IMPACT ASSESSMENT OF LONG TERM TREATED WASTEWATER DISCHARGE ON HEAVY METAL CONCENTRATION IN SOILS FROM PALAPYE EAST, BOTSWANA

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A Thesis submitted to the Faculty of Sciences in Fulfilment of the Requirements of the Award of the Degree of Master of Science by Research in Environmental Science

------- September 2017 -------

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I, Ndiye Michael Kebonye, hereby declare that this thesis is my own original work and that it has not been presented and will not be presented to any other university for a similar or any other degree award.

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CERTIFICATION

We the undersigned certify that we have read and hereby recommend for acceptance by the Faculty of Sciences a thesis titled: "*Impact assessment of long term treated wastewater discharge on heavy metal concentration in soils from Palapye East, Botswana*", in fulfilment of the requirements for the degree of Master of Science in Environmental Science in BIUST.

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Date: 11 Sept., 2017

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Date: 11 Sept., 2017

DEDICATION

To my wife, Tebogo Ndiye Kebonye and my parents, Mr Edward Motsipe and Mrs Tolani Bameno Kebonye for their love and support.

ACKNOWLEDGEMENT

I wish to thank God Almighty for the strength and ability to complete this work. I am also thankful to my supervisors, Professor Dr Felicia O. Akinyemi and Dr Peter N. Eze for their encouragement and mentorship throughout the entire research period. They have greatly contributed to my scientific career and writing skills. Also, the Botswana International University of Science and Technology (BIUST) for the MSc scholarship provided, transport facilitation to do field work and for the platform to carry out selected laboratory experiments particularly in the Department of Earth and Environmental Science.

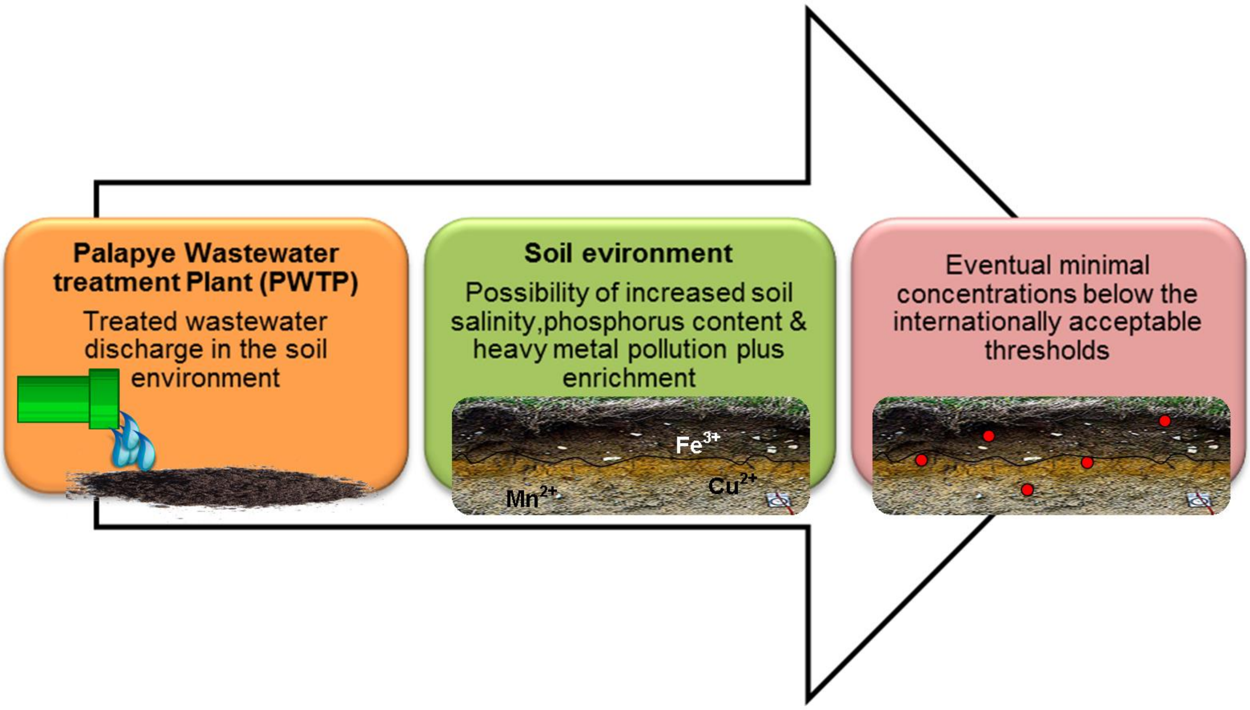
Special thanks are due to the Palapye Wastewater Treatment Plant (PWTP) staff under the Botswana Water Utilities Corporation (BWUC) for providing data on water (i.e. the treated wastewater). The Government of Botswana's research permit as a postgraduate Research Assistant on the United States Agency for International Development (USAID)/Botswana International University of Science & Technology (BIUST) funded Land Degradation Index Mapping (LDIMapping) project (SERVIR/E&S/2014/004) is also duly acknowledged. I also thank some local farmers residing near the study area for allowing accessibility into their farms in order to locate certain sampling points on the other side of their properties.

ABSTRACT

Issues on environmental soil quality continue to attract much global attention. Domestic wastewater is a potential source of contaminants capable of degrading the soil environment. This study reports the accumulative effects of 21 years (1995 – 2016) of treated wastewater discharge on heavy metal concentration levels in the proximal environment of Palapye wastewater treatment Plant (PWTP), Central Botswana. Soil samples were collected from eight geo-referenced pedons: four situated along the treated wastewater channel and four on an adjacent well-drained channel (control). Selected physico-chemical properties of the soils were determined using routine laboratory procedures and heavy metal concentrations with portable XRF (Olympus Delta Premium Analyser SN: 550255, USA). Results of the study show that heavy metal (Fe, Cu, Zn, Mn, Pb and U) concentrations in the two drainage classes (poorly drained and somewhat excessively drained) did not vary significantly ($p > 0.05$). There was strong correlation between organic matter (OM) and Fe ($R^2 = 0.896$, $p < 0.01$), OM and Cu ($R^2 = 0.908$, $p < 0.01$), OM and Zn ($R^2 = 0.956$, $p < 0.01$) and OM and Mn ($R^2 = 0.954$, $p < 0.01$) in control soils, while treated wastewater affected soils showed strong correlation for OM and Fe ($R^2 = 0.765$, $p < 0.01$), OM and Zn ($R^2 = 0.770$, $p < 0.01$) and OM and Mn ($R^2 = 0.802$, $p < 0.01$). Source apportionment of heavy metals using PCA shows one component in the control soils accounted for 77% of the total variance, while two components accounted for 97% of the total variance in treated wastewater affected soils. Geochemical mass balance plots for selected profiles showed fluctuations for Fe and Mn at various depths while Zn maintained an almost constant trend. The geoaccumulation (Igeo) and pollution load (PLI) indices both show all soils to be unpolluted. Conclusion is made that two decades of treated wastewater discharge has not led to the degradation of environmental soil quality in Palapye. However, it is strongly recommended that heavy metal levels be

checked intermittently as a routine environmental monitoring exercise. Manganese which showed severe enrichment in two profiles 7 and 8 might indicates possible soil pollution, but their speciation and bio-accessibility, rather than simply total concentrations, have to be established.

Graphical Abstract



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CHAPTER ONE

GENERAL INTRODUCTION

1.1 Overview of anthropogenic activities and soil quality

Soil is a naturally occurring body that facilitates plant growth, water and nutrient movement in the environment (Wang *et al.,* 2003), and provides other ecosystem services (Legaz *et al.,* 2017). These ecosystem services include carbon sequestration, water purification and soil contaminant reduction, climate and flood regulation, biogeochemical nutrient cycling habit for organisms, and sources of pharmaceuticals and genetic resources (FAO, 2015). Soil quality is soil's potential to function, to sustain animal and plant life and to improve water and air quality (Doran, 2002; Legaz *et al.,* 2017). Recently though, issues on soil quality have attracted great attention (Liu *et al.,* 2016a) as alterations primarily brought about by anthropogenic activities continue to affect soil parameters. In modern and urban societies, soil quality is mostly affected by anthropogenic activities including agriculture, industries, waste treatment, mining and roadside vehicular emissions (Karim *et al.,* 2014).

The nature and mode by which pollutants are deposited in the environment through these anthropogenic activities is unique. Some pollutants are retained and transported by either air or water, settling and accumulating in soil environments through leaching, adsorption and infiltration where they degrade soil quality. Effluent from households, construction, industrial and sometimes mining drainage systems collected in reservoir ponds to undergo various treatment processes before either being discharged into the environment or rechannelled to various activities to be reused is known as wastewater. There is a high reliance on wastewater for urban agricultural projects in arid, semi-arid and mediterranean regions where water availability is usually a challenge (Farahat and Linderholm, 2015; Elgallal *et al*., 2016;

Bardhan *et al*., 2016). Although reusing treated wastewater has been reported to supplements some deficient nutrients required by plants in soils, its unceasing use may prove detrimental to soil environments particularly with regards to quality (Andrews *et al.*, 2016). Single or at times combined techniques used to treat wastewater for environmental and domestic suitability do not ensure overall cleanliness of these waters due to limitations arising from complexity of these effluents (Ahmed and Ahmaruzzaman, 2016). Some of the non – degradable metallic pollutants and organic compounds are still masked and retained in treated wastewater at the end (Speir *et al.*, 2003; Nagel *et al.*, 2003; Klay *et al.*, 2010). Characterisation of wastewater is based on physical, chemical and biological parameters (Table 1.1). The quality and composition of wastewater is often described in terms of the aforementioned parameters (von Sperling, 2007).

Table 1.1: Selected parameters that characterise wastewater

Physical characteristics	Chemical characteristics	Biological characteristics
Temperature	Total solids	Algae
Colour	Organic matter	Bacteria
Odour	Total nitrogen	Archaea
Turbidity	Total phosphorus	Fungi
	pH	Protozoa
	Oils and grease	Viruses
	Chlorides	Helminths

Source: von Sperling, (2007)

1.2 Wastewater effects on soils

In many countries, population growth is a key driver of increased production of wastewater (Ledón *et al*., 2017). Therefore, huge amount of money is regularly invested because of the demand for more sophisticated wastewater treatment methods (Ledón et al., 2017). Once treated, wastewater is either used for irrigation or discharged directly into the soil environment; retained pollutants harboured by these treated wastewaters are released into the environment where they affect soil biological, physical and chemical properties. Some impacts on soil attributed to wastewater application include but not limited to high microbial pollution (Stark *et al.*, 2016), decrease in soil organic matter, soil structural and textural alteration, high soil salinity, increase in soil bulk density (Azouzi *et al.*, 2016), decrease in soil porosity and hydraulic conductivity (Aiello *et al.*, 2007), rapid soil nutrient accumulation and mineral pollution (Liu *et al.*, 2016b). A wide documentation has been done on soil microbial pollution, soil salinity and soil mineral pollution (e.g. phosphorus and heavy metals) (Flores-Márgez *et al.*, 2013; Thongtha *et al.*, 2014; Farahat and Linderholm, 2015; Andrews *et al.*, 2016; Stark *et al.*, 2016).

High microbial pollution in soil is a consequence of inadequate treatment of wastewater. In view of this, antibiotic resistant microbes are then favoured by these conditions (Di Cesare *et al.*, 2016). Irrigation or discharge of inadequately treated wastewater tends to encourage the deposition of potentially harmful microbial organisms into soil. The increase in microbial population (e.g. some bacteria such as *Escherichia coli* and *Vibrio cholera*, protozoa and viruses) may interfere with soil ecosystem functioning and eventually affect plant growth. Salinization on the other hand affects over one third of the world's irrigated land (Singh, 2015). According to Klay *et al.* (2010) irrigation with treated wastewater is responsible for high salinity levels in soils. High soil salinity inhibits vegetation growth resulting in bare patches on the ground and triggers the formation of salt crystals on soil surfaces as well as reduces crop yields (White, 2006).

Meanwhile, reasonable amounts of phosphorus contained in wastewater may also accelerate environmental eutrophication of water (Nguyen *et al.*, 2016). In addition to high microbial pollution, salinity and phosphorus enrichment in soil, treated wastewater may still contain reasonably high concentrations of retained heavy metal quantities as sourced from a wide range of urban activities which include metal plating, mining activities, tanneries, smelting and alloy industries (Hegazi, 2013). Lee *et al.* (2016) also ascertains that wastewater from industrial plating contains reasonable amounts of heavy metals including Cr, Ni and Cu of toxic and persistent nature once in the environment. These pollutants are detrimental to the environment (Järup, 2003; WHO, 2011) since they are non-biodegradable (Wang *et al.,* 2015; Liu *et al.,* 2016b). Consequently, irrigation or discharge of treated wastewater into the environment may result in long term accumulation and persistence of these potentially toxic metals in soil to eventually affect general soil physical and chemical properties by means of denaturing or lowering microbial activity (Khan, 2008; Ding *et al.*, 2017).

1.3. Problem statement

The Palapye Wastewater treatment plant (PWTP) releases treated wastewater directly into the immediate environment where it has now created a wetland channel which flows in the Lotsane sub-basin (catchment). The area is predominantly agrarian in nature, therefore, if by any chance discharged treated wastewater has retained potential toxic metals such as lead (Pb), Arsenic (As) and Uranium (U) due to flaws in treatment techniques; possibilities of eventually posing threat to the entire food chain due to accumulation are imminent. In several studies in China, wastewater sourced from various activities was ascertained to increase the levels of various heavy metals (HMs) in agricultural soils. For instance in Lechang Guangdong Province, South China a paddy field used for rice planting was enriched with cadmium (Cd) as a result of continuous irrigation with untreated wastewater from mining activities (Yang *et al.*, 2006). Also in 1960 another paddy field in Dabaoshan in Shaoguan, Guangdong Province was found to contain high levels of Zn, Cd, Cu and Pb attributed to continuous irrigation with acid mining wastewater (Zhou *et al.*, 2007).

Although no documented complaints from local farmers and residents around the plant concerning effects of the treated wastewater have been raised as yet, depending only on primary and secondary wastewater treatment methods is untimely more so that they only improve water quality while metallic deposits are still retained (Klay *et al.,* 2010). Most of the documented studies in respective places in Botswana widely studied effects of direct irrigation of treated wastewater in cultivated soils and crops (e.g. Dikinya and Areola, 2009; Dikinya and Areola, 2010; Mosime *et al*., 2011; Likuku and Obuseng, 2015) rather than effects of continued channelled discharge in soil environments used for communal grazing.

1.4 Rational and justification

As the demand for water continues to increase, treated wastewater provides an alternative solution to reduce pressure on potable water sources in arid and semi-arid regions like Botswana (Zaibel *et al.,* 2016). Although treated, Klay *et al.* (2010) establishes that some metallic compounds are still retained and these may facilitate the accumulation of heavy metals (HMs) in soil. In Botswana, even though conclusions drawn from several Glen Valley studies (Dikinya and Areola, 2009; Dikinya and Areola, 2010; Mosime *et al*., 2011) show that treated wastewater adversely affect physical, chemical and biological parameters in vegetables products, Likuku and Obuseng, (2015) highlight the need to assess the accumulative impacts of treated wastewater reuse in the entire food chain. In conjunction to this, soil being an important component that begins the whole process of plant growth ought to be assessed for heavy metal concentration levels periodically. Besides, there is still limited information on heavy metal pollution in Botswana as a whole. Furthermore, according to Gharaibeh *et al*. (2016) there is still a level of uncertainty as to whether the benefits of treated wastewater outweigh its potential to degrade soil quality, thus a greater level of understanding is still needed before widely recommending it for irrigation purposes. This study seeks to fill gaps in knowledge by contributing on the effects of long term discharge of treated wastewater at the Palapye wastewater treatment plant on soil heavy metal concentration levels.

1.5 Aims and objectives

The overarching aim of this study is to assess heavy metal concentration levels due to treated wastewater discharge on soil proximal to Palapye Wastewater Treatment Plant (PWTP).

Specific objectives of the study include:

i. To characterize soils exposed to long term discharge of treated wastewater using selected physical, chemical and geochemical properties (particularly heavy metals);

ii. To assess treated wastewater impacts on studied soil properties by comparing treated wastewater affected with no – treated (control) soils and;

iii. To undertake potential risk assessment of heavy metal pollution in the soils around the wastewater treatment plant.

1.6 Thesis layout

This thesis contains four chapters.

CHAPTER ONE: General introduction and a review of contemporary literature on treated wastewater and soil quality.

CHAPTER TWO: Methodology; geological and geographical settings of the study area, and field and laboratory procedures applied in the study.

CHAPTER THREE: Results

CHAPTER FOUR: Discussions of the research findings

CHAPTER FIVE: Synthesis, conclusion and recommendations for further studies

CHAPTER TWO

MATERIALS AND METHODS

2.1. Geographical setting of study area

The study was carried out within 1 km periphery of the Palapye Wastewater Treatment Plant (PWTP), in the Central District of Botswana. The area is found approximately within latitude ranges of 22°31' and 22°32'S, and longitude of 27°10' and 27°12' E (Fig. 2.1). Altitudes for the locations ranged from 900 to 922 m above sea level. The study area is flanked to the north by Dikabeya Farms – a large commercial irrigation farm (approximately 8 km from PWTP), to the south by Botswana International University of Science & Technology (BIUST) (approximately 6 km from PWTP), Palapye (2 km from PWTP), and to the west and east by large expanse of arable lands.

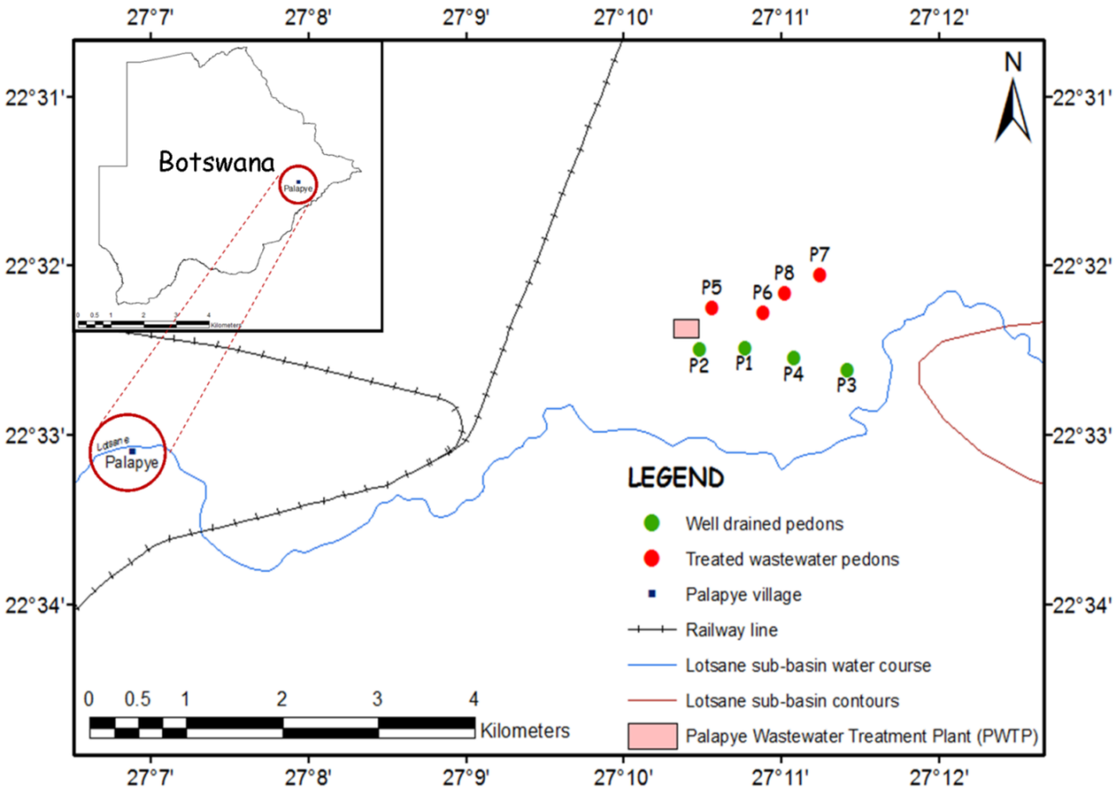


Figure 2.1: Pedon locations relative to the wastewater treatment plant

2.2. Site description

2.2.1. Climate

Palapye is predominantly a tropical semi-arid climate characterized by erratic rainfall patterns annually averaging between 371 mm and 396 mm and temperature ranges from 32 ^{o}C to 39 ^{o}C (Zhai *et al.*, 2009). The area is prone to dryness in synchrony to occasional prolonged periodic droughts (Phuthego, 2007; Mphale, 2014).

2.2.2. Soils and geology

The soils of Palapye are predominantly sandy, sandy loam to sandy clay loam (alluvial and colluvial) in nature and mostly made up of ochric horizon (Burgess, 2006). According to the Soil Taxonomy soil classification system, soils from the study all qualify as Ustic Quartzipsamments, an FAO/WRB equivalent of Ferralic Arenosols (De Wit and Nachtergaele, 1990). The geology of the area is the Lotsane Formation composed mainly of sandstone, shale and limestone deposits (Jones and Hepworth, 1973).

2.2.3. Vegetation and landuse

Vegetation is predominantly mixed mopane bushveld consisting of *Colophospermum mopane* permanent stands mixed with other species like *Acacia nigrescens, Combretum apiculatum, Acacia tortilis, Burkea Africana, Combretum imberbe, Acacia mellifera, Acacia erioloba, Terminalia prunioides, Terminalia sericea* and *Catophractes alexandri* (Bekker and De Wit, 1990; Burgess, 2006). The dominant anthropogenic activity around the study area relates to agriculture particularly pastoral and arable farming.

2.3. Field sampling

A total of eight soil profiles (e.g. Fig. 2.2) within the proximity (radius of 1.5 km) of the treatment plant (Fig. 2.1) were dug for this study. The pedons had to be away from obvious disturbances and at least 400 m apart per transact. Four pedons were situated along the treated wastewater channel (affected by treated wastewater) and four on a well – drained transect (control, an area not affected by treated wastewater) away from the plant. These pedons were named P1: Pedon 1, P2: Pedon 2, P3: Pedon 3, P4: Pedon 4 for the control, P5: Pedon 5, P6: Pedon 6, P7: Pedon 7 and P8: Pedon 8 for the treated wastewater channel respectively (Fig. 2.1). Hand samples were collected from each horizon of the profiles and transferred to the laboratory in plastic zip-lock bags for further analyses. The soil samples were each collected and described in the field following the Guideline of FAO for Soil Profile Description (2006). Soil colour was determined using Munsell soil colour system (Munsell Color Company, 2015). Also the general soil macromorphological properties were described in accordance with the guidelines for soil profile description (FAO, 2006).

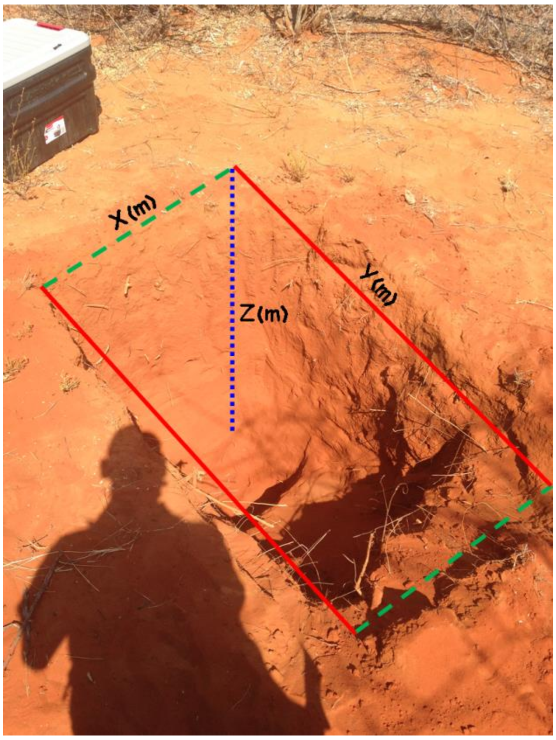


Figure 2.2: Field observations showing pedon dimensions in the control channel

A background sample (parent material) (Fig. 2.3: depicted by red arrow) of the study area was also identified and collected for total elemental analysis.

2.4. Laboratory analyses

All soil samples were pre-treated by gently grinding and passing them through 2 mm sieve to separate soils from gravels and roots/rhizomes. Each soil sample was then stored separately in a corresponding pre labelled plastic bottle container to await routine laboratory procedures. Soil particle size distribution was determined by the Bouyoucos hydrometer method (Bouyoucos, 1962). Soil bulk density (BD) followed the core sampler method (Daddow and Warrington, 1983). Soil potential hydrogen (pH) was determined in water and in 0.01 M $CaCl_2$ solution (both at 1: 2.5 soil to solution ratio: w/v) using a Bante 210 Benchtop pH/mV meter. The electric conductivity (EC) was determined in water (1: 2.5 soil to solution ratio:w/v) through a HACH EC meter.

Figure 2.3: In situ rock outcrop located in the study area

Phosphorus (P) determination followed the Bray and Kurtz P-1 method (Bray and Kurtz, 1945) further determining its levels using a UNICAM Spectrometer. Cation exchange capacity (CEC) was determined by the summation of exchangeable cations, Ca^{2+}, Mg^{2+}, K^{+} and Na^{+} using a computer. This method of determining CEC in soils suffices where the pH (H_2O) is not below 5.50. Calcium (Ca) and Magnesium (Mg) were determined by water extraction (1:1) followed by Ethylene Diaminetetraacetic Acid (EDTA) titration method using filtration apparatus and a burette (Barrow sand Simpson, 1962). As for Potassium (K) and Sodium (Na) the ammonium acetate extraction followed by Flame photometry method were employed using a Corning 410 Flame photometer (Lavkulich, 1981). Soil organic matter (OM) was determined through the estimation of organic matter by loss on ignition (ASTM D 2974) method using a Carbolite AAF 1100 furnace pre-set at 440^{o}C.

Heavy metals analysis was carried out with Portable X-Ray Fluorescence (PXRF) Spectrometer (Olympus Delta Premium Analyser SN: 550255, USA), a device widely used in recent years to assess elemental concentrations in soils. It has varying operational modes which enables quantification of a wide range of concentration levels in soils. Furthermore, it is considered effective in determining total soil heavy metal concentrations based on linear regression models between fluorescence intensity and specific heavy metal concentration levels (Kibride *et al.*, 2006). All these characteristics of the PXRF allow it to tally well with other analytical techniques such as ICP-MS and AAS. Moreover it is advantageous in that it can be used in both field and in the laboratory as compared to other analytical techniques which are only limited to the laboratory.

PXRF is a device that uses Energy Dispersive X-Ray Fluorescence (EDXRF) principles. A sample is first directly excited with incident radiation from a primary source in the form of energy photons (Fig. 2.4). A sample's chemical composition is immediately measured without the sample being destroyed (no sample preparation therefore no destruction) (Appolonia and Melquiades, 2014). This measurement happens as fluorescent X-Ray feedback per element together with Compton and Rayleigh scatter energies from the sample are simultaneously measured by the X-Ray detector mounted within the PXRF.

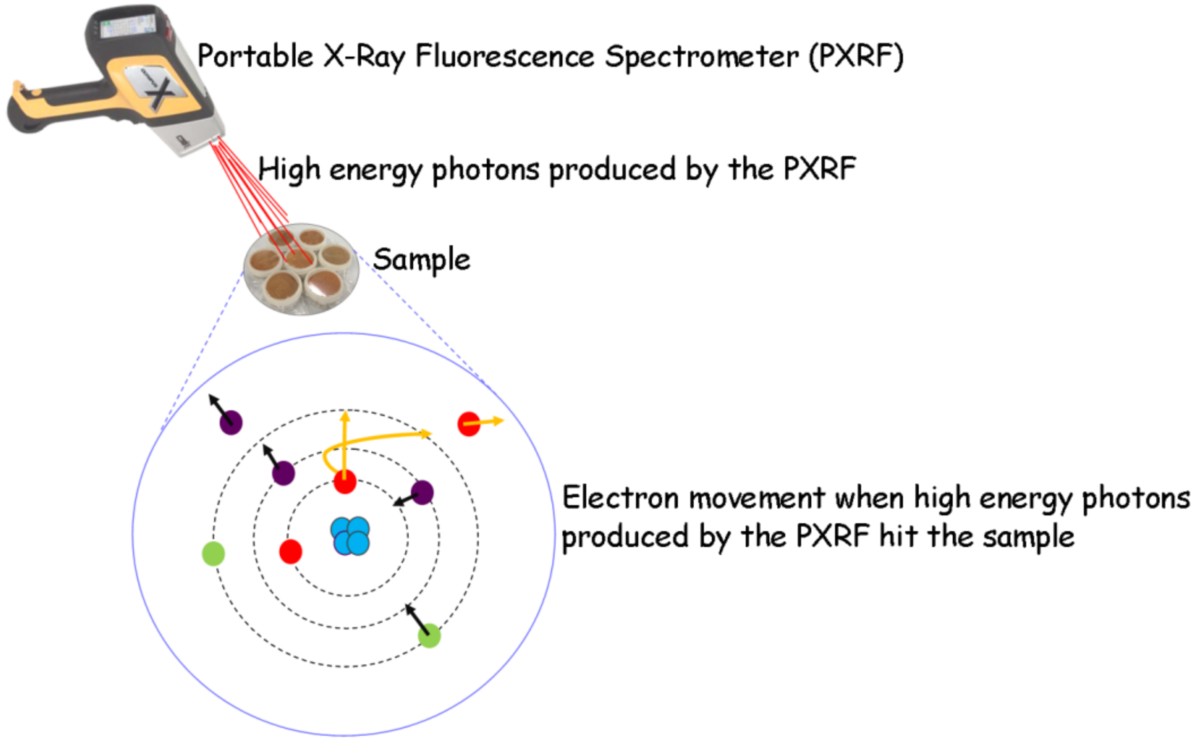


Figure 2.4: Simplified schematic representation showing the principle behind the PXRF

Sample pre-treatment for rapid heavy metals analysis with PXRD includes pulverising using a Planetary Micro Mill Pulverisette 7 (Fritsch) in order to further reduce their particle sizes and for homogeneity. For the background sample (parent material) all weathered and/or contaminated edges were cut off, following grinding of the sample using a rock grinder, then pulverisation for a finer homogenous sample. The pulverised soils and parent material samples (Fig. 2.5) were properly packaged in small plastic containers each covered with a thin plastic film for specific use in the XRF (0.25 mil (6µ) thick; 2.75 x 300). Before sample scanning, a calibration check (cal. check) using a 316 stainless steel cal. check coupon was performed on the PXRF to ensure its proper functioning in accordance with the User manual guidelines. Soil reference materials, NIST 2710a and 2711a (Table 2.1) were used for references. All measurements were taken in triplicates.

Figure 2.5: Pulverised samples

Table 2.1: Elemental concentration levels in Standard Reference Material (SRM) 2710a and 2711a in ppm

Element	NIST 2710a			NIST 2711a		
	Measured value	Certified Value*	Recovery (%)	Measured value	Certified Value[#]	Recovery (%)
	---------------------------ppm---------------------------			---------------------------ppm--------------------------		
As	1511	1540 ± 100	98	53	107 ± 5	50
Cu	3355	3420 ± 50	98	111	140 ± 2	79
Pb	5443	5520 ± 30	99	1363	1400 ± 10	97
U	17	9.11 ± 0.30	187	nd	3.01 ± 0.12	-
Zn	4092	4180 ± 150	98	360	414 ± 11	87
Fe	42104	43200 ± 800	97	21412	28200 ± 400	76
Mn	2119	2140 ± 60	99	575	675 ± 18	85

nd: No data; *National Institute of Standards and Technology, (2009a); [#]National Institute of Standards and Technology, (2009b)

2.5. Soil pollution level assessment

Heavy metal pollution levels in both control and treated wastewater affected soils were assessed using three mathematical indices, the Enrichment Factor (EF), Geoaccumulation Index (Igeo) and Pollution Load Index (PLI) respectively. These indices have been widely used to understand the extent and complexities in pollution for different environments (Addo *et al.*, 2012; Sakan *et al.*, 2015; Xu *et al.*, 2017).In this study, these indices were employed particularly in soils.

2.5.1. Enrichment Factor (EF)

The EF has been used by several researchers to measure contamination in different environmental matrices (Singh *et al.*, 2010; Yuan *et al.*, 2014; Zeng *et al.*, 2014; Xu *et al.*, 2017). In using the EF index, Al or Fe are widely used as normalising elements in order to capture outlier metal contributions (Sakan *et al.*, 2015). In this study Fe was used as a normalising element thus EF was computed by Equation 1:

$$\mathrm{EF} = \frac{\left[\frac{\mathrm{C_x}}{\mathrm{C_{Fe}}}\right]\mathrm{Sample}}{\left[\frac{\mathrm{B_x}}{\mathrm{B_{Fe}}}\right]\mathrm{Background}}$$

………..Equation 1

Where:

C_x over C_{Fe} and B_x over B_{Fe} represent the heavy metal of interest to Fe ratios in the study sample over that of the background sample.

In general, for EF determination, five categories were used to weigh the levels of pollution. An EF < 2 denoted minimal enrichment, EF from 2 to 5 for moderate enrichment, EF from 5 to 20 for severe enrichment, EF from 20 to 40 for very high enrichment and EF > 40 for extremely high enrichment (Addo *et al.*, 2012).

2.5.2. Geoaccumulation Index (Igeo)

Similar to EF the Geoaccumulation index (Igeo) assesses levels of pollution in the environment and it is given by the Equation 2:

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n}\right] \quad \text{………..Equation 2}$$

Where:

C_n = measured concentration of the element in the tested sample;

B_n = geochemical background value of the element of interest and

Constant 1.5 = Minimizes the effect of possible variations in the background values which may be attributed to lithologic variations.

The geoaccumulation index (Igeo) scale ranges were: Igeo ≤ 0 (Partially unpolluted), 0 < Igeo < 1 (Unpolluted to moderately polluted), 1 < Igeo < 2 (Moderately polluted), 2 < Igeo < 3 (Moderately to strongly polluted), 3 < Igeo < 4 (strongly polluted), 4 < Igeo < 5 (Strongly to extremely polluted) and Igeo > 5 (Extremely polluted) respectively.

2.5.3. Pollution Load Index (PLI)

The PLI is first computed from the contamination factor (CF) which is the ratio between the heavy metal of interest in the study sample and in the background sample (Equation 3).

$$CF = \frac{\text{Cm sample}}{\text{Cm background}} \quad \text{……….. Equation 3}$$

Pollution load index is then computed from Equation 4 where n is the total number of metals studied.

$$PLI = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x} \ldots \text{x } CF_n)^{\frac{1}{n}} \quad \text{……….. Equation 4}$$

The interpretations of results for PLI were given by: PLI < 1 denoting perfection, PLI = 1 for only baseline levels of pollutants is present and PLI > 1 for a deteriorating site quality.

2.6. Geochemical mass balance plot

In quantifying the total result for pedogenic weathering throughout the soil profile, geochemical mass balance plots were computed through Equation 5. This expression assumes an immobile element like Zirconium (Zr) as used in the study exists separately. It is then used to correct mobile element concentration levels during weathering processes (Du *et al.*, 2010).

$$\tau_{i.j} = \left(\frac{C_{i.p}}{C_{i,w}}\right)\left(\frac{C_{j,w}}{C_{j,p}}\right) - 1$$

……….. Equation 5

The dimensionless coefficient (τ_i) represents the product concentration ratio of interest where C refers to concentrations of either mobile or immobile elements (subscripts j and i respectively) for weathered samples (subscript w) or parent material (subscript p) all minus 1 (Chadwick *et al.*, 1990; Du *et al.*, 2010; Ling *et al.*, 2014).

2.7 Wastewater sample characterisation

Treated wastewater data was obtained from PWTP. This plant uses water based procedures following the Botswana Bureau of Standards (BOBS) regulations and or protocols. Its Quality Control section ensures strict adherence to standard laboratory practices in all their analyses. Thus their data is very much reliable for use. Moreover, the wastewater data is quite detailed in that it does not only capture daily chemical, biological and physical property changes but also caters for seasonal changes as well. The data was mainly physical, chemical and microbiological properties including pH, temperature, free chlorides (Cl_2), total chlorides (Cl_2), chemical oxygen demand (COD) and total coliforms. This data was used to infer on the possible effects the treated wastewater has in the soil environment. Potential hydrogen (pH) and temperature were measured using a pH meter equipped with a pH electrode and a temperature compensation probe as done by Estefan *et al.,* (2013). Free and total chlorides were ascertained using the N, N, diethyl-p-phenylene diamine (DPD) indicator through a pocket colorimeter as done in Palin, (1957). For chemical oxygen demand (COD) the titrimetric method as used by Chen *et al.* (2001) was employed. As for total coliforms, the membrane filtration method was used (EPA, 2002). The PWTP conducts daily monitoring of the effluent and for this study the monthly averages per parameter were used.

2.8. Statistical Analysis

Heavy metal concentration levels were subjected to basic ANOVA at ($p < 0.05$) for determining statistical significances for distinct parameters per drainage class. For correlation between various parameters (e.g. heavy metal, organic matter and clay content) Pearson correlation coefficients were obtained using a bivariate procedure as in Pan *et al.* (2016). Source apportionment of heavy metals was done by extracting components through factor analyses. Hierarchical cluster analyses were also done to further assess interactions between various parameters studied. Boxplots and whisker descriptive summaries showing minimum, maximum, 1st quartile, median and 3rd quartile data for EF, Igeo and PLI values were also documented. All mentioned statistical procedures were performed in the IBM Statistical Package for Social Sciences (SPSS) 20. While using SPSS, missing value (no data) cells were replaced with -99999 according to IBM, (2011) procedures.

CHAPTER THREE

RESULTS

3.1. Properties of the treated wastewater

The results of selected biological, chemical and physical properties of the treated wastewater from PWTP are presented in Table 3.1. The monthly pH values ranged from 7.3 – 8.4 (i.e. from slightly – strongly alkaline) and averaged 7.9. Wastewater temperatures per month ranged from 18 – 30 ^{o}C and averaged 25 ^{o}C. Free chloride (Cl_2) ions ranged between 0.2 to 0.4 mg L^{-1} with five out of the six months measured recording 0.2 mg L^{-1}. Total chloride (Cl_2) values ranged from 0.2 – 0.6 mg L^{-1}. Chemical oxygen demand (COD) measured between 20.0 and 115.9 mg L^{-1} with slightly higher monthly average COD's of 115.9 and 105.5 mg.L^{-1} in June and July respectively. This study shows that the total coliform concentrations of the wastewater varied between sampling campaigns. Total coliforms ranged from 2362 – 14533 CFU/100 mL and averaged 8384 CFU/100 mL.

Table 3.1: Selected parameters assessed in treated wastewater from PWTP in 2016

Month	pH	Temp. ^{o}C	Free Cl_2 (mg L^{-1})	Total Cl_2 (mg L^{-1})	COD (mg L^{-1})	Total coliforms (CFU/100ml)
January	7.7	31	0.2	0.6	51	2362
February	7.8	29	0.2	0.5	35	2900
March	7.3	30	0.2	0.3	20	3711
April	8.0	27	0.2	0.3	34	3733
May	7.9	23	0.4	nd	35	nd
June	7.9	22	0.2	0.2	116	14150
July	8.2	18	nd	0.5	106	7300
August	8.4	21	nd	0.4	nd	13900
September	7.8	24	nd	0.4	nd	14533
October	7.9	25	nd	0.3	nd	12867
Average	7.9	25	0.2	0.4	57	8384
WUC limits	5.5 – 9.0	35	1.0	1.0	150	20000

nd: no data; WUC: Water Utilities Corporation

3.2. Macromorphology and field observations

There were considerable variations in the macromorphological properties of the soils (Table 3.2). Soils on the adjacent well-drained landscape (control) were generally deeper than soils on the wastewater flow channel (Figs 3.1 to 3.7). Soils sampled from the well – drained channel were in total 22 (n = 22) while only 10 (n = 10) were sampled from the treated wastewater channel (Table 3.3). Horizon designation of the pedons follows the traditional A-B-C convention. Six genetic horizons were identified for pedon 1 (P1); seven for pedon 2 (P2); four for pedon 3 (P3); five for pedon 4 (P4); three for pedon 5 (P5); two for pedon 6 (P6); three for pedon 7 (P7); and two for pedon 8 (P8) (Figs 3.1 – 3.7).

Soil colour for each drainage class varied widely in both dry and moist state. The control soils varied from yellowish red (5YR 4/6) to very dark brown (7.5YR 2.5/2) in dry state and dark reddish brown (2.5YR 2.5/4) to very dark brown (7.5YR 2.5/2) in moist state. Treated wastewater affected soils were predominantly dark brown (7.5YR 3/4) in dry state and dark brown (7.5YR 3/4) to very dark brown (7.5YR 2.5/2) in moist state. Soil from horizon Btgb in pedon 7 of colour 7.5YR 3/1 (very dark grey) is an example of a Dystric Gleysol soil. Generally, this study showed remarkable variations in soil colour within and across the profiles. The structure of the control soils was predominantly sub-angular blocky (sblk) relative to a more angular blocky (ablk) structure observed for treated wastewater affected soils.

Table 3.2: Profile description of the macromorphological characterisation of control and treated wastewater affected soils

Horizon	Depth (cm)	Colour		Structure[1]	Roots	Boundary[2]	Consistence		Field texture[3]	Cementation	React HCl	Other features
		Dry	Moist				Dry	Moist				
					Control pedons							
Pedon 1												
A1	0-13	5YR 4/6 (Yellowish red)	2.5YR 3/4 (Dark reddish brown)	2sg	none	CS	Loose	Loose	Sandy	None	Moderate	None
A2	13-30	5YR 4/6 (Yellowish red)	2.5YR 2.5/4 (Dark reddish brown)	2sblk	few	GS	Soft	Very friable	Sandy	None	Moderate	None
A3	30-54	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	2sblk	few	GS	Soft	Very friable	Sandy	None	None	None
AB	54-91	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	2sblk	few	GS	Slightly hard	Very friable	Sandy	None	None	None
B1	91-154	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	3sblk	few	GS	Soft	Very friable	Lo.Sa	None	None	None
B2	154-170$^+$	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	3sblk	none		Slightly hard	Very friable	Lo.Sa	None	None	None
Pedon 2												
A1	0-7	2.5YR 3/6 (Dark red)	2.5YR 3/3 (Dark reddish brown)	1sblk	common	CS	Soft	Friable	Sandy	None	None	None
A2	7 - 35	10R 3/4 (Dusky red)	2.5YR 2.5/4 (Dark reddish brown)	1sblk	few	GS	Soft	Very friable	Sandy	None	None	None
AB	35-70	10R 3/4 (Dusky red)	2.5YR 2.5/4 (Dark reddish brown)	3sblk	few	GS	Soft	Very friable	Sandy	None	None	None
B1	70-96	2.5YR 3/6 (Dark red)	2.5YR 3/4 (Dark reddish brown)	1sblk	few	GS	Soft	Very friable	Sandy	None	Moderate	None
B2	96-108	2.5YR 3/6 (Dark	2.5YR 2.5/3 (Dark	2sblk	few	GS	Soft	Very	Lo.Sa	None	Moderate	None

		red)	reddish brown)					friable				
B3	108-143	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	2sblk	few	GS	Soft	Very friable	Lo.Sa	None	Moderate	None
B4	143-160^{+}	2.5YR 3/6 (Dark red)	2.5YR 2.5/4 (Dark reddish brown)	3sblk	few		Soft	Very friable	Lo.Sa	None	None	None
<u>Pedon 3</u>												
A	0-8	7.5YR 4/3 (Brown)	7.5YR 2.5/2 (Very dark brown)	3m	occasional	CS	Very hard	Very firm	Lo.clay	Strong	None	None
AB	8-22	7.5YR 2.5/3 (Very dark brown)	7.5YR 2.5/3 (Very dark brown)	3ablk	none	GS	Hard	Firm	Lo.clay	Strong	None	None
B1	22-74	7.5YR 3/3 (Dark brown)	7.5YR 2.5/3 (Very dark brown)	3ablk	few	GS	Very hard	Friable	Lo.clay	Strong	Moderate	None
Bk	74-98^{+}	5YR 3/3 (Dark reddish brown)	5YR 2.5/2 (Dark reddish brown)	3ablk	none		Very hard	Friable	Lo.clay	Strong	Moderate	Carbonate (CO_3) nodules
<u>Pedon 4</u>												
A1	0-11	5YR 4/6 (Yellowish red)	2.5YR 2.5/4 (Dark reddish brown)	3ablk	occasional	CS	Soft	Very friable	Sandy	None	Moderate	None
A2	11-40	5YR 4/6 (Yellowish red)	2.5YR 3/4 (Dark reddish brown)	3ablk	occasional	GS	Slightly hard	Very friable	Sandy	None	Moderate	None
AB	40-61	2.5YR 4/6 (Red)	2.5YR 3/4 (Dark reddish brown)	2ablk	occasional	GS	Slightly hard	Very friable	Sandy	None	Moderate	None
B1	61-98	2.5YR 4/6 (Red)	2.5YR 3/4 (Dark reddish brown)	3ablk	few	GS	Hard	Very friable	Lo.Sa	None	Moderate	None
B2	98-130^{+}	2.5YR 3/6 (Dark red)	2.5YR 3/6 (Dark red)	3ablk	none		Hard	Very friable	Lo.Sa	None	Moderate	None

Treated wastewater affected pedons

<u>Pedon 5</u>

Ap	0-11	7.5YR 3/4 (Dark brown)	7.5YR 2.5/3 (Very dark brown)	2ablk	many	CS	Slightly hard	Very friable	Sa.Lo	None	None	None
A2	11-49	7.5YR 3/4 (Dark brown)	5YR 3/4 (Dark reddish brown)	2ablk	few	GS	Slightly hard	Very friable	Sandy	None	Moderate	None
A3	49-75^{+}	7.5YR 3/4 (Dark brown)	5YR 3/4 (Dark reddish brown)	2ablk	few		Slightly hard	Very friable	Sandy	None	None	None
<u>Pedon 6</u>												
Ap	0-10	7.5YR 3/2 (Dark brown)	7.5YR 3/2 (Dark brown)	2ablk	many	CS	Hard	Very friable	Lo.clay	None	Moderate	None
Btg	10-30^{+}	7.5YR 3/4 (Dark brown)	7.5YR 3/4 (Dark brown)	2ablk	none		Hard	Very friable	Lo.clay	None	None	None
<u>Pedon 7</u>												
A	0-10	7.5YR 3/4 (Dark brown)	7.5YR 2.5/2 (Very dark brown)	3ablk	many	CW	Very hard	Friable	Sa.Lo	None	Moderate	Evidence of round shaped gravel
AB	10-38	7.5YR 4/4 (Brown)	7.5YR 3/4 (Dark brown)	3sblk	many	CI	Slightly hard	Very friable	Lo.clay	None	Moderate	Evidence of round shaped gravel
Btgb	38-50^{+}	7.5YR 3/4 (Dark brown)	7.5YR 3/1 (Very dark grey)	m	many		Very hard	Friable	Clay.Lo	None	Moderate	None
<u>Pedon 8</u>												
Ap	0-8	7.5YR 3/4 (Dark brown)	7.5YR 2.5/3 (Very dark brown)	2ablk	many	CS	Slightly hard	Friable	Loamy	None	None	None
Btg	8-40^{+}	7.5YR 3/4 (Dark brown)	7.5YR 2.5/3 (Very dark brown)	2ablk	occasional		Slightly hard		Loamy	None	None	None

1– Weak; 2 – medium; 3 – strong; m – massive; sbk – subangular blocky; ablk – angular blocky; a – abrupt; c – clear; s – smooth; g – gradual; w – wavy; i – irregular; ClayLo – clay loam; LoSa – loamy sand; SaLo – sandy loam

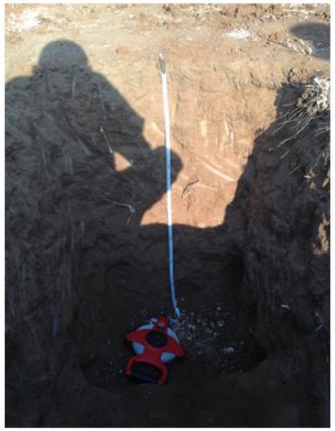
Table 3.3: Site description for each pedon location

Pedon	Location Altitude (m)	Geographic location		Horizon	Depth (cm)	Description of the surrounding area	Drainage class
		Latitude	Longitude				
				Control pedons			
Pedon 1	909	22° 32.487'S	27° 10.768'E	A1 A2 A3 AB B1 B2	0-13 13-30 30-54 54-91 91-154 154-170+	Grazing area, good soils suitable for plants and grasses (Good biomass), good tree cover (70%), *Colophospermum mopane* (40%), *Ximenia caffra* (30%), *Dichrostachys cinerea* (20%), Boscia foetida (10%) and *Grewia flavescens* (20%) (shrubland)	Somewhat excessively drained (control)
Pedon 2	913	22° 32.498'S	27° 10.479'E	A1 A2 AB B1 B2 B3 B4	0-7 7 - 35 35-70 70-96 96-108 108-143 143-160+	Grazing area, good tree cover with *Acacia mellifera* (70%) (shrubland)	Somewhat excessively drained (control)
Pedon 3	900	22° 32.616'S	27° 11.419'E	A AB B1 Bk	0-8 8 -22 22-74 74-98+	Grazing area, abundant with *Acacia tortilis*, Dry claylike soils, less vegetated area, carbonate nodules found at 98cm depth, few abundant roots in profile, stench available in profile (open shrubland)	Somewhat excessively drained (control)
Pedon 4	905	22° 32.548'S	27° 11.082'E	A1 A2 AB B1 B2	0-11 11-40 40-61 61-98 98-130+	Grazing area, Grewia species (60%), *Dichrostachys cinerea* (Moselesele) (60%), few roots observed in profile (open shrubland).	Somewhat excessively drained (control)
				Treated wastewater affected pedons			
Pedon 5	911	22° 32.248'S	27° 10.563'E	Ap A2 A3	0-11 11-49 49-75+	Grazing area, *Combretum apiculatum* (50%), *Cynadon dactylon* (90%), few *Grewia flavescens* (50%) and *flava* species (open shrubland)	Poorly drained
Pedon 6	922	22° 32.276'S	27° 10.888'E	Ap Btg	0-10 10-30+	Covered with *Cynadon dactylon*, *Grewia flava* area, grazing area, waterlogged	Poorly drained
Pedon 7	900	22° 32.057'S	27° 11.248'E	A AB Btgb	0-10 10-38 38-50+	Natural land, tall vegetation composition of *Acacia* species and *Colophospermum mopane* (closed shrubland)	Poorly drained
Pedon 8	909	22° 32.162'S	27° 11.023'E	Ap Btg	0-8 8-40+	Near farmland, grazing area, last profile pit, no clear horizon. Boundary water table (40cm), strictly covered with *Cynadon dactylon* (carpet grass).	Poorly drained

3.1

3.2

3.3



3.4

3.5

3.6

3.7

Figures 3.1 – 3.7: The studied pedons

Structure also varied within the pedons. Soil in the lower horizons had stronger structure than the overlying soils. Generally, most horizons in control soils had fewer roots compared to treated wastewater affected soils. Soil consistence in control soils varied from loose to very hard in dry state and loose to very friable in moist state. On the other hand, in treated wastewater affected soils, consistence varied from slightly hard to very hard in dry state and friable to very friable in moist state. Cementation was observed in pedon 3 and it had secondary precipitates of carbonate nodules at the 98 cm depth. In pedon 7, round shaped gravel granules were observed from the 0 – 38 cm depth (Table 3.2).

3.3. Laboratory analyses

3.3.1. Physico-chemical properties

Both control and treated wastewater affected soils were mainly sandy to sandy loam in nature (Table 3.4), with particle size distribution for sand in the control soils ranging from 725 – 955 g kg^{-1} while that of treated wastewater affected soils ranged from 725 – 950 g kg^{-1}. Some pedons were predominantly sandy (e.g. pedons 1, 2, 5, 6 and 8) containing sand particles ≥ 800 g kg^{-1} in all horizons. Silt for control soils ranged from 0 – 85 g kg^{-1} relative to treated wastewater affected soils of range from 10 – 45 g kg^{-1}. Furthermore, clay particle distribution ranged from 40 – 190 g kg^{-1} for control soils whereas in treated wastewater affected soils it ranged from 40 – 230 g kg^{-1}. There were no significant differences ($p > 0.05$) in means of sand, silt and clay contents between the drainage classes (Table 3.5). An increased mean clay content of 172.5 g kg^{-1} was evident in pedon 3 for the control soil which was slightly higher compared to any of those pedons in both drainage classes. Generally, particle size distribution seemed to fluctuate with varying soil depths throughout all pedons.

There were no statistical differences in mean P levels ($p > 0.05$) between the drainage classes (Table 3.5). The Phosphorus (P) content of the soils showed more remarkable variations within profiles than across profiles. In all the soils, top horizons (A) had higher contents of P than the underlying horizons – a trend similar to that of organic matter contents. For EC, there were statistical differences in means between the two drainage classes ($p < 0.05$) (Table 3.5). Treated wastewater affected soils had slightly higher mean EC values. On another note, both classes had statistically similar mean OM contents ($p > 0.05$), with means for studied pedons ranging from 0.84 – 3.71 %.

Table 3.4: Selected physico-chemical properties of control and treated wastewater affected soils

Pedon	Horizon	Depth (cm)	Sand	Silt	Clay	Texture (IUSS)	Phosphorus (ppm)	EC ($dS.m^{-1}$)	OM (%)	CEC (meq/100g)	pH	
			-------<2mm, (g kg^{-1})--------								H_2O	$CaCl_2$
						Control pedons						
Pedon 1	A1	0-13	955	5	40	Sand	8.54	0.10	1.03	0.24	6.78	6.00
	A2	13-30	905	25	70	Sand	0.67	0.07	0.90	0.24	6.06	5.42
	A3	30-54	910	20	70	Sand	0.53	0.10	0.81	0.29	6.39	5.66
	AB	54-91	915	5	80	Sand	0.47	0.10	0.90	0.31	6.98	6.12
	B1	91-154	915	5	80	Sand	0.93	0.09	0.84	0.30	6.73	5.34
	B2	154-170^{+}	895	15	90	Sand	7.84	0.12	1.11	0.29	6.71	6.40
Pedon 2	A1	0-7	925	25	50	Sand	7.00	0.19	1.29	0.39	7.26	6.50
	A2	7 - 35	920	20	60	Sand	1.60	0.11	0.68	0.32	6.72	6.58
	AB	35-70	905	35	60	Sand	1.40	0.13	0.72	0.33	6.87	6.55
	B1	70-96	935	5	60	Sand	1.00	0.15	0.71	0.40	6.85	6.24
	B2	96-108	920	10	70	Sand	0.73	0.12	0.84	0.27	7.06	6.40
	B3	108-143	925	5	70	Sand	1.27	0.14	0.82	0.23	7.28	6.58
	B4	143-160^{+}	930	0	70	Sand	1.00	0.15	0.82	0.24	7.22	6.48
Pedon 3	A	0-8	725	85	190	Sandy loam	6.65	0.32	4.75	1.93	7.53	6.55
	AB	8 - 22	800	50	150	Sandy loam	0.93	0.25	3.32	1.11	7.58	6.79
	B1	22-74	790	30	180	Sandy loam	1.20	0.27	3.60	0.58	7.38	6.61
	Bk	74-98^{+}	805	25	170	Sandy loam	0.60	0.26	3.17	0.67	7.69	6.54
Pedon 4	A1	0-11	920	20	60	Sand	7.63	0.12	1.51	0.60	6.92	6.21
	A2	11-40	855	55	90	Loamy sand	1.07	0.08	1.01	0.51	6.22	4.99

	AB	40-61	900	20	80	Sand	0.87	0.08	1.09	0.48	6.05	4.75
	B1	61-98	860	10	130	Loamy sand	0.53	0.06	1.20	0.52	6.12	4.64
	B2	98-130$^+$	870	0	130	Loamy sand	0.60	0.08	1.47	0.54	5.50	4.53
						Treated wastewater affected pedons						
Pedon 5	Ap	0-11	950	10	40	Sand	1.80	0.74	2.41	1.73	7.14	6.47
	A2	11-49	900	30	70	Sand	1.27	0.19	0.88	0.66	7.24	6.64
	A3	49-75$^+$	890	30	80	Sand	1.13	0.20	0.79	0.64	7.45	6.35
Pedon 6	Ap	0-10	930	20	50	Sand	6.37	2.23	2.25	8.14	8.66	7.67
	Btg	10-30$^+$	910	20	70	Sand	1.20	0.22	1.04	0.98	7.32	6.60
Pedon 7	A	0-10	885	25	90	Sand	12.60	0.28	2.39	1.36	7.39	6.73
	AB	10-38	910	20	70	Sand	3.08	0.20	1.10	0.76	7.65	7.50
	Btgb	38-50$^+$	725	45	230	Sandy clay loam	0.47	0.31	4.33	1.86	7.52	7.04
Pedon 8	Ap	0-8	875	35	90	Sand	3.01	0.98	2.83	5.01	7.82	6.99
	Btg	8-40$^+$	875	35	90	Sand	0.67	0.22	1.26	1.22	7.55	6.66

Table 3.5: Summary average levels for physico-chemical properties per drainage class

Drainage class	Sand	Silt	Clay	Phosphorus	EC	OM	CEC	pH (H_2O)	pH ($CaCl_2$)
	---------------------g kg^{-1}---------------------			(ppm)	(dS.m^{-1})	(%)	(meq/100g)		
Somewhat excessively drained	885.45a	21.36a	93.18a	2.41a	0.14a	1.48a	0.49a	6.81a	5.99a
Poorly drained	885.00a	27.00a	88.00a	3.16a	0.56b	1.93a	2.24b	7.57b	6.87b

There is no significant difference between mean values in a column with a similar letter (t-test, $\alpha = 0.05$).

Organic matter was highest in pedon 3. There were statistical differences in mean CEC levels between the two drainage classes ($p < 0.05$) (Table 3.5). Cation exchange capacity (CEC) levels in both control and treated wastewater affected soils were relatively low, 0.23 – 1.93 meq/100g and 0.64 – 8.14 meq/100g respectively. Meanwhile, there were statistical differences between mean soil pH in both media (water and $CaCl_2$ and water) ($p > 0.05$) (Table 3.5). Bulk density (BD) was assessed for treated wastewater affected soils alone. The results also show that sandy soils had higher BD than sandy clay loam soils (Table 3.6).

3.3.2. Geochemistry

3.3.2.1 Heavy metal (HMs) concentrations

As a trend for both drainage classes, mean concentration levels showed a decreasing order from Fe > Mn > Zn > Cu > Pb > U respectively. Control soils had higher mean concentration levels of Fe and Cu (9756.77 and 8.59 ppm respectively) than treated wastewater affected soils (9367.40 and 7.58 ppm respectively) (Table 3.7 and 3.8). The study showed no significant differences between mean soil HM concentration levels of Fe, Cu, Zn, Mn, Pb and U in both drainage classes ($p > 0.05$) (Table 3.9).

Table 3.6: Bulk density determination for treated wastewater affected soils

Pedon	Geographic location		Horizon	Depth (cm)	STC (IUSS)	Soil BD (g/cm^3)	GWC (θg)	VWC (θ)	Porosity (ϕ)	Effective saturation (Se)	Inches of water/ft soil
	Latitude	Longitude									
Pedon 5	22° 32.248'S	27° 10.563'E	Ap	0-11	Sa	1.75	0.18	0.31	0.34	0.91	3.71
			A2	11-49	Sa	1.76	0.27	0.48	0.33	1.44	5.77
			A3	49-75$^+$	Sa	1.70	0.35	0.59	0.36	1.64	7.04
			Mean			1.74	0.27	0.46	0.34	1.33	5.51
Pedon 6	22° 32.276'S	27° 10.888'E	Ap	0-10	Sa	1.91	0.23	0.44	0.28	1.56	5.22
			Btg	10-30$^+$	Sa	1.79	0.19	0.34	0.33	1.05	4.10
			Mean			1.85	0.21	0.39	0.31	1.31	4.66
Pedon 7	22° 32.057'S	27° 11.248'E	Btgb	38-50$^+$	Sa.cl.lo	1.48	0.84	1.24	0.44	2.81	14.87
			Mean			1.48	0.84	1.24	0.44	2.81	14.87
Pedon 8	22° 32.162'S	27° 11.023'E	Ap	0-8	Sa	1.84	0.10	0.18	0.30	0.58	2.11
			Btg	8-40$^+$	Sa	1.77	0.28	0.49	0.33	1.48	5.91
			Mean			1.81	0.19	0.34	0.32	1.03	4.01

STC: Soil textural class; BD: Bulk density, Sa: Sand, Sa.cl.lo: Sandy clay loam; GWC: Gravimetric water content; VWC: Volumetric water content

Table 3.7: Heavy metal concentrations in control pedons

Control pedons								
Pedon	Depth (cm)	Fe	Cu	Zn	As	Mn	Pb	U
		ppm						
Profile 1								
A1	0-13	5594	nd	5.9	nd	48	5.9	nd
A2	13-30	6963	nd	6.8	nd	132	5.7	nd
A3	30-54	7668	nd	4.7	nd	75	6.7	nd
AB	54-91	8390	5.7	6.5	nd	78	7.2	nd
B1	91-154	8583	5.5	5.4	nd	76	6.6	nd
B2	154-170^{+}	9387	nd	7.2	nd	71	8.3	nd
Profile 2								
A1	0-7	5738	5.7	5.2	nd	65	7.2	nd
A2	7-35	6363	nd	6.7	nd	77	6.5	4
AB	35-70	6903	nd	6.2	nd	74	5.2	nd
B1	70-96	6673	6.3	5.1	nd	58	5.4	nd
B2	96-108	8416	nd	6.9	nd	70	6.3	nd
B3	108-143	7822	7.1	7.3	nd	60	7.8	nd
B4	143-160^{+}	8445	6.5	7.4	nd	69	5.6	nd
Profile 3								
A	0-8	21800	20	28.2	nd	395	6.9	nd
AB	8-22	14451	11	17.1	nd	252	5.5	nd
B1	22-74	14908	10.7	15.4	nd	264	6.1	nd
Bk	74-98^{+}	13634	9.9	15.4	nd	245	7.5	nd
Profile 4								
A1	0-11	9747	nd	9.6	nd	184	7.6	nd
A2	11-40	7488	6.8	6.9	nd	122	8	nd
AB	40-61	9508	nd	8	nd	80	8.5	nd
B1	61-98	11896	nd	9.4	nd	76	6.6	4.5
B2	98-130^{+}	14272	7.9	10.4	nd	87	7.8	4.6
Thresholds								
Mean	-	9756.77	8.59	9.17	nd	120.82	6.77	4.37
Local Parent Material	-	41314	nd	399	6.7	171	nd	10
Global concentration in soils[#]	-	35000	14	30-100	<0.1-67	10-9000	27	<0.4-96
Upper continental crust*	-	30890	25	71	2	600	20	2.8

nd: no data; *GERM Reservoir database, (2017); [#] Kabata-Pendias and Szteke, (2015)

Table 3.8: Heavy metal concentrations in treated wastewater affected pedons

Treated wastewater affected pedons								
Pedon	Depth (cm)	Fe	Cu	Zn	As	Mn	Pb	U
		-----	-----	-----	ppm	-----	-----	-----
Profile 5								
Ap	0-11	5569	nd	4.6	nd	88	5.9	nd
A2	11-49	6392	nd	5.2	nd	71	7.5	nd
A3	49-75+	7584	nd	7.8	nd	60	5.7	nd
Profile 6								
Ap	0-10	7075	7.2	8	nd	132	6	4.6
Btg	10-30+	7054	nd	6.7	nd	79	8.6	nd
Profile 7								
A	0-10	9895	8.4	12.3	nd	264	8.6	nd
AB	10-38	5945	nd	7.8	nd	141	7.9	nd
Btgb	38-50+	22433	7	24.3	3	411	7.1	6
Profile 8								
Ap	0-8	10444	7.7	8.9	nd	245	10.8	nd
Btg	8-40+	11283	nd	9.1	nd	239	7.5	nd
Thresholds								
Mean	-	9367.4	7.6	9.5	3.0	173.0	7.6	5.3
Local Parent Material	-	41314	nd	399	6.7	171	nd	10
Global concentrations in soils#	-	35000	14	30-100	<0.1-67	10-9000	27	<0.4-96
Upper continental crust*	-	30890	25	71	2	600	20	2.8

nd: no data; *GERM Reservoir database, (2017); # Kabata-Pendias and Szteke, (2015)

Table 3.9: Mean heavy metal concentration levels per drainage class

Drainage class	Fe	Cu	Zn	As	Mn	Pb	U
	-----	-----	-----	ppm	-----	-----	-----
Somewhat excessively drained	9756.77a	8.59a	9.17a	-	120.80a	6.77a	4.37a
Poorly drained	9367.40a	7.58a	9.47a	-	173.00a	7.56a	5.30a

Mean Arsenic (As) levels could not be computed virtually because of shortage of data entries. There is no significant difference between mean values in a column with a similar letter (t-test, $\alpha = 0.05$).

Treated wastewater affected soils on the other hand had slightly higher mean concentration levels of Zn, Mn, Pb and U compared to control soils. Generally, most mean HM concentration levels in control soils were within various thresholds (e.g. local parent material, global concentration in soils and the upper continental crust) except for mean U concentration level relative to the upper continental crust (Table 3.7). Similarly, mean HM concentration levels in treated wastewater affected soils were within thresholds except mean Mn relative to the local parent material as well as mean levels for As and U against the upper continental crust (Table 3.8).

In pedons 2 and 4 particularly horizons (A2) and (B1, B2) respectively there were traces of U though averagely their concentration levels were lower by at least half of the mean for the local parent material. The same was observed for pedon 6 (Ap) and pedon 7 (Btgb) with reference to means for As and U. Their mean concentration levels were lower by almost half when compared to individual mean levels in the local parent material. Generally, pedon 3 compared to other pedons showed relatively high concentration levels of Fe ranging from 13634 – 21800 ppm for all its horizons. Moreover, pedon 3 had the highest mean concentration levels of Cu (12.90 ppm), Zn (19.03 ppm), Mn (289.00 ppm) as well as mean clay content (172.50 g kg^{-1}) of all pedons studied. Pedon 7 had the highest mean concentration levels of As and U than all other pedons (3.00 ppm and 6.00 respectively). Lead (Pb) was measured at the highest concentration level in pedon 8 (9.15 ppm).

3.3.2.2. Geochemical mass-balance

In the study, geochemical mass balance plots for selected profiles (Fig. 3.8 a-d and Fig. 3.9 a-b) show Zn maintained an almost constant trend while fluctuations were observed for Fe and Mn at various depths. In the control channel, Zn displayed neither increase nor decrease throughout the profiles and this was similarly observed in the treated wastewater channel. A repetitive fluctuation was mostly observed for Fe and Mn in control than treated wastewater pedons.

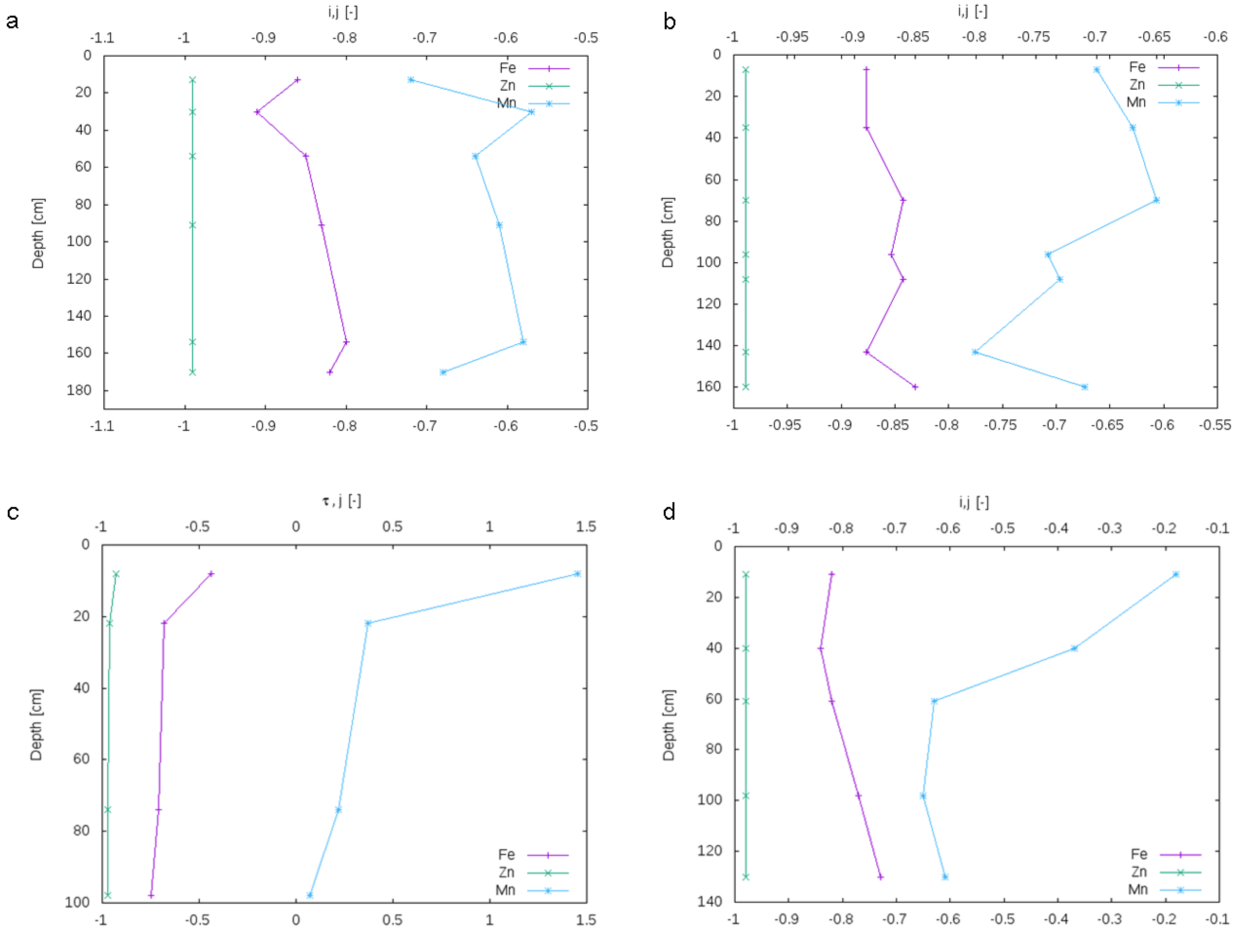


Figure 3.8 a-d: Geochemical mass balance plots for control soils

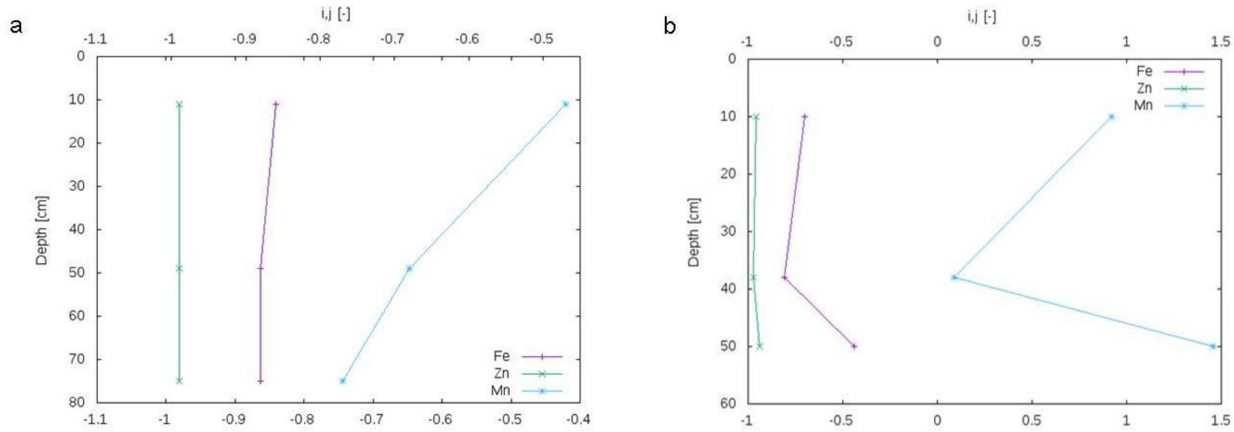


Figure 3.9 a-b: Geochemical mass balance plots for treated wastewater affected soils

3.4. Pollution indices

3.4.1. Enrichment Factor (EF)

The EF values in control soils for Fe were all 1.00, Zn ranged from 0.06 to 0.13, Mn ranged from 1.47 to 4.58 and U ranged from 1.33 to 2.60 (Figs 3.10 and 3.12). Mean EF levels showed decreasing order from 2.83 (Mn) > 1.83 (U) > 1.00 (Fe) > 0.09 (Zn) respectively (Table 3.10). In treated wastewater affected soils, Fe levels were all 1.00, Zn ranged from 0.08 to 0.14, As was 0.82, Mn ranged from 1.91 to 6.45 and U ranged from 1.10 to 2.69 (Figure 3.11 and 3.13). On average the EF values for treated wastewater affected soils decreased from 4.30 (Mn) > 1.90 (U) > 1.00 (Fe) > 0.82 (As) > 0.10 (Zn) respectively (Table 3.10). EF values for Cu, As and U could not be computed in both drainage classes because no data was captured for these individual elements in the parent material. Both figures 3.10 and 3.11 display EF values for control and treated wastewater affected soils in various pedons and horizons studied. The figures also show delineations for various pollution levels measured from severe enrichment (SE), moderate enrichment (ME) and deficient enrichment (DE) respectively.

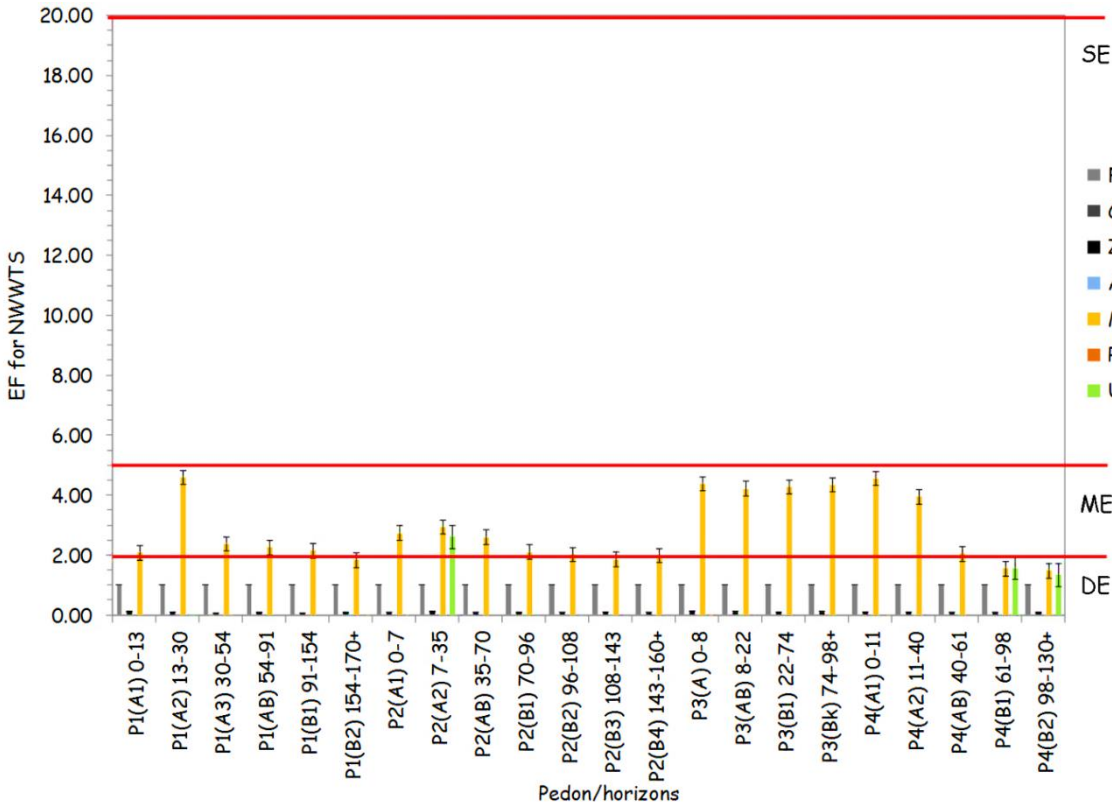


Figure 3.10: EF values for control soils. Abbreviations SE, ME and DE stand for severe enrichment, moderate enrichment and deficient enrichment

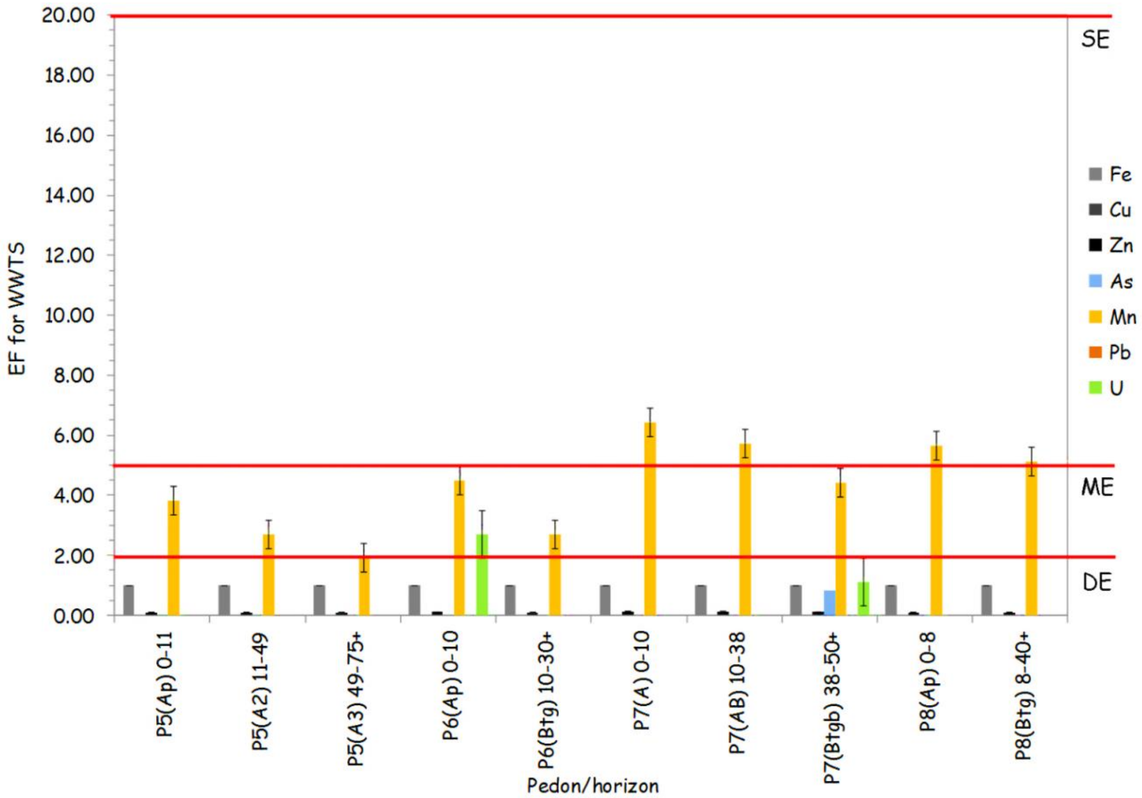


Figure 3.11: EF values for treated wastewater affected soils. Abbreviations SE, ME and DE stand for severe enrichment, moderate enrichment and deficient enrichment

Table 3.10: Mean EF values for both drainage classes

	Control soils							Treated wastewater affected soils						
Heavy metal	Fe	Cu	Zn	As	Mn	Pb	U	Fe	Cu	Zn	As	Mn	Pb	U
Mean	1.00	nd	0.09	nd	2.83	nd	1.83	1.00	nd	0.10	0.82	4.30	nd	1.90

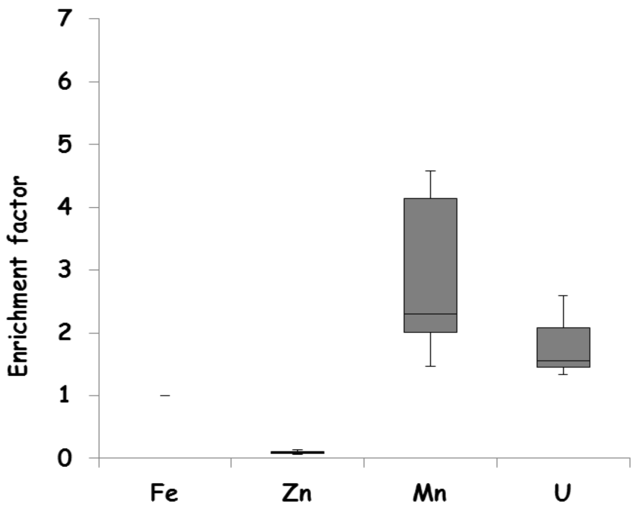


Figure 3.12: Boxplot and whisker for EF values in control soils

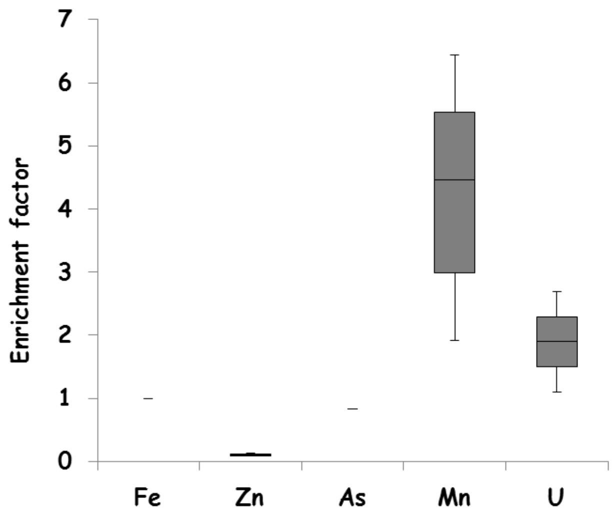


Figure 3.13: Boxplot and whisker for EF values in treated wastewater affected soils

3.4.2. Geo accumulation Index (Igeo)

The Igeo for control soils for Fe ranged from -3.47 to -1.51, Zn from -6.99 to -4.41, Mn from -2.42 to 0.62 and U from -1.91 to -1.71 (Figs 3.14 and 3.16). Mean Igeo values for control soils decreased in order from Mn (-1.36) > U (-1.78) > Fe (-2.76) > Zn (-6.20) respectively (Table 3.11). Alternatively, for treated wastewater affected soils Fe ranged from -3.48 to -1.47, Zn from -7.02 to -4.62, As only -1.74, Mn from -2.10 to 0.68 and U from -1.71 to -1.32 (Figs 3.15 and 3.17). Treated wastewater affected soil mean Igeo levels decreased in order from Mn (-0.85) > U (-1.51) > As (-1.74) > Fe (-2.86) > Zn (-6.14) respectively (Table 3.11).

Based on the Igeo scale (PU: Partially unpolluted, U-MC: Unpolluted to moderately polluted, MC: Moderately polluted, M-SC: Moderately to strongly polluted, SC: Strongly polluted, S-EC: Strongly to extremely polluted and EC: Extremely polluted) all study soils were considered unpolluted (Figs 3.14 and 3.15).

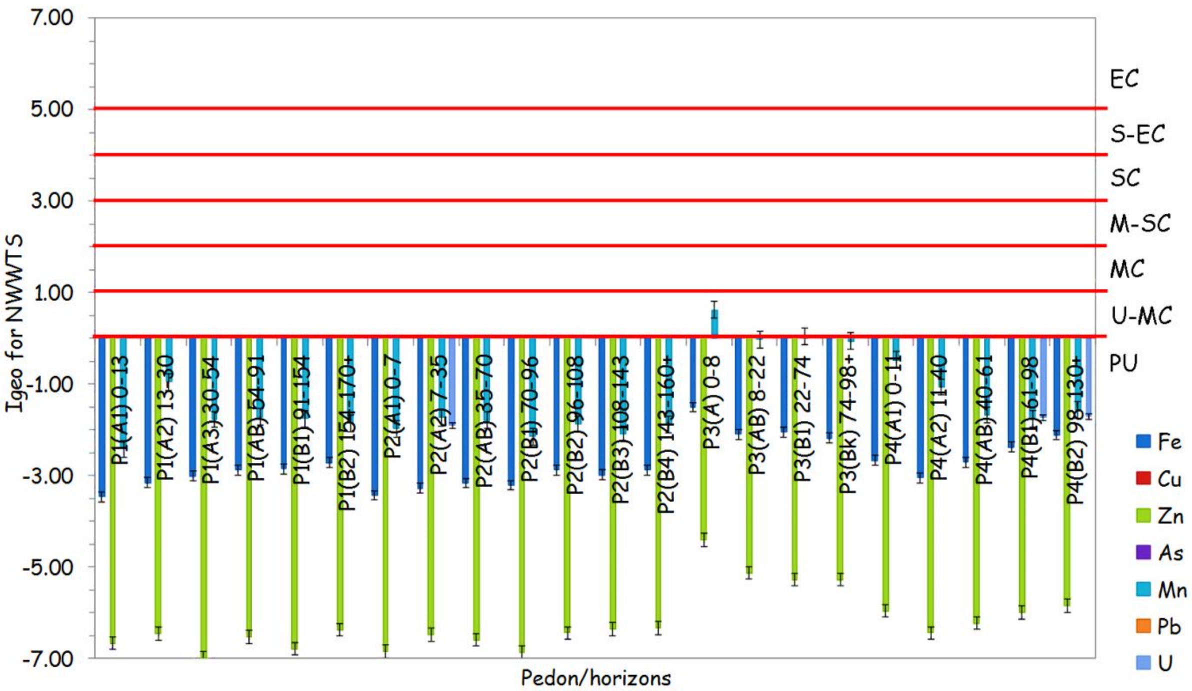


Figure 3.14: Igeo values for control soils. Abbreviations PU: Partially unpolluted, U-MC: Unpolluted to moderately polluted, MC: Moderately polluted, M-SC: Moderately to strongly polluted, SC: Strongly polluted, S-EC: Strongly to extremely polluted and EC: Extremely polluted

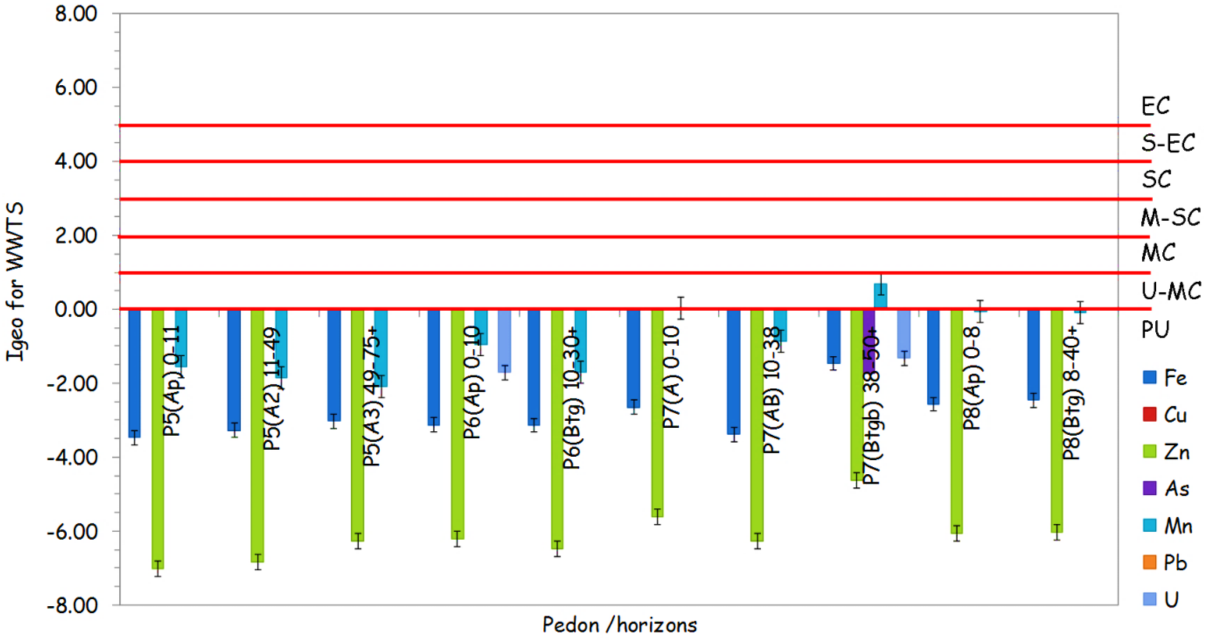


Figure 3.15: Igeo values for treated wastewater affected soils. PU: Partially unpolluted, U-MC: Unpolluted to moderately polluted, MC: Moderately polluted, M-SC: Moderately to strongly polluted, SC: Strongly polluted, S-EC: Strongly to extremely polluted and EC: Extremely polluted

Table 3.11: Mean Igeo values for both drainage classes

	Control soils							Treated wastewater affected soils						
Heavy metal	Fe	Cu	Zn	As	Mn	Pb	U	Fe	Cu	Zn	As	Mn	Pb	U
Mean	-2.76	nd	-6.20	nd	-1.36	nd	-1.78	-2.86	nd	-6.14	-1.74	-0.85	nd	-1.51

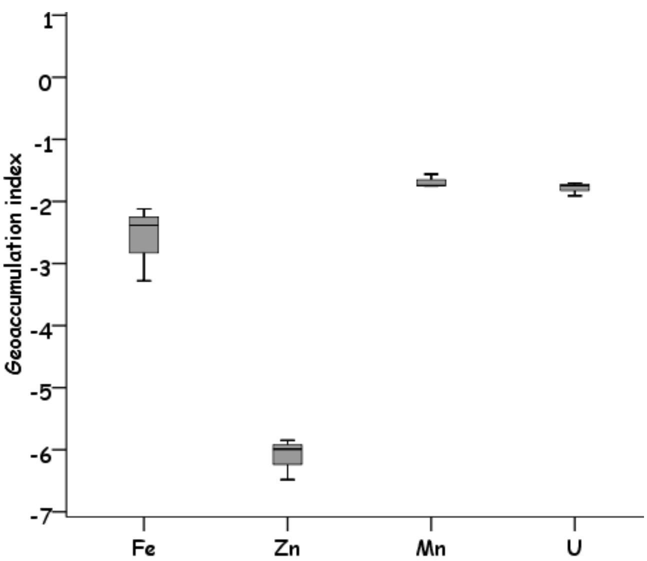


Figure 3.16: Boxplot and whisker for Igeo values in control soils

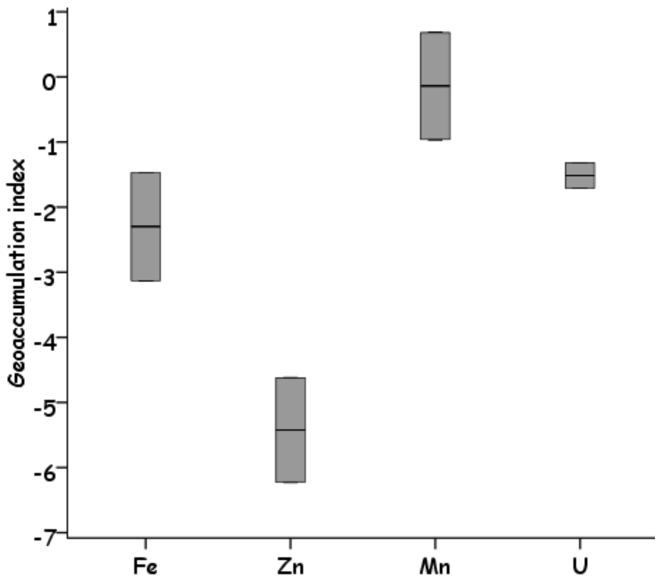


Figure 3.17: Boxplot and whisker for Igeo values in treated wastewater affected soils

3.4.3. Pollution Load Index (PLI)

Pollution load index values for control soils ranged from 0.33 to 0.70 (Figs 3.18 - 3.20) with mean of 0.43 (Table 3.12) while treated wastewater affected soils ranged from 0.35 to 0.58 (Figs 3.19 and 3.20) with mean value of 0.44 (Table 3.12).

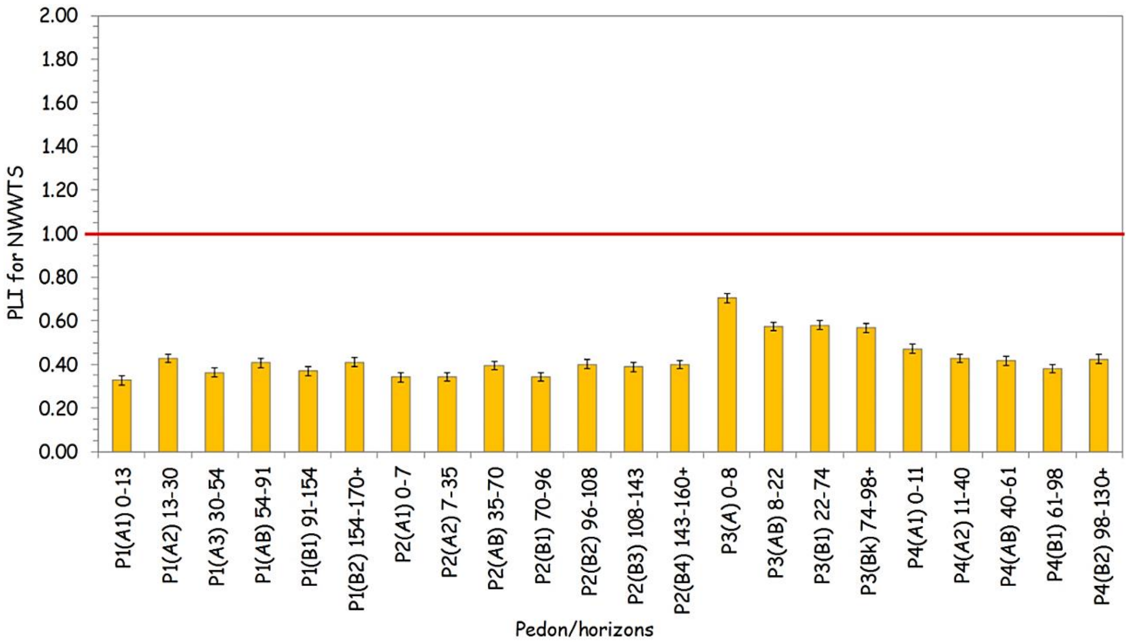


Figure 3.18: PLI values for control soils

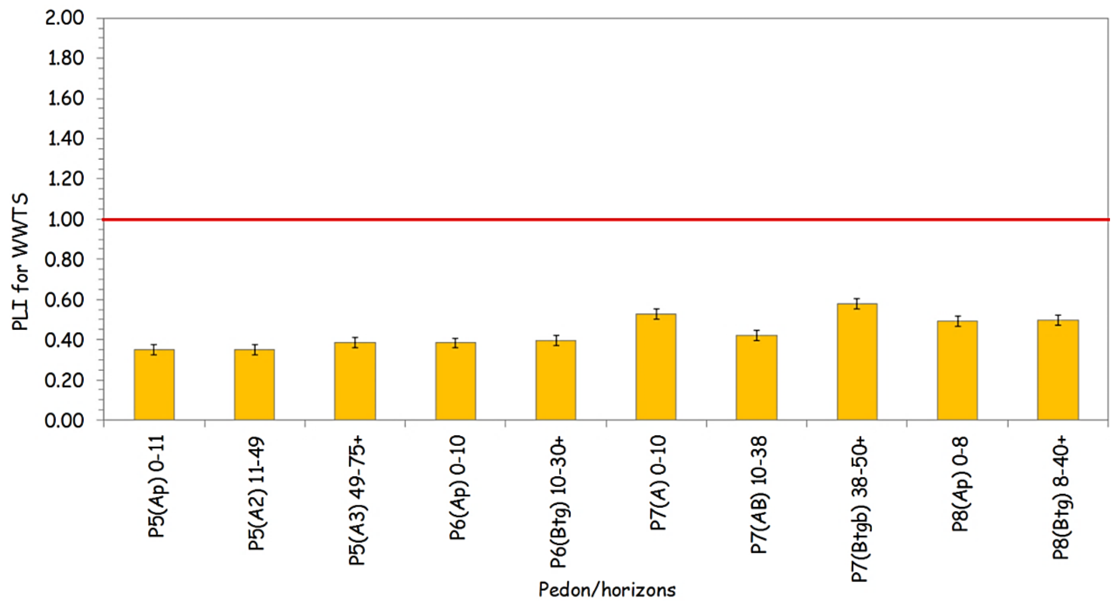


Figure 3.19: PLI values for treated wastewater affected soils

Table 3.12: Mean PLI values for both drainage classes

	Control soils	Treated wastewater affected soils
Mean PLI	0.43	0.44

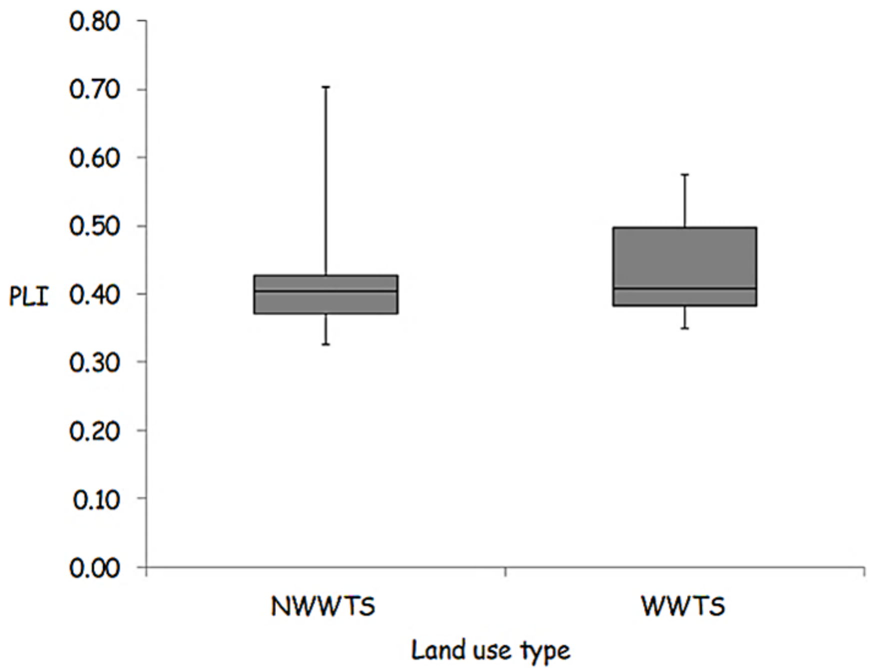


Figure 3.20: Boxplot and whisker for PLI in both drainage classes

3.5 Source apportionment of heavy metals in soils

In this study, PCA was used for source apportionment of heavy metals based on eigenvalue greater than 1. The results conceded a single component (PC1) accounting for 77% of the total variance in control soils. Independently, this component (PC1) explained 77% of the total variance, with positivity relating to Fe, Cu, Zn and Mn (Table 3.13). As for treated wastewater affected soils, two components were extracted of which accounted for 97% of the total variance. The PC1 explained 72% of the total variance, with positivity for Fe, Zn and Mn while PC2 explained only 25% of the total variance, strongly observed for Pb alone.

Table 3.13: Source apportionment of heavy metal contents in control and treated wastewater affected soils

	Initial Eigenvalues			Element	Rotated Component Matrix	
	Total	% Variance	Cumulative %		PC1	PC2
	Total variance explained				Component matrixes	
Control soils						
1	**3.838**	**76.753**	**76.753**	Fe	**0.965**	
2	0.995	19.901	96.654	Cu	**0.979**	
3	0.097	1.941	98.595	Zn	**0.997**	
4	0.064	1.281	99.876	Mn	**0.971**	
5	0.006	0.124	100.000	Pb	-0.103	
Treated wastewater affected soils						
1	**2.880**	**72.005**	**72.005**	Fe	**0.973**	-0.152
2	**1.005**	**25.113**	**97.118**	Zn	**0.964**	-0.205
3	0.078	1.959	99.077	Mn	**0.969**	0.100
4	0.037	0.923	100.000	Pb	0.258	**0.964**

3.6 Hierarchical cluster analysis of heavy metals for both control and treated wastewater affected soils

In the study, agglomeration schedules per drainage class were done using the nearest neighbour cluster method coupled with the Euclidean distance measure. Since HM data were in varying units, thousands, hundreds and tens, the data was initially standardized using the -1 to 1 range. Based on the HCA output for control soils a dendrogram yielded two clusters. One of the clusters showed strong associations between Cu/Mn and Zn/Fe (Figure 3.22). These findings strongly confirmed findings attained through the various control soil correlation matrices (CMs) showing strong positively significant ($p < 0.01$) correlations of 0.932** and 0.943** respectively (Figure 3.24). The second cluster showed a weak association between Pb and other element. As for treated wastewater affected soils, strong associations were observed between Fe/Zn and Fe/Mn (Figure 3.23). For CM results, strong positively significant ($p < 0.01$) correlations between each pair of elements (Fe/Zn and Fe/Mn) were 0.962** and 0.902** respectively (Figure 3.25).

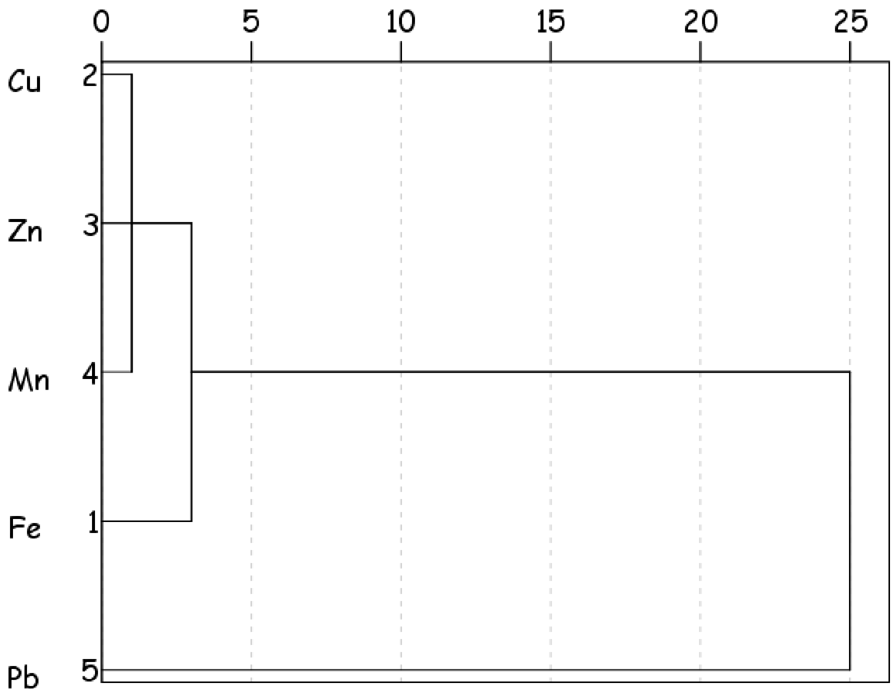


Figure 3.22: Dendrogram output from a hierarchical cluster analysis of heavy metals in control soils

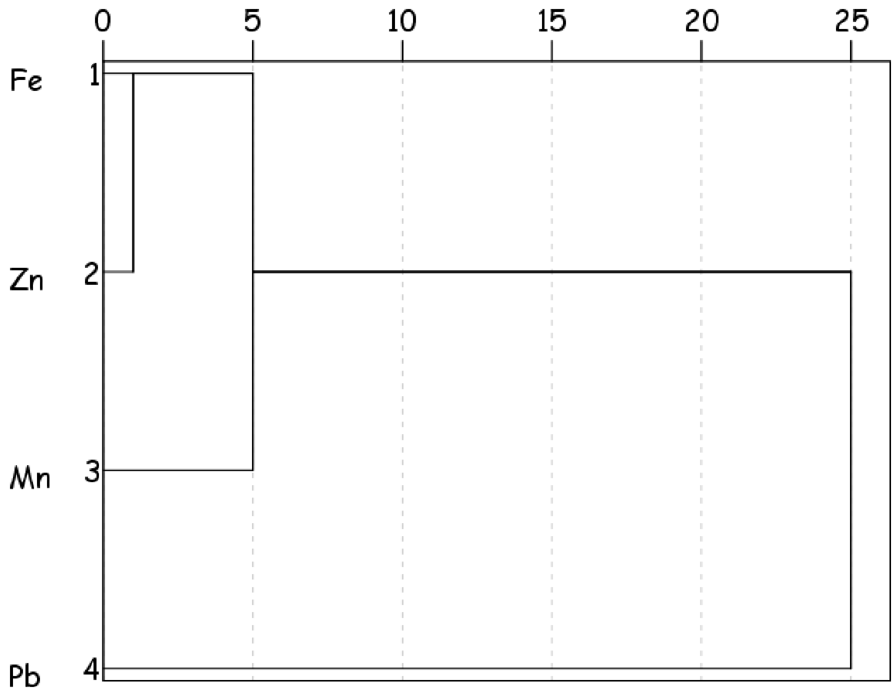


Figure 3.23: Dendrogram output from a hierarchical cluster analysis of heavy metals in treated wastewater affected soils

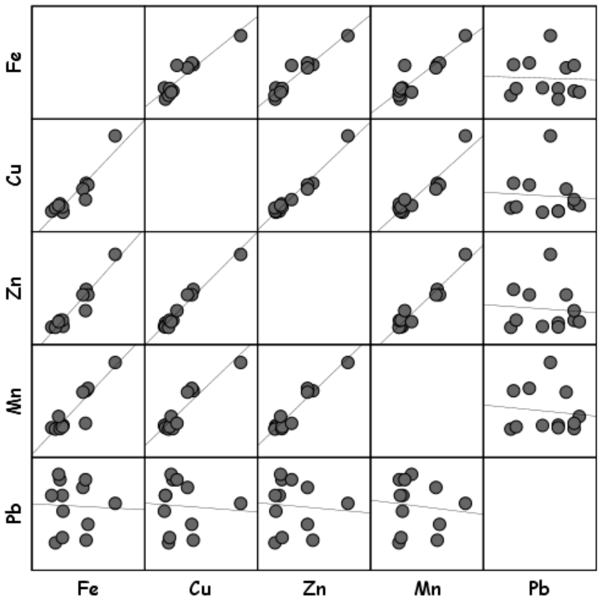


Figure 3.24: Inter – elemental association between HMs in control soils (*Line of best fit passing at or near the origin denotes very good association)

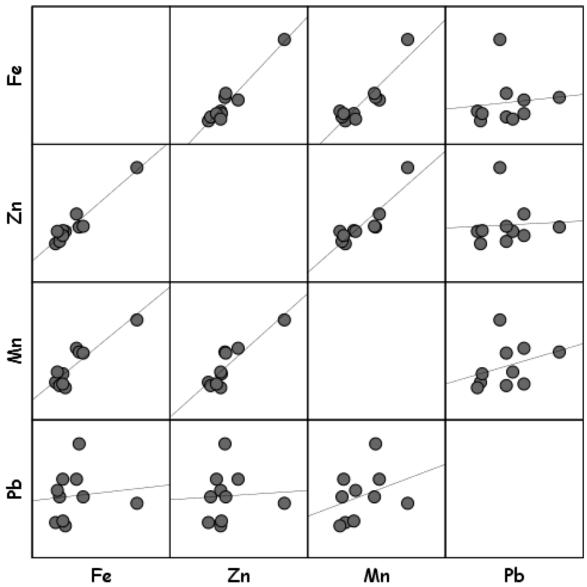


Figure 3.25: Inter – elemental association between HMs in treated wastewater affected soils (*Line of best fit passing at or near the origin denotes very good association)

3.7 Correlation matrix between heavy metals and selected soil parameters for both drainage classes

3.7.1 Organic matter and HMs interactions for both drainage classes

The Table 3.14 shows correlation matrix between OM and HMs in both control and treated wastewater affected soils. There were positively strong correlations between Fe/OM (0.896**), Cu/OM (0.908**), Zn/OM (0.956**) and Mn/OM (0.954**) for control soils. In the case of treated wastewater affected soils strong correlations were noted between Fe/OM (0.765**), Zn/OM (0.770**) and Mn/OM (0.802**).

Table 3.14: Correlation matrix between HMs and OM in control and treated wastewater affected soils

	Fe	Cu	Zn	Mn	Pb	OM
Control soils						
Fe	1.000	0.922**	0.943**	0.852**	0.121	**0.896****
Cu	0.922**	1.000	0.979**	0.932**	-0.067	**0.908****
Zn	0.943**	0.979**	1.000	0.942**	0.019	**0.956****
Mn	0.852**	0.932**	0.942**	1.000	-0.023	**0.954****
Pb	0.121	-0.067	0.019	-0.023	1.000	-0.007
OM	0.896**	0.908**	0.956**	0.954**	-0.007	1.000
Treated wastewater affected soils						
Fe	1.000		0.962**	0.902**	0.111	**0.765****
Zn	0.962**		1.000	0.890**	0.058	**0.770****
Mn	0.902**		0.890**	1.000	0.332	**0.802****
Pb	0.111		0.058	0.332	1.000	0.128
OM	0.765**		0.770**	0.802**	0.128	1.000

**Represents correlation significant at the 0.01 level (2-tailed)

3.7.2 Clay content and HMs interactions for both drainage classes

There were significant positive correlations observed between Fe/clay (0.929**), Cu/clay (0.817**), Zn/clay (0.868**) and Mn/clay (0.821**) in control soils (Table 3.15). Treated wastewater affected soils on the other hand showed strong correlation between Fe/clay (0.973**), Zn/clay (0.962**) and Mn/clay (0.833**). Strong positive correlation between Mn and clay was observed for both drainage classes.

Table 3.15: Correlation matrix between HMs and clay content in control and treated wastewater affected soils

	Fe	Cu	Zn	Mn	Pb	Clay content
Control soils						
Fe	1.000	0.922**	0.943**	0.852**	0.121	**0.929****
Cu	0.922**	1.000	0.979**	0.932**	-0.067	**0.817****
Zn	0.943**	0.979**	1.000	0.942**	0.019	**0.868****
Mn	0.852**	0.932**	0.942**	1.000	-0.023	**0.821****
Pb	0.121	-0.067	0.019	-0.023	1.000	0.089
Clay content	0.929**	0.817**	0.868**	0.821**	0.089	1.000
Treated wastewater affected soils						
Fe	1.000		0.962**	0.902**	0.111	**0.973****
Zn	0.962**		1.000	0.890**	0.058	**0.962****
Mn	0.902**		0.890**	1.000	0.332	**0.833****
Pb	0.111		0.058	0.332	1.000	0.100
Clay content	0.973**		0.962**	0.833**	0.100	1.000

**Represents correlation significant at the 0.01 level (2-tailed)

3.7.3 Potential hydrogen (pH) in H_2O and HMs interactions for both soil drainage classes

There were significant differences observed for mean pH (in both water and $CaCl_2$) among the two drainage classes ($p < 0.05$) respectively. The values for pH (in water) in control and treated wastewater affected soils ranged from 5.50 – 7.69 (moderately acidic – slightly alkaline) and 7.14 – 8.66 (Neutral – strongly alkaline) respectively. For pH (in $CaCl_2$), control soils ranged from 4.53 – 6.79 (very strongly acidic – neutral) while treated wastewater affected soils ranged from 6.35 – 7.67 (slightly acid – slightly alkaline). The only positive interaction observed were between pH (H_2O) with Zn (0.444*) and Mn (0.489*) for control soils (Table 3.16).

Table 3.16: Correlation matrix between HMs and pH (in water) for control and treated wastewater affected soils

	Fe	Cu	Zn	Mn	Pb	pH
Control soils						
Fe	1.000	0.922**	0.943**	0.852**	0.121	0.260
Cu	0.922**	1.000	0.979**	0.932**	-0.067	0.394
Zn	0.943**	0.979**	1.000	0.942**	0.019	**0.444***
Mn	0.852**	0.932**	0.942**	1.000	-0.023	**0.489***
Pb	0.121	-0.067	0.019	-0.023	1.000	-0.258
pH	0.260	0.394	0.444*	0.489*	-0.258	1.000
Treated wastewater affected soils						
Fe	1.000		0.962**	0.902**	0.111	0.006
Zn	0.962**		1.000	0.890**	0.058	0.058
Mn	0.902**		0.890**	1.000	0.332	0.110
Pb	0.111		0.058	0.332	1.000	-0.055
pH	0.006		0.058	0.110	-0.055	1.000

**Represents correlation significant at the 0.01 level (2-tailed); *Represents correlation significant at the 0.05 level (2-tailed)

3.7.4 Electric conductivity (EC) and HMs interactions for both drainage classes

Mean EC levels between drainage classes were significantly different ($p < 0.05$). Study results further established significant interactions ($p < 0.01$) between EC and HMs particularly Fe/EC (0.671**), Cu/EC (0.795**), Zn/EC (0.799**) and Mn/EC (0.815**) in control soils (Table 3.17).

Table 3.17: Correlation matrix between HMs and EC for control and treated wastewater affected soils

	Fe	Cu	Zn	Mn	Pb	EC
Control soils						
Fe	1.000	0.922**	0.943**	0.852**	0.121	**0.671****
Cu	0.922**	1.000	0.979**	0.932**	-0.067	**0.795****
Zn	0.943**	0.979**	1.000	0.942**	0.019	**0.799****
Mn	0.852**	0.932**	0.942**	1.000	-0.023	**0.815****
Pb	0.121	-0.067	0.019	-0.023	1.000	-0.170
EC	0.671**	0.795**	0.799**	0.815**	-0.170	1.000
Treated wastewater affected soils						
Fe	1.000		0.962**	0.902**	0.111	-0.150
Zn	0.962**		1.000	0.890**	0.058	-0.129
Mn	0.902**		0.890**	1.000	0.332	-0.059
Pb	0.111		0.058	0.332	1.000	-0.164
EC	-0.150		-0.129	-0.059	-0.164	1.000

**Represents correlation significant at the 0.01 level (2-tailed)

CHAPTER FOUR

DISCUSSION

4.1. Properties of the treated wastewater

The alkaline pH conditions in the treated wastewater could be attributed to chloride ions sourced from chlorine used to treat the wastewater. Chemical oxidation processes using oxidants including chlorine, chlorine dioxide and ozone have been widely used for wastewater treatment and are effective tools for blocking the release of micropollutants (e.g. pesticides, industrial chemicals, pharmaceuticals and personal care products: PPCPs) and hormones to the aquatic and terrestrial environments (Lee and Gunten, 2010). Biokinetic parameters define the rate of microbial cell growth and substrate consumption and are known to depend on temperature (Sollfrank *et al*., 1992). With a seemingly consistent ambient temperature, biokinetic processes, stoichiometry and the treated wastewater composition would not be affected. According to the Environmental Protection Agency (EPA) (1997), COD for urban wastewater is expected to range from 250 – 800 mg L^{-1} which is slightly higher than study results. On the basis of these low COD levels relative to thresholds by EPA, it can be inferred that there is considerably low amount of oxidizable pollutants in the wastewater discharged from the treatment plant.

In some cases however, the presence of organic molecules (e.g. pyridine and benzene) which are relatively resistant to oxidation may give a falsely low COD. For a more robust assessment of wastewater quality, it is better to use a combination of COD and biological oxygen demand (BOD) data as the latter is capable of measuring all organic contaminants, including those that are not biodegradeable. Various studies ascertain COD to be higher than BOD_5 in treated wastewater (Mekki *et al*., 2016; Bohórquez *et al*., 2017). The colony forming unit of the wastewater were at all times below the WUC threshold of 20000 CFU/100 mL – an indication of a low possible microbiological contamination of the environment by the discharged treated wastewater. All the selected properties assessed in treated wastewater were below the thresholds set by Botswana Water Utilities Corporation (BWUC) which suggests no to low chances of pollutants of biological origin being released into the soil environments.

4.2. Macromorphology and field observations

Depth to water table had a remarkable impact on the soils as the pedons on the treated wastewater channel had shallow depths compared to the control pedons. While the control soils were generally well drained, the soils on the treated wastewater channel had abundant redoximorphic features owing to poor drainage and high water table. Soil colour for horizon Btgb in pedon 7 indicated depletion in oxygen as a result of prolonged waterlogging (Bedard-Haughn, 2011). Hue, Value and Chroma are the three indices used for the description of soil colour. In order of redness, 2.5YR is the strongest, followed by 5YR and lastly 7.5YR. Redness of soils indicates the presence of iron oxides, especially hematite (Schwertmann, 1993). Value shows the degree of lightness/darkness of the soil colour. A Value of 8 is the lightest of any particular soil colour while 1 is the darkest in any given colour spectrum.

Soil structure could be explained in terms of the clay contents which also varied within pedons. The amount and nature of clays have been severally reported to affect soil structure especially when it combines with organic matter to act as cementing agents (Chenu *et al*., 2000; Bronick and Lal, 2005; Rillig and Mummey, 2006). Adequate soil moisture regimes are most likely to account for more roots in the flooded soils. In addition to suitable pH and available nutrients, plant cells require water for survival and optimum physiological performance (Flanagan and Johnson, 2005; Deutsch *et al*., 2010). Organic matter content, particle size distribution and moisture content are factors that mostly affect soil consistence (McNabb *et al*., 2001; Silva *et al*., 2007). Gile *et al*. (1966) reported that, arid regions are common for horizons with authigenic carbonate deposits (Bk horizons) as observed in pedon 3. Furthermore, formation of secondary carbonates in arid and semi-arid environments is strongly linked to soil aggregate dynamics (Bronick and Lal, 2005). Evidence of pebbles in pedon 7 suggested these were transported from elsewhere more so as this particular pedon was located on the lower part of the terrain when compared to others in the same soil drainage class. Slope and climatic factors including rainfall have huge impacts on the depositional characteristics of rock fragments (Wieczorek and Glade, 2005).

4.3. Physico-chemical properties

The nature of the parent material had strong influence in the texture of the soils. As have been reported in many environments with similar parent material, sandstone undergoes weathering to produce soils that are predominantly sandy (Pettijohn *et al*., 2012; Eze and Meadows, 2014). Illuviation of clays could possibly account for the outlier as observed in Pedon 3 which is much in agreement with the reported ability of clay illuviation to affect soil profile texture (Pal *et al*., 2003; Phillips, 2007). Moreover, pedon 3 relative to other pedons evidently contained higher amounts of OM (3.71%) which is expected to improve the overall soil structure (Six et al., 2000; Bot and Benites, 2005). Soil organic matter loading is usually shown by a much darker colour than soils with less organic matter content. This pedogenic process is termed as “melanisation”, an occurrence resulting from additional of humus.

Phosphorus is strongly tied to clay minerals as inorganic P and organic matter in the form of organic P (Kronvang, 1992). Organic P therefore accounts for higher P contents in the topsoils than subsoils which is evident in the study. Phosphorus content below 10 ppm is generally considered low in soils (Tree Fruit Research and Extension Center, 2004). Most soils had low P level except for Pedon 7 (with the highest P of 12.60 ppm). The treated wastewater affected soils had more P contents than control soils because usually wastewater tend to carry organic residues which could contribute to increased P content in soils. The form as well as availability of P in soils is strongly dependant on soil pH. Slightly higher pH (alkaline) conditions anticipated for treated wastewater affected soils could result in more water-soluble forms of P due to reactions with Ca^{2+} ions in soils. Meanwhile this is unexpected at lower pH soils where P reacts mostly with Al^{3+} ions to form less water-soluble salts which are usually unavailable for plants. Generally, study P levels were incapable of causing any detrimental problems such as water eutrophication in the environment. Degree of weathering and erosion, nature of parent material, climate, crop removal and fertilization are factors that affect P availability in soils. Only the topsoil of pedon 7 had optimal P content the rest were low which could be attributed to the nature of the parent material and crop removal.

With EC contents below 1.2 dS/m in all the soils, they can be described as low in salinity and less likely to have soluble salt related problems in accordance to Hach Company guideline (1992). The soils also had low organic matter content which could be attributed to poor vegetation, typical of arid and semi-arid environments (Aranda *et al*., 2011). Low rainfall, low nutrient status (CEC) (as shown in this study) and high rate of mineralisation hinder biomass production and accumulation in soils. Although generally low in both drainage classes, CEC levels in treated wastewater affected soils were fairly higher than in control soils (e.g. mean CEC for pedon 6 and 8) attributed to the existing alkaline conditions. High pH levels force the negatively charged hydroxide (OH^-) ions to displace hydrogen (H^+) ions from existing hydroxide groups of clay minerals thus concentrating mostly the negatively charged OH^- ions. These negatively charged conditions then elevate CEC levels in soils.

Cation exchange capacity of soils infers its ability to retain nutrients at the exchange surface of soil colloids and depends on organic matter, type and quantity of clay minerals (Thomas *et al*., 2007). In view of this, CEC is then used to tell a story of soil clay mineralogy and OM content. With CEC of less than 10 meq/100g, it can be inferred that the soils are dominantly rich in kaolinite ($Al_2Si_2O_5(OH)_4$), a 1:1 clay mineral consistent with very low clay and OM contents (i.e. 40 – 230 g kg^{-1} and 0.68 – 4.75% for this study) (Schaetzl and Anderson, 2005; White, 2006). Kaolinites have low CEC (Ma and Eggleton, 1999). Moreover, it is noted that pedotransfer functions have successfully established a strong correlation between CEC and clay mineralogy (Lambooy, 1984).

The dry water status of the control soils coupled with their sandy nature made collection of undisturbed core samplers impossible for BD determination. Studies by Schaetzl and Anderson, (2005); Montagne *et al*., (2009); Kumar *et al*., (2014) established that high soil BD equates to low soil porosity and vice versa and this is in agreement with the study results. Soils with high OM are associated with low BD because of the high microbial activity which facilitates pore formation in soils (Schaetzl and Anderson, 2005). This may well explain why pedon 7 had the least BD (1.48), the highest porosity (0.44), effective saturation (2.81) and inches of water per feet of soil (14.87) respectively. Schaetzl and Anderson (2005) opine that BD in natural soils increases with sampling depth due to lower organic matter contents in lower horizons. However, study results conversely showed Ap horizons of pedon 6 and 8 to have higher BD than lower horizons, an occurrence assumed from effects of high waterlogging in lower horizons due to rapid infiltration of treated wastewater. It is probable that treated wastewater eventually creates pore spaces in soils that contribute to lower BD measures. Soils BD for selected pedons are shown in Table 4.1.

Table 4.1: Summary soil bulk densities for treated wastewater affected soils

Pedon	Horizon	Depth (cm)	STC (IUSS)	Soil BD (g/cm^3)
Pedon 5	Ap	0-11	Sa	1.75
	A2	11-49	Sa	1.76
	A3	$49\text{-}75^+$	Sa	1.70
Pedon 6	Ap	0-10	Sa	1.91
	Btg	$10\text{-}30^+$	Sa	1.79
Pedon 7	Btgb	$38\text{-}50^+$	Sa.cl.lo	1.48
Pedon 8	Ap	0-8	Sa	1.84
	Btg	$8\text{-}40^+$	Sa	1.77

STC: Soil textural class; BD: Bulk density, Sa: Sand, Sa.cl.lo: Sandy clay loam

4.4. Heavy metal (HMs) concentrations

The occurrence of soil Fe and Cu is predominantly influenced by various soil activities along with the parent material (Kabata-Pendias and Pendias, 2001). Treated wastewater affected soils because of their slightly higher mean organic matter (OM) content (1.93%) than control soils (1.48%) could have somewhat increased Fe and Cu fixation (chelation) (Ponizovsky *et al*., 2006; Lindsay, 1991) causing their rapid migration and transportation in these soils. This may well explain why low mean concentration levels of Fe and Cu are observed for treated wastewater affected than control soils. Both elements are highly available in the slightly acid conditions of the control soils than the slightly alkaline ones for the treated wastewater affected soils.. In the study, HM concentrations were not assessed in the treated wastewater, but treated wastewater has been reported to contain heavy metals including Pb, Cr, Ni, Zn, Cu, Hg, Cd and Ni (Meng, 2006) which might have been retained after treatment. Though not proven in the study, it was assumed that the slightly higher mean concentration levels observed in treated wastewater affected soils than the other drainage class may have been due to the wastewater. A 2 ppm mean difference between Mn in treated wastewater affected soils and the local parent material may suggest some level of Mn enrichment, though necessary to confirm whether it depicts pollution or not.

High Fe levels in pedon 3 could possibly be tied to the levels of OM content (3.17 – 4.75%) contained in these horizons which may have caused Fe to take up a chelated form (Lindsay, 1991). Heavy metals tend to have strong affiliation with inorganic colloids like clay minerals (Bradl, 2004) thus explain why pedon 3 had the highest mean concentration levels of Cu, Zn and Mn. Pedon 7 compared to other pedons of the same drainage class was located at lower end of nearly flat terrain suggesting possible deposition and transportation of these HMs. According to Du Laing *et al*., (2009) topography greatly influences the amount and bioavailability of HMs in soils due to effects of runoff, infiltration and leaching. Pedon 8 in particular, was closest to farmlands where Pb based fertilisers, lime and agrochemical applications are used on a routine basis. Agricultural practices are known to elevate the levels of various HMs in agricultural soils (Udeigwe *et al*., 2011).

4.5. Geochemical mass-balance

Elemental redistribution in soils follows pedogenic and or chemical weathering processes. In the case of control soils, pH < 7 postulated a possible reduction in adsorption of Zn^{2+} ions likely to facilitate mobility and leaching of Zn in the soil (Kabata-Pendias and Pendias, 2001). This explains why Zn seemed to maintain a constant trend throughout selected control soil profiles. The only explanation given for selected profiles in the treated wastewater channel may be that Zn was at equilibrium throughout the horizons. Elements including As, Cu, U and Pb were not displayed because they occurred haphazardly in just two profiles. Bai *et al*., (2011) reported factors like OM, soil texture, pH and CEC to affect the mobility of elements in soils. For Fe and Mn, positive correlation between these respective elements with OM in both drainage classes may explain the various fluctuations observed within different pedons. Supposedly, transport of heavy metals of geogenic and/or anthropogenic origin from dissolution by treated wastewater is responsible for heavy metals redistribution in the soils

4.6. Pollution indices

The results show that control soils were moderately enriched while in treated wastewater affected soils there was severe enrichment of Mn in pedons 7 and 8 (5.12 – 6.45) assumed from the discharged treated wastewater. Although EF values for Mn showed severe enrichment for some treated wastewater affected soils, Mn speciation and bio-accessibility by plants, rather than simply total concentrations, have to be further established so as to ascertain possibility of pollution occurrence allied to treated wastewater. As per the Igeo and PLI scales, study soils were considered unpolluted. Generally, study EF and Igeo values are in comparison similar to those assessed by Banerjee and Gupta (2017) for agricultural soils irrigated with untreated industrial wastewater.

4.7 Source apportionment of heavy metals in soils

Several studies have widely used multivariate approaches including the Principal Component Analysis (PCA) and Correlation Matrix (CM) in order to apportion sources of environmental heavy metal pollution (Chabukdhara *et al*., 2016; da Silva, *et al*., 2016; Aminiyan *et al*., 2017). For PC1, there were positively significant correlations between Fe/Cu (0.922**), Fe/Zn (0.943**) together with Fe/Mn (0.852**) in control soils which could be of geogenic origin. Iron is one of the most common elements in the parent material (Qiutong and Mingkui, 2017) thus strong interaction between it with other elements would presume these particular elements to be of geogenic origin. Moreover, treated wastewater affected soils suggested the same, with positively significant correlations observed between Fe/Zn (0.962**) and Fe/Mn (0.902**) for PC1.

However, an interesting observation showing no correlation whatsoever between Fe/Pb (0.111) for PC2 in wastewater treated soils could be of anthropogenic origin. Sources of Pb in the environment are mainly tied to natural erosion and nonpoint origin (e.g. agricultural pollution). Some of these sources include fertilizers, manure, sewage sludge (biosolids), sewage effluents, pesticides, vehicular exhausts and industrial fumes (Bradl, 2005). As is the case in this study, cattle manure/dung was the only possible culprit to be the source of Pb levels observed in wastewater affected soils. These animals directly drink treated wastewater released near the plant as well as forage around the study area (Fig. 4.1). Most likely some traces of Pb may be continuously introduced in their diets during feeding and drinking. According to Eneji *et al*., (2003), Leclerc and Laurent, (2017), Yang *et al*., (2017a) cattle manure has been found to contain notable amount of accumulated heavy metals resulting from unmonitored incorporation of metals in their diets. So possibly it may explain why Pb levels were associated with the anthropogenic influence as presumed from retention in the treated wastewater.

Figure 4.1: Cattle grazing activities in the treated wastewater affected channel (highlighted in yellow)

4.8 Hierarchical cluster analysis of heavy metals for both control and treated wastewater affected soils

A Hierarchical Cluster Analysis (HCA) has been widely used to ascertain results obtained from a Principal Component Analysis (PCA) (Asaduzzaman *et al*., 2017; Beattie *et al*., 2017; Li *et al*., 2017; Ebqa'ai and Ibrahim, 2017). Reflecting on the results for the first cluster in control soils, a strong affiliation between Cu and Mn tied both elements to a common source while Zn and Fe indicated both elements are of geogenic origin more so that Fe is common in the parent material (Qiutong and Mingkui, 2017). Strong affinity for Fe by both Zn and Mn in treated wastewater affected soils discriminated these elements to geogenic sources whereas weak association between Pb and Fe suggested it to be of anthropogenic origin.

4.9 Correlation matrix (CM) between heavy metals and selected soil parameters for soil drainage classes

According to Tipping, (2002), OM is confirmed to have a binding effect on most substances in soils especially multi-charged elements like Fe^{3+} and Al^{3+} which is in agreement with the study results. Charged minerals of Fe and Al (e.g. Fe hydroxide or Fe oxides) facilitate the adsorption of OM in soils (Feng *et al*., 2005; Sodano *et al*., 2016). Yet again OM has a significant influence on the formation of Fe oxides (Zhu *et al*., 2010). This is mainly facilitated by existing attractions between positively charged surface groups of Fe oxides and negatively charged surface groups of organic matter (Schaetzl and Anderson, 2005). In the case of Cu, its versatility in soils enables it to exhibit a great ability of chemically interacting with mineral and organic components (Kikuchi *et al*., 2017) such as phenols for the formation of inner sphere complexes (Udeigwe *et al*., 2016). This fact is also confirmed by Latrille *et al*., (2003) who established an affinity between Cu and organic matter plus allophane ($Al_2O_3 \cdot (SiO_2)_{1.3\text{-}2} \cdot (2.5\text{-}3)H_2$).

Soil organic matter is also capable of holding and or fixing Zn quite strongly (Hafeez *et al*., 2013) and that may explain why there is a strong correlation in both drainage classes studied.

Furthermore, basic organic compounds such as amino acids and hydroxyl acids are effective in complexing Zn thus enabling its mobility and solubility within the soil environment (Kabata-Pendias and Pendias, 2001). Organic matter has a potential to fix Mn in soils thus facilitating the formation of organic complexes of Mn (Kabata-Pendias and Pendias, 2001). So, this may explain why a positive interaction is observed between the two parameters for each drainage class.

Clay fractions or minerals have binding potential. It may be the case that Fe is held up by these minerals and fractions. Clay fractions are known to contribute significantly to the level of Cu in soils (Kabata-Pendias and Pendias, 2001) which may explain why 82% correlation is observed in control soils. Zinc adsorption and retention in soils demonstrate that clays are capable of holding Zn quite strongly (McBride, 1994). Both results per drainage class are in agreement with these findings as per the positive correlation observed. Manganese in study soils positively associates with clay content possibly facilitated by existing bonds in soils and this may explain the degree of interaction observed.

Though, EC levels in soils studied were relatively low, its presence in soils is known to decrease pH readings by at least 0.2 – 0.3 thus the 0.01 M $CaCl_2$ solution was used to satisfy possible effects of salt availability in study soils (USDA, 1999). Soil pH greatly affects nutrient availability for plants (USDA, 1999) in that as minerals dissolve in soils, nutrient availability for plants is induced. Moreover, pH has a strong affinity with metals in that it ascertains metal speciation, mobility and bioavailability in soils (Zhao *et al*., 2010). In soils, acidic compared to neutral and alkaline conditions favour the solubility of most minerals (e.g. Fe, Mn, Zn and Cu etc.) (USDA, 1999). These acidic conditions facilitate extraction of these various minerals into dissolved and exchangeable forms that are readily available and easily used by plants (Zeng *et al*., 2011).

A positive interaction between pH (H_2O) with Zn (0.444*) and Mn (0.489*) for control soils suggested some level of influence pH has on the elemental concentration of these soils. Furthermore, lower mean pH (H_2O) levels observed for some pedons (pedon 1: pH of 6.61 and pedon 4: pH 6.16) in the control channel validate this claim. Study results are consistent with other findings (e.g. Violante *et al*., 2010; Zeng *et al*., 2011; Adamczyk-Szabela *et al*., 2015). In the case of treated wastewater affected soils, the presence of dissolved chloride ions sourced from chlorine used to treat wastewater might have resulted in slight increment in mean pH levels for soils under this drainage class (pedon 5: pH of 7.28, pedon 6: pH of 7.99, pedon 7: pH of 7.52 and pedon 8: pH of 7.69 respectively). Thus, this may explain why no interactions are observed between pH and HMs in wastewater treated soils suggesting no influence on the solubility, mobility and bioavailability of respective HMs.

According to the USDA, (1999) EC scale, studies EC levels in both control and treated wastewater affected soils were generally low, 0.06 – 0.32 (non – saline) and 0.19 – 2.23 (slightly – saline) $dS.m^{-1}$ respectively. Moreover, because the study soils are assumed to belong to the kaolinite clay mineral group characterised by low CEC levels, simultaneously their EC levels are expected to be low as evidenced by the study results. Though EC was generally low in both drainage classes, treated wastewater affected soils had slightly higher levels compared with control soils. The only possible explanation given was attributed to the dissolved chloride ions (Cl^-) sourced from the chlorine used by the plant to treat wastewater.

While these Cl^- ions are discharged alongside these waters into soil environments, they combine with existing soil minerals in order to form inorganic mineral including sodium chloride ($NaCl$), calcium chloride ($CaCl_2$) and potassium chloride (KCl) which then slightly increase soil EC levels. Therefore, possible effects of EC levels on plants occurring under control soils are anticipated to be lower than those in treated wastewater affected soils. The EC similar to pH may have an influence particularly on the bioavailability and mobility of Fe, Cu, Zn and Mn in these particular soils. For instance, higher mean levels of these HMs in pedon 3 than any other pedon (Fe: 16198.25 ppm, Cu: 12.90 ppm, Zn: 19.03 ppm and Mn: 289.00 ppm).

Treated wastewater affected soils showed no interaction between EC and HMs. Furthermore, interesting to note about EC is that higher EC levels were observed for pedons and horizons with small soil particles relative to larger particles. This is because grain size texture affects soil EC, clay soils tend to have higher EC compared to silt soils and sandy soils respectively (clay > silt > sand) (Bai *et al*., 2013). For instance, horizon Btgb in pedon 7 with sandy clay loam texture had clay content of 230.00 g kg^{-1} and all horizons in pedon 3 with sandy loam texture had clay contents ranging from 150 – 180 g kg^{-1}. Their EC levels were 0.31 $dS.m^{-1}$ and ranging from 0.25 – 0.32 $dS.m^{-1}$ respectively. Exceptions were made though for Ap horizons in pedons 5, 6 and 8 which seemed to show consistently high EC levels irrespective of grain size texture. All these pedons were located in the treated wastewater affected channel; treated wastewater may be responsible for higher EC levels observed in these upper most horizons. In addition, treated wastewater could increase the CEC of soils if it contains dissolved cations. Higher CEC levels, in most cases, are indicative of more OM and clay contents. With an increase in CEC, cations are adsorbed on the negatively charged surfaces of clays and OM. This could lead to the formation of organo-complexes which immobilises cation in soils. Immobilisation thrives on the principle of double ionic layer theory.

CHAPTER FIVE

SYNTHESIS AND CONCLUSIONS

5.1 Background

Amid geogenic and anthropogenic sources of environmental heavy metal pollution, those based on anthropogenic activities are most predominant (Karim *et al*., 2014; Yang *et al*., 2017b). Some of these include mining activities, industrial effluent reuse or discharge and vehicular emissions from mobile sources (Yıldırım and Tokalıoğlu; 2016; Mehr *et al*., 2017). In drier regions of the world shortage of water for the sustenance of various activities including construction and agricultural production has encouraged the reuse of treated wastewater as an alternative (Elgallal *et al*., 2016; Andrews *et al*., 2016; Ganjegunte *et al*., 2017). Unfortunately, wastewater is a potential host of heavy metals including but not limited to Pb, Mn, Cr, Ni and Cu which in their accumulation may pose serious environmental and health hazards. As an alternative measure to curb shortage of water meant for irrigation in agricultural production, treated wastewater reuse is slowly rising in Botswana evidently noted in several Glen valley studies (Dikinya and Areola, 2009; Dikinya and Areola, 2010; Likuku and Obuseng, 2015).

With the uncertainty as to whether benefits of treated wastewater outweigh its potential to degrade soil quality, there is still more to be understood before firmly recommending the reuse of treated wastewater (Gharaibeh *et al.,* 2016). Therefore, this study helps provide knowledge to fill the gaps along the aforementioned subject matter. This chapter is a synthesis of all aspects studied on heavy metal concentration levels in soils exposed to treated wastewater discharged from PWTP. So far, nothing on soil exposure to heavy metals assumed from discharge of treated wastewater has been documented in the study area. The overarching aim of this study was to assess heavy metal concentration levels due to treated wastewater discharge on soil proximal to PWTP. Specific objectives of the study included:

i. To characterize soils exposed to long term discharge of treated wastewater using selected physical, chemical and geochemical properties (particularly heavy metals);

ii. To assess treated wastewater impacts on studied soil properties by comparing treated wastewater affected with no – treated (control) soils and;

iii. To undertake potential risk assessment of heavy metal pollution in the soils around the wastewater treatment plant.

5.2 Synthesis of key findings

Sufficiently, this study has successfully assessed heavy metal concentration levels in soils continuously exposed to treated wastewater discharged from the Palapye Wastewater Treatment Plant (PWTP) relative to soils unaffected by treated wastewater as similarly observed in related studies (e.g. Asgari and Cornelis, 2015; Gola *et al*., 2016; Hidri *et al*., 2016). The study establishes that even though treated wastewater is continuously discharged into the proximal environment to the plant, its effects in soils is minimal contingent on regular treatment methods employed. The current study as per the objectives yielded the following findings:

- Source apportionment via PCA revealed that Zn, Cu and Mn in soils for both drainage classes are mainly of geogenic origin because of their strong affinity with Fe. Iron is one of the most abundantly occurring elements in the earth’s crust and elements showing a strong affinity with Fe will be of similar origin. In control soils correlations showed positively strong correlations between Fe/Cu (0.922**, $p < 0.01$), Fe/Zn (0.943**, $p < 0.01$) and Fe/Mn (0.852**, $p < 0.01$) while treated wastewater affected soils showed positively strong correlations between Fe/Zn (0.962**, $p < 0.01$) and Fe/Mn (0.902**, $p < 0.01$).

- Selected pollution indices including the EF, Igeo and PLI verified that treated wastewater discharge has not lead to HMs pollution in the soil environments (treated wastewater affected soils) within the proximity of PWTP. Suggesting that the continued application of treated waste water into nearby land areas is not a possible treat for heavy metal contamination in soil.

- Moreover, Mn which showed enrichment in profiles 7 and 8 might indicate possible soil pollution, but its speciation and bio-accessibility rather than simply total concentrations, have to be further established so as to conclude on likely pollution occurrence as attributed to treated wastewater.

5.3 Conclusion

The study compared selected soil properties (i.e. physical, chemical and geochemical) of treated wastewater affected and a control soils occurring in the proximity of the Palapye Wastewater Treatment Plant (PWTP). Particularly, respective mean heavy metal concentration levels in both drainage classes showed no variations statistically ($p > 0.05$). Based on various thresholds (see chapter 3) used, most mean HMs concentration levels per drainage class were generally low (below internationally allowable limits) suggesting minimal influence from the discharged treated wastewater. These concentration levels were further explained using various soil properties (e.g. pH, EC, OM, CEC). Pollution level assessment through the EF index showed some level of Mn enrichment in soils from pedon 7 and 8 while Igeo and PLI indices revealed soils to be unpolluted. Future assessment should deal with availability, speciation and movement of heavy metals within the pedon. HM fractionation is recommended to characterize the heavy metal contents in soil.

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APPENDIX

This thesis was published in Geoderma regional as title: Long term treated wastewater impacts and source identification of heavy metals in semi-arid soils of Central Botswana.

The citation is given by:

Kebonye, N. M., Eze, P. N., & Akinyemi, F. O. (2017). Long term treated wastewater impacts and source identification of heavy metals in semi-arid soils of Central Botswana. Geoderma Regional, 10, 200-214. (See attached pdf).