration. No Cr was detected in the water samples. The mean values for the metal concentration in the water are displayed in Table 16.

The concentration of metals in the ash is presented in Table 17. Only one ash sample was brought to Sweden for analysis of Cr and Pb. However, the mean values of Zn, Cu and Cr were all found in higher concentrations in the ash then in the soil. The concentration of Fe and Pb were lower in the ash than in the soil samples.

Table 17 - Mean concentration of metals in water samples (mg/L), analysed at the University of Malawi

Name	**Fe**	**Zn**	**Cu**	**Cr**	**Pb**
Before treatment	0.6	0.8	0.5	0	0.2
Pond 1	0.8	1.1	0.5	0	0
Pond 2	0.6	0.5	0.6	0	0
Outlet to stream	1.3	0.3	0.5	0	0

Table 18 - Concentration of metals in ash samples (mg/kg ash) collected at the waste dump, analysed at the University of Malawi.

	Fe	Zn	Cu	Pb	Cr
Ash 1	1602	174	88	45	16
Ash 2	2146	109	63	-	-
Ash 3	1332	225	61	-	-
Mean	*1693*	*170*	*71*	*45*	*16*

6. Discussion

The main objectives of this study was to find out if the two assessed areas are contaminated with heavy metals, and if they have a higher, lower or equal nutrient status compared to a reference site. A more general objective was to investigate and discuss the forces that lead to a situation where food is cultivated on areas we in Sweden would routinely classify as contaminated or at high-risk for contamination.

6.1 Hypothesis testing

The hypothesis formed before the study was as follows:

Null hypothesis: There is no difference between the reference site and WD and/or WWTP regarding:

- *a) Concentration of Fe, Zn, Cu, Cd, Pb and Cr in soil*
- *b) Concentration of Fe, Zn, Cu, Cd, Pb and Cr in plants*
- *c) Nutrient status*

In statistical hypothesis testing the null hypothesis can be rejected if the P-value is lower than the significant level, in this case <0.05. We can then say that with a certainty of 95 %, there is a difference between at least two of the tested groups. However, my null hypothesis was that there were no different in metal concentration between the reference site and WD and/or WWTP. The difference between WD and WWTP is not of interest in this study. Therefore the P-value alone (Table 19) is not enough information for rejecting or not rejecting this null hypothesis. Therefore the grouping information from Tukey’s test is also used. The results for Cd will not be included in the hypothesis testing, as explained under “Results”.

According to the P-values for the soil samples there are significant differences between sites for all metals. However, the grouping information shows that only the concentration of Zn shows any significant difference between the reference and both of the other sites. For Cu and Fe the difference indicated from the P-value is between the two sites WD and WWTP, but not the reference. Hypothesis (a) is therefore rejected regarding only Zn, and not rejected for any of the other metals. Regarding Pb and Cr the number of samples analysed is assumed to be too low to give sufficient certainty for a statistical hypothesis test. In the same way we can reject the null hypothesis (b) for Zn (both at WD and WWTP for maize, only WWTP for pumpkin leaves) and for Cu (regarding maize at WD). For all other metals we cannot reject the null hypothesis (b).

Regarding hypothesis (c) the number of samples analysed are not sufficient to make a qualified decision about rejecting or not rejecting the null hypothesis.

Table 19 - P-values compared with significant level

	Fe	Zn	Cu
Soil	$P < 0.05$	$P < 0.05$	$P < 0.05$
Pumpkin leaves	$P < 0.05$	$P < 0.05$	$P > 0.05$
Maize	$P > 0.05$	$P < 0.05$	$P < 0.05$

6.2 Flaws in method

A displayed inability to repeat the analysis and acquire similar concentrations makes the results for Cd-content in the samples unreliable. A simple explanation for the irregularity would be that the result from the Buck Scientific 200 AAS used at University of Malawi is faulty, due to the machine being developed in the early 80's and the lamps being hand-me-downs from other universities. However, the calibration curves created with this machine showed a correct linear response in increasing absorbance with increasing concentration of metal in the calibration solutions. Therefore the response to the variation of Cd concentration between the two analyses is to exclude both of them from the study.

A possible explanation for the higher concentration showed in the analysis at University of Malawi is background interference from particles due to the flame not being at a sufficient temperature. This is shown to give a higher absorption (García & Báez 2012). There might also have been problems with the radiation source or the monochromator that made other elements interfere with the results. All this speculations can however not be proved without further testing of the instrument.

An important thing to remember regarding the assessment of contamination is the limitations given by the method of analysis. An AAS instrument has, like all other instruments, a detection limit. This limit is dependent on the instrument, the chosen wavelength, the solvent and a number of other factors (Van Loon 1980). If the concentration in the sample is below the limit of detection, the analysis will give a result of zero. This does not mean that the sample is free from the actual substance. To make sure that eventual presence of metals are detected one can either change method of analysis to one with lower detection limit, or change the method for extraction to get samples with higher concentration. This can be done by increasing the amount of sample used for extraction from ~1 to ~10 g or even more. Higher concentrations are easier to handle and the standard deviation between replicates will have a lower impact on the certainty of the result. In further studies I also recommend that the methods for sample preparation are changed to simpler ones. It's also important to use a blank with the same acids as in the sample preparation, and to use standards prepared with the same acids.

Other flaws in this study are the problem with broken equipment, the short time period and the short contact time with local experts and residents. The choice of metals to analyse was also determined by availability of equipment to analyse them, and not by any qualified suspicions of which ones might be relevant in the case.

6.3 Interpretation of results

General guideline values were used to give a reference value to compare with the found concentrations. To only compare with the reference site would be insufficient, since there we lack knowledge about previous use of the land. The reference site was considered to have a lower risk of contamination and was chosen to represent a “general” field, but one cannot be certain that the reference is free from contaminations.

The concentration of Pb at the waste dump (WD) in the samples is above the general guideline values given by the Swedish Agency for Environmental Protection (NV 2009). At WWPT, the concentration of Pb in the three samples analysed was above the guideline value. However, Sillanpää and Janson reported in 1994 that Pb contamination were not a problem in agricultural production in Malawi. Another factor that needs to be considered in the interpretation of these results is the concentration of Pb in plants. As mentioned earlier, the measured Pb concentration in the plants is unexpectedly high compared with other studies. All those unexpectedly high values combined with lack of support from earlier studies indicates that these results should be treated with scepticism until further studies can confirm the accuracy of them. The mean value for Cu was also above guideline values, but the high standard deviation of the data need to be taken into consideration.

For all metals except Zn, the results for the metal content in plants were in some way unreliable, as described earlier. Therefore no evaluation of risk from consumption of plants from the site will be performed. Since there seemed to be a trend of unreasonable high concentration for all assessed metals there might have been some errors in the way that the samples were prepared.

It is however important to keep in mind that even though it seems likely that the concentration of a metal is low at the sites right now, there might be a future risk for contamination. Also, even if the unreliable results from this study cannot prove any contamination, they can also not prove any lack of contamination. There is also a possibility of presence of metals and organic compounds not analysed in this study. It might therefore be motivated to use these results to plan and perform a second, improved, study.

The analysis of the soils content of phosphorus and nitrogen were not performed with a method that gives results suitable to be compared with other studies, unless they used the same methods of extraction and analysis. However, the results can be compared with each other to give a ranking between the sites. This ranking indicates that the crop production at these areas can acquire positive benefits from nutrients leaching from the waste water treatment plant or from the waste dump. Both carbon content and CEC are unexpectedly high. Large amounts of organic matter can give a high CEC, but since the soil had a light colour and the method for measuring total carbon is inexact, the values shouldn’t be trusted.

6.4 Agricultural situation

6.4.1 Access to land

In the case of the waste dump, the land is owned by the city assembly and the use of it for crop production can be considered squatting. The person I met during the sample collecting told me that he had no other land to cultivate but this. On the waste water treatment plant the usage of the land was a benefit for the people working for the city assembly. They were assigned one piece of land each, and rotated places.

6.4.2 Access to inputs

None of the farmers addressed in this study benefited from FISP and both sites were unfertilised, but according to the people cultivating crops on the waste dump and at the waste water treatment plant the sites gave good yields without use of fertilisers. Especially the fields at the waste dump were said to give extraordinary amounts of maize without any inputs. From this point of view the cultivation of those areas is benefiting the farmers, since they get a higher yield without investment in fertilisers.

6.5 Social, economic and political aspects of contamination

The third objective for this study was to “discuss the political, economic and social forces that make people need to grow food on areas with suspected contamination”. To make a complete assessment of those forces is of course impossible, but a more general discussion of what I believe is the main problems for the agricultural practice in Malawi is carried out below.

6.5.1 Food security

I believe that the low food security is the main cause of risky behaviour regarding land use. In the current situation with low use of agricultural input and technology combined with small average plot size, farmers can’t “afford” not to cultivate all available land. This is especially true when the sites also give benefits in form of nutrients.

There are two ways for a country like Malawi to ensure food security. The first is to promote self-sufficiency of food, and the other is to develop a well-functioning import system. To be able to rely on import, access to foreign currency is critical, and can be acquired by a focus on cash crops for export or on industry (Harrigan, 2008). A problem with the second approach is that the poor infrastructure gives high import prices and leads to delayed arrivals of food in times of need. The starving events that occurred in 2001–02, 2004–05, and 2007–09 were all connected to the same pattern of a low maize harvest leading to a rise in price followed by a ban of private trading and delayed import (Ellis & Manda 2012). Malawi’s dependency on import in episodes of food shortages combined with the poor infrastructure have resulted in situations where the strategy to fight off high maize prices with external trade fails to deliver results in time, leading to starvation in the country (Ellis & Manda 2012). Historically Malawi has had a focus on national self-sufficiency of maize, combined with export of cash crops to promote economic growth. According to Chilowa (1998) food security in Malawi has been viewed as synonymous to “production of enough maize”. This strategy has failed to provide food security for the majority of the population. A different approach could be to focus on self-sufficiency at a household level, since a national self-sufficiency of maize does not guarantee an even distribution of food in the population. The Farm Input Subsidy Program may have helped to increase maize production, but critics like Pauw *et al* (2014) shows that the intended poverty reduction failed to occur.

A secondary issue worth mentioning is that the programs for subsidising and distributing fertilisers in Malawi might have consequences on the soil quality and public health. It’s widely known that inorganic fertiliser can be contaminated with cadmium, and most high-income countries have regulation regarding Cd-concentration in fertilisers used in agriculture. However, according to the Malawi Bureau of Standards no control of the Cd concentration is performed on the imported fertilisers. My effort to find out the origin of the apatite used in production was also fruitless, and there seems to be a lack of documentation in this area. However, in 1992 Malawi was reported to have low levels of Cd in soil and plants and this study does not indicate any drastic increase in those levels.

7. Conclusions

According to this study, the general guideline values (NV 2009) were exceeded for lead in at least one sample on both WD and WWTP. On WWTP the mean value of Cu exceeds the guideline value 80 mg Cu/kg soil (7 out of 17 samples exceed). The results for Pb are however unexpectedly high compared with earlier similar studies, and the concentration of Cu at WWTP showed a large standard deviation. There is also the earlier mentioned problem with the results for Cd concentration. All this means that no conclusion about the presence of Cd, Pb or Cu can be drawn from this study, even if a brief look at the results might indicate contamination. The only certain conclusion from this experimental study is that the used methods are insufficient. In future studies at the area it might be recommended to send samples to a laboratory with a higher standard and better accuracy in the analyses.

The concentration of nitrogen and phosphorus on both sites are higher than the reference levels. At the waste water treatment plant the soil pH was extremely low (3.71). To prevent losses of yield and to decrease the availability of some metals liming might be considered.

From the results presented here there might be some arguments to perform another risk assessment of the areas using the suggested improvements. A risk assessment on the hygienic and pathogenic aspects would also be motivated. Another important factor not covered in this study is the proportion of arable land close to potential sources of contaminating substances and the number of people affected by it.

When this study was performed some gaps in the existing research were found. For example, there is very little written about the average levels of metals in arable soil in Malawi. This is information needed to perform accurate risk assessments. There is also a lack of information regarding origin and Cd-content of the inorganic fertilisers imported to Malawi.

Malawi has a history of subsidy programs to give small-scale farmers access to fertilisers and seeds. I do not believe that the idea to break the poverty trap by giving smallholders access to agricultural is bad. The problem is when modern technology such as inorganic fertilisers or improved seeds is used to conceal the long term consequences of agricultural malpractice and bad politics. These programs must be combined with actions to secure safe access to land, fair ways of trading and over-all poverty reduction. Food security for all of the populations needs to be achieved to prevent food production on contaminated areas. If the alternative is starvation, the use of the land and the utilisation of the leaching nutrients might be the best alternative for the farmers even if there is a risk for negative health effects from contamination. The most important thing is that information about the risk and benefits is handed to the local farmers and the city assembly so they can make a qualified decision about the future use of the areas.

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Appendices

These appendices were made in cooperation with Sofie Orvestedt, and appear in a similar form in her work titled “Waste management and impact on people’s health when cultivating on sites contaminated with heavy metals - Minor field study made in Zomba, Malawi” (2015).

Appendix 1 – Sampling performance

This sampling strategy contains a detailed description of how the sampling was performed. It contains descriptions and situational planning such as the area of sampling, locations for the sampling points and how the samples were taken and handled.

The aim of this sampling plan was to 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 or other reasons for changes. This is the final document describing in detail how the sampling was performed.

Sampling scale

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

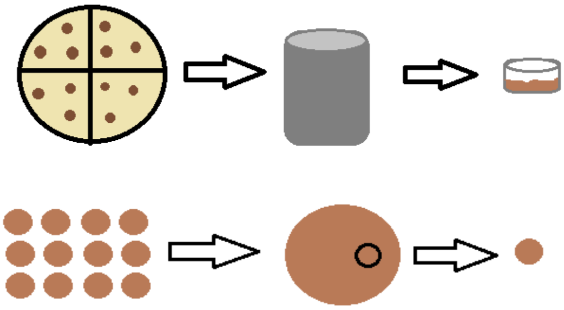

Figure 5 - An illustration of the composite samples from 12 individual samples to 1 composite sample and one aliquot for further analysing.

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, Back, Engelke, Sego, & Wik, 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 after the severity of the consequences coming from committing the 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 6 - Type I and type II errors

Pilot study

The sampling began with a pilot study to de 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 of course further reduce the number of samples but was not a problem in this study.

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

Soil samples

To be able to quantify the amount of heavy metals in the soil surface and to be able to create a map over 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 the 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 an acceptable risk for type I and type II errors.

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

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 measured out

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 analyse as soon as possible (Swedish geotechnical society, 2013)

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:

- 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).

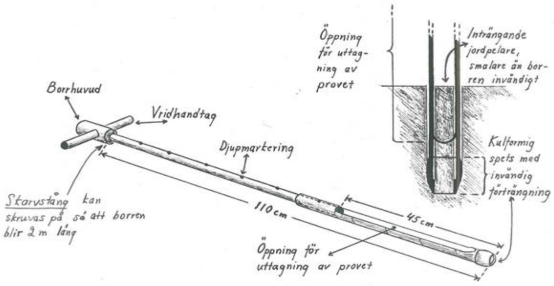

Figure 7 - Soil survey drill "Trekantenborr"

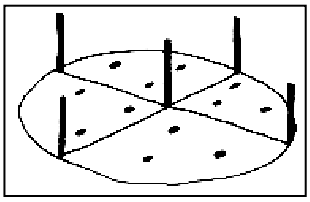

Figure 4 - Illustration of the sample circle and how the surface soil samples were taken

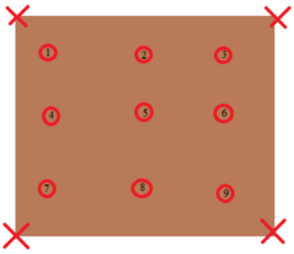

Figure 5 - Sampling grid without fixed distance

Crop samples

Materials:

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

Method:

- Plant samples were planned to be taken 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 edible plants as maize and pumpkin leaves were sampled

Water samples

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 was taken to be as representative as possible, which is why the samples was 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 it was clear if there were several sampling vessels for the same sampling point
- Rubber gloves were put on
- The bottle was brought down vertically in the water with the opening first so that the water surface was not included in the sample.

Packing, transport and storage

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

Appendix 2 – Analysis performance

This is a detailed description of how the analyses were performed. 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.

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 weight 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 analyse was not possible to perform at Chancellor College which is why they were sent to a lab at the Forest department. 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

Source: Samson Mkali Idruss Sajidu, *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.

Total Organic Carbon (Walkley and Black 1934)

The organic carbon in the sample is oxidized with potassium dichromate and sulphuric acid. The excess potassium dichromate is titrated against ferrous ammonium sulphate.

Reagents

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

Procedure

- Weigh 1 g soil into a 500 ml conical flask.
- Add 10 ml of 1 N $K_2Cr_2O_7$ and 20 ml of conc. H_2SO_4.
- Swirl the flask carefully and allow it to stand for 30 minutes.
- Slowly add 200 ml distilled water and 10 ml H_3PO_4.
- Add 1 ml of diphenylamine indicator and titrate against 0.5 N Ferrous ammonium sulphate solution until green colour starts appearing indicating the end point.
- Run a blank simultaneously.

Total Nitrogen (Kjeldahl method)

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

Total phosphorous - Vanadomolybdophosphoric yellow colour method

Reagents

- *Solution A:* Dissolve 25 g of ammonium molybdate in 300 ml warm distilled water and cool it.
- *Solution B:* Dissolve 1.25 g of ammonium metavandate in 300 ml boiled distilled water. Cool and add 250 ml conc. HNO_3. Cool solution B and mix with solution A and make up to one litre.
- *Standard P solution:* Dissolve 0.2195 g of dried KH_2PO_4 in distilled water, acidify with 25 ml of 7N H_2SO_4 and make the volume up to one litre to get 50 mg/l P solution.

Procedure

- Place 10 ml of acid digests (see chapter B-13) of soil sample in a 50 ml volumetric flask, add 10 ml of the vanadate-molybdate reagent and dilute to 50 ml.

- Mix well and read the P concentration after 10 minutes using spectrophotometer at 420 nm.
- Take 0, 1, 2, 3, 4 and 5 ml of the 100 mg/l P solution in 50 ml volumetric flask and develop colour in identical manner.
- Calibrate the spectrophotometer with known P concentration and read the concentration of sample.

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 weight was 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

- Acid was added to prevent microbial growth
- 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 were 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 3 - Calculations

Moisture

The soils moisture content and the moisture correction factor were calculated for all sample points using equation 1 and 2.

$$\mathrm{M} = \frac{(\mathrm{B}-\mathrm{C})\times 100\%}{(\mathrm{C}-\mathrm{A})} \qquad \text{Equation 1}$$

$$\mathrm{mcf} = \frac{100+\mathrm{M}(\%)}{100} \qquad \text{Equation 2}$$

Where
M = Moisture content (%)
A = Empty Beaker weight
B = Sample + Beaker weight
C = Final weight

Heavy metal content in surface soil

Two aliquots per sample point was analysed for Cd, Cu, Zn and Fe using AAS, with measures absorbance. Before analyse 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. The calibration curve and equation for Cd is shown as an example (equation 3, figure 6).

The absorbance values from the samples were then recalculated to ppm using the equation from the calibration curve. After that the value in ppm was recalculated to mg/kg soil using equation 4.

$$C_{Cd}\,(ppm) = \frac{A}{0.029} \qquad \text{Equation 3}$$

$$C_{Cd}(mg/kg) = \frac{C_{Cd}\,(ppm)*MCF*0.1}{Sample\ weight} * 1000 \qquad \text{Equation 4}$$

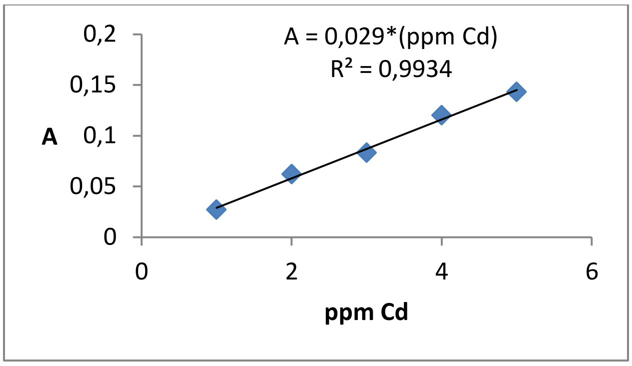

Figure 8 - Calibration curve for Cd. All trend lines used for calculation of concentration goes through zero.

Phosphorous

Three sample points per site was analysed, using the same samples as for metal analysis. 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.

$$P\ (\mu g/g) = \frac{R*50}{10} * \frac{100}{Sample\ weight\ (g)} \qquad \text{Equation 5}$$

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.

Cation Exchange Capacity (CEC)

For determination of CEC, a known concentration of Cu^{2+} -diethylenediamine complex 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 6.

Equation 6

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