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The Feasibility of Treating Heavy Metals Present in Wastewater Sludge (WWS) as found in Eswatini and the Sustainable Disposal thereof.

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DECLARATION

I declare that this dissertation is my own original work, except where duly acknowledged. It is only submitted for the Master of Science degree in the University of KwaZulu-Natal. I also certify that no plagiarism was committed in writing this work and has not been previously submitted partly or fully for a degree to any other University.

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ABSTRACT

Sewerage content found in wastewater treatment sludge is known to be rich in nutrients and organic matter, rendering it an alternative solution for commercial fertilizers. However, wastewater treatment sludge may contain toxic heavy metals that could be detrimental to the environment and can pose a threat to human life if entered the food chain. Several studies globally have reported success in immobilizing heavy metals, but the long-term sustainability cannot be ascertained.

This research aims to determine the heavy metals present in the Eswatini wastewater treatment sludge, in order to enhance is potential for sustainable use. Triplicate wastewater sludge sampled from Matsapha and Nhlambeni Wastewater Treatment Plants were first tested for electrical conductivity (salinity), moisture content, pH, nutrients and heavy metals and organic matter.

Both Matsapha and Nhlambeni Wastewater Treatment Plant samples were treated with di-hydrogen sulphate (H_2PO_4) and sorption analysis was conducted to determine phosphorus adsorbed by each sample. The sorption analysis samples were further tested for seepage of heavy metals using a Toxicity Characteristic Leaching Procedure (TCLP). Spinach and grass were planted on both samples to determine plant uptake of heavy metals and leachability was determined through a column study on the mixture of soil and sludge samples using recommendations from the South African legislation. Analysis for acid digested samples and leached water were conducted through ICP-OES. Results indicated significant immobilization of heavy metals present in the wastewater sludge samples, which was confirm by the TCLP test. However, leached samples from column study could not confirm the reality of immobilized heavy metals over long term since the soil itself contained some heavy metals, which its availability for plant uptake is not known.

This research will inform, mainly the African local municipalities and parastatals that attempt to treat industrial wastewater sludge (aimed at reducing the solubility of heavy metals) for possible use in agriculture.

Keywords:

Wastewater treatment sludge, heavy metals, di-hydrogen sulphate (H_2PO_4), immobilizing, sorption analysis, TCLP, plant uptake, column study, ICP-OES.

I dedicate this work to:

My late dad

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LIST OF ABBREVIATIONS

Abbreviation	Definition
Al	Aluminium
As	Arsenic
B	Boron
Be	Beryllium
Ca	Calcium
$CaCl_2$	Calcium Chloride
Cd	Cadmium
CH_4	Methane
CO_2	Carbon Dioxide
Co	Cobalt
Cr	Chromium
Cu	Copper
EWSC	Eswatini Water Treatment Plant
Fe	Iron
FSTs	Final Sedimentation Tanks
GHG	Greenhouse Gases
H_2O	Water
H_2S	Hydrogen Sulphide
ISO	International Organisation for Standards
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
ISTs	Intermediate Settlement Tanks
IWWTP	Industrial Wastewater Treatment Plant
K	Potassium
KCl	Potassium Chloride
KH_2PO_4	Potassium dihydrogen phosphate
MC	Moisture Content
MCL	Maximum Contaminated Level
Mg	Magnesium
Mn	Manganese
Mo	Molybdenum
MWWTP	Matsapha Wastewater Treatment Plant
N	Nitrate
Ni	Nickel

Na	Sodium
NREL	National Renewable Energy Laboratory
P	Phosphorus
Pb	Lead
pH	Potential for Hydrogen
PSTs	Primary Sedimentation Tanks
S	Sulphur
Sb	Antimony
SDGs	Sustainable Development Goals
Se	Selenium
Si	Silicon
Sn	Tin
TCLP	Toxicity Characteristic Leaching Procedure
Ti	Titanium
Tl	Thallium
UN	United Nations
UNEP	United Nations Environmental Program
UNESWA	University of Eswatini
USEPA	United States Environmental Protection Act
V	Vanadium
WHO	World Health Organisation
WSP	Water and Sanitation Program
WWTP	Wastewater Treatment Plant
Zn	Zinc
Zr	Zirconium

CHAPTER 1: Introduction

1.1 Background of the study

"In the middle of difficulty lies opportunity." - ***Albert Einstein***

This quote attributed to Albert Einstein is proven to be true in relation to wastewater sludge. As a result, many scientists and engineers are researching sustainable opportunities that will reduce the environmental impacts of waste and introducing reuse technologies that are in line with circular economy. However, the truth of the matter is that the issues of waste management must be supported at political level (i.e., become legislated) first to be effectively implemented.

Wastewater sludge is a by-product of wastewater treatment processes and can be classified in five (5) categories: (1) raw sludge, (2) primary sludge, (3) activated sludge, (4) aerobically stabilised sludge and (5) digested sludge (Demirbas et al., 2017). Wastewater sludge is reported to have higher concentration of nutrients and organic matter than the wastewater itself making it a valuable material for use in agriculture as soil amendment (Gupta et al., 2020a). While there are several direct and indirect recognizable advantages of re-using wastewater sludge and wastewater as a resource (Jiménez et al., 2009a), there are growing concerns about the presence of heavy metals that from Wastewater can pollute the environment. If these metals enter the food chain or animal feed and get absorbed in excess of permissible limits, they may cause complicated illnesses to human beings and animals that may ultimately lead to death (Agoro et al., 2020a) & (Gunatilake, 2015a). In South Africa, Water Research Commission documented five (5) volumes of guidelines that provides guidance for the utilization and disposal of wastewater. Suggested disposal options are based on the quality of generated wastewater sludge, which is measured by the quantity of microbiological contaminants, stability and pollution content (Snyman & Herselman, 2009).

Eswatini wastewater treatment plants are currently putting more efforts into treating the wastewater to meet the required Eswatini Environmental Authority (EEA) standards. The sludge generated through treatment processes is currently kept onsite, mainly because there are no ISO accredited sludge testing laboratories nationally. Instead, there is only one laboratory in Mhlume City, East of Eswatini which has an ISO accreditation for testing soil samples for agricultural use.

Several studies have been conducted on heavy metals present in industrial wastewater sludge, but there is insufficient information on solid effluent treatment aimed at reducing the solubility of heavy metals and analysis of sludge to be used in agricultural fields in developing countries with a low level of wastewater treatment. Therefore, it is envisaged that this research will inform wastewater managers and other interested parties in developing countries who may attempt to treat industrial wastewater sludge (by reducing the solubility of heavy metals) for possible use in agriculture.

1.2 Problem Statement

Eswatini Water Services Corporation (EWSC) is a government parastatal responsible for potable water supply, treatment and disposal of wastewater. One of its largest treatment plants with a capacity of 20Ml/day is in Matsapha. Matsapha Watewater Treatment Plant receives wastewater from the country's main industrial area, an international airport, a high security prison, police training college, residential developments, landfills, and predominantly industrial activities. Currently the treatment plant discharges a significant amount of sludge from the industrial wastewater treatment plant (IWWTP) which has a potential to be used as an agricultural resource. Nutrients in wastewater sludge can be recovered for agriculture and aquaculture while organic carbon can be recovered for soil amendment or energy generation (Drechsel et al., 2015a). Influent and effluent tests conducted at all EWSC wastewater treatment plants (WWTP) indicated the presence of high concentrations of heavy metals, which may have detrimental effects on human and the physical environments (Peng et al., 2011), if used for crop production or animal feed. The concern of leaching/solubility of heavy metals from the sludge, if used in agriculture without prior treatment can possibly contaminate the environment, including surface and underground water. Sustainable treatment and disposal methods need to be identified for the use of this material in agriculture.

The research questions to be answered by this study are:

1) Which heavy metals of environmental concern are present in the Matsapha and Nhlambeni Wastewater Treatment Plant (MWWTP) sludge?
2) How does the concentration of heavy metals in MWWTP sludge compare to the effluent and the allowable national and regional heavy metal limits?
3) How effective is the phosphorus-based material in immobilizing heavy metals in the industrial wastewater sludge from MWWTP?
4) How does the treatment method affect the essential plant nutrients in the sludge when used in agriculture as a soil amendment?
5) How do immobilized heavy metals change over time?

1.3 Aims & Objectives:

The main aim of the study is to establish the concentration of heavy metals in the local sludge, improve its potential use in agriculture as a soil amendment (or soil fertility improver) by treating it with phosphate-based chemical(s) to reduce metal solubility.

The objectives are;

1) Determine the concentration of metals present in the MWWTP sludge.
2) Compare the concentration levels of heavy metals in MWWTP sludge to the aqueous solution and the available listed standards in the local and regional regulations.
3) Evaluate and compare the effectiveness of immobilising heavy metals present in MWWTP using phosphorus-base material, KH_2PO_4.
4) Evaluate the effects of immobilisation of heavy metals to essential plant nutrients (i.e., K, Ca, Mg.)
5) Monitor the changes of immobilised heavy metals through column leaching.
6) Use the findings to develop recommendations for possible sustainable sludge disposal methods.

1.4 Local Information

EWSC has a total of six (6) wastewater treatment plants nationally and four (4) wastewater treatment ponds. Wastewater samples are taken daily for testing in an ISO certified laboratory to ensure that treated effluent meets the acceptable national standards sets by the Eswatini Environmental Authority. However, In all the existing treatment plants no quality tests are conducted on the wastewater sludge which is currently disposed onsite at all the six WWTP.

Nhlambeni Wastewater Treatment Plant receives waste from residential and commercial customers. Mastapha wastewater Treatment Plant receives waste from the industrial and commercial areas, airport and hotels and residential areas. The industries comprise of brewery, Coca Cola concentrates company, poultry, textile, paint manufactures and garages. Knowing that wastewater sludge has a higher contamination rate when compared to wastewater fluids(Gupta et al., 2020), it is highly possible that the sludge contains some metals that are not detected in the effluent. Therefore, it is important to determine the metals present in the wastewater sludge and compare the findings with those found in wastewater effluent. Also, EWSC has farms which can be used for closing the loop of wastewater sludge disposal by using it as fertilizer instead of disposing it to the landfill site. The wastewater sludge needs to be treated before disposal (Snyman, 2018) to reduce solubility effects of the heavy metals. This has never been done before in Eswatini and this research would provide scientific information to EWSC for objective business decisions.

1.5 Overall Approach:

Chapter 1 of this dissertation introduces the study. ***Chapter 2*** presents the detailed literature review conducted for this study. In ***Chapter 3*** the materials and the methodology are outlined, and the research study limitations are discussed as well. Presentation, analysis and interpretations of results are given in ***Chapter 4***. Finally, Conclusions and recommendations are presented in ***Chapter 5***.

CHAPTER 2 – Literature Review

2.1 Introduction

This chapter discusses heavy metals in sludge and their implications in agriculture, the generation of wastewater sludge, followed by a review of different recovery potential studies. The subsequent sections present literature on recovery of wastewater sludge for soil amendment and looks at treatment methods for heavy metals. Finally, the chapter concludes by stating the hypotheses derived from the literature in relation to treatment of heavy metals present in wastewater for use in agriculture.

2.2 Heavy Metals in Sludge and Agricultural Implications

As indicated in Chapter One, wastewater sludge has potential fertilizer properties, but it could contain heavy metals which are toxic to the environment and fraught with health hazards if entered a food chain untreated. Heavy metals are described as elements with a high atomic weight and a density at least 5 times greater than water (Tchounwou et al., 2012). These heavy metals originate both naturally (i.e., weathering of metals-containing rocks and volcanic eruptions) and anthropogenic (i.e., industrial emissions, mining, smelting, and agricultural activities like application of pesticides and phosphate fertilizers) (Ali et al., 2019). As a result of rapid anthropogenic activities, human exposure has also increased dramatically. From agricultural application point of view, wastewater sludge contains undesirable substances such as heavy metals, pathogens, pharmaceuticals, and other substances which are detrimental to the environment and human life (Nicholas et al., 2010; Efsa, 2012 & Snyman, 2018). African countries like South Africa and Kenya have followed global trends by categorizing their wastewater sludge in accordance with its toxicity for different disposal requirements (Snyman, 2018). The categorization is meant to make it easier for wastewater sludge generators and / or end users to select most appropriate resource recovery method. However, since this study is on heavy metals, the other pollutants present in wastewater will not be reviewed in detail but will only be mentioned as appropriate.

Stylianou et al., (2007) recognized that the principal pollutant elements such as copper (Cu), zinc (Zn), chromium (Cr), nickel (Ni), and lead (Pb) are limiting sludge recycling to agricultural land. The study conducted for Eswatini heavy metals in sewage revealed that wastewater sludge is within the regulatory limits set by USEPA, South Africa and EU; however, Cu, Cr, Zn and Ni, were above the recommended Chinese guidelines in sludge samples collected from Matsapha, and only Cu exceeded Chinese guidelines in Nhlambeni (Tiruneh et al., 2014). Environmental engineers and scientists around the world are conducting investigations pertaining the treatment of heavy metals for use as soil amendment. Gunatilake, (2015) reviewed different methods of removing heavy metals from industrial wastewater and concluded that chemical treatment is the most effective compared to physical and biological treatments when treating toxic inorganic compounds. This basically means wastewater sludge contaminated with heavy metals can be treated to meet the required guidelines or standards. Although the sorption methods depend mostly on high soil pH (Gunatilake, 2015), whereas the nutrients are more soluble on lower pH (Kazem, 2012). Lake, (2000) reported that essential nutrients such as Phosphorus (P), magnesium (Mg) and calcium (Ca) become less available at low pH, whereas elements such as iron (Fe), aluminium (Al) and manganese (Mn) strive with a possibility of becoming toxic to plants.

2.3 Production of Wastewater Sludge

Wastewater sludge originates from households, institutions, industrial and commercial developments. Wastewater consist of harmful substances such as pathogens, pharmaceuticals, heavy metals, and others that are considered unsafe for the environment and human life (Nicholas et al., 2010; Tchounwou et al., 2012; Efsa, 2012; Snyman, 2018) . The generators of wastewater either treat their effluent or discharge in wastewater systems for treatment, or both depending on the legislative requirements. Activities occurring in textile, brewery, and metal industries, generate heavy metals contaminated effluents that end up in wastewater facilities. In case of Eswatini, published National Sanitation and Hygiene Policy in Eswatini enforces that the wastewater generators, especially industries with contaminants exceeding design capacity of the wastewater treatment plant, to pre-treat their wastewater before safe discharge to a wastewater treatment plant (FAO, 2019). By design, wastewater treatment plants discharge sludge at different points of the process; referred to as raw sludge, primary sludge, activated sludge, aerobically stabilised sludge and digested sludge (see Table 2.1).

Eswatini is currently facing challenges in finding effective and practical solutions for treatment and sustainable disposal of wastewater sludge. However, it is widely understood that indiscriminate disposal of wastewater sludge may cause harm to the environment, enter the food chain and cause chronic illness that could ultimately lead to death. As much as there are concerns about anaerobic composting of wastewater sludge when disposed of at landfills which could introduce environmental emission (Okoh et al., 2007), unavailability of engineered lined landfill space in Eswatini as well as other municipalities in South Africa is an additional problem. It is therefore necessary to explore sustainable disposal options of generated sludge within the country.

Table 2. 1: Types of Sludge According to Origin, Characteristics and Operating Condition

Type of sludge	Characteristics	Origin and operating condition	Reference
Raw sludge	- high portion of organic matters, as faeces, vegetables, fruits, textiles, paper. -Bad odour	Solid extracted at inlet works, after screening and the grit chamber and consists of unstable wastewater contaminations. It may be organic solids that settle to the bottom of the primary sedimentation and gets extracted and transferred to the anaerobic digester for treatment.	(Demirbas et al., 2017 & Jiménez et al., 2009)
Primary sludge	-Floating sludge -high turbidity	Solids found in the primary settlement tank which moves to the next treatment process for aeration (e.g., aeration basin that forms activated sludge or bio-trickling filter)	(Demirbas et al., 2017 & Jiménez et al., 2009)
Activated sludge	-This consortium of microorganisms, the biological component of the process, is known collectively as activated sludge - Minimal or no smell	solid found in the aeration basin where treatment process is by a community of microorganisms. Once the aeration is complete, the settling bacteria in the next settlement tank form a sludge blanket which becomes Return Activated sludge (RAS). the RAS continuously recycled to primary clarification to assist with breaking down the organic matter of the incoming sewage until it is ineffective and becomes waste activated sludge (WAS) which moves on to covered tanks called aerobic sludge digesters.	(Demirbas et al., 2017 & Jiménez et al., 2009)
Aerobically stabilised sludge	Settling bacteria from WAS	In this process the bacteria in activated sludge begin to digest another until most sludge disappears. This sludge moves to dewatering facility.	(Demirbas et al., 2017 & Jiménez et al., 2009)
Digested sludge	Sludge cakes or solids	It is produced after the de-watering process by conventional drying beds, mechanical equipment (such as belt press, centrifuge de-watering plant). This sludge can be recovered as a resource	(Demirbas et al., 2017 & Jiménez et al., 2009)

2.4 Wastewater Recovery of Nutrients and Organic Matter

Wastewater sludge is rich in nutrients and organic matter (Jiménez, 2006), which has increased global interest of using it as a fertilizer. Organic carbon improves soil structure for plants roots once it is stabilized and can also be used for energy or fuel recovery. Nutrients like phosphorus and nitrogen are essential for plant growth and can be a beneficial natural fertilizer. Therefore, it is necessary to treat wastewater sludge for pathogens, heavy metals, and pharmaceutical before land application (Nicholas, 2010).

Recovery of nutrients from sludge presents the opportunity to contribute directly and indirectly towards the global Sustainable Development Goals (SDGs). Application of sludge as fertilizer requires an extensive study to ensure that the benefiting environment and human beings do not suffer the effects because of untreated contaminants. The process of sludge application as fertilizer has caught the attention globally and locally. In fact, the Eswatini Observer published an article entitled "Farmers Abandoning Production Due to Shortage of Fertiliser" on the 1st of August 2022. This clearly indicates the need to accelerate research for treatment of the existing contaminated wastewater sludge.

2.4.1 Sludge Re-Use for Agriculture Globally

Global organizations such as UN-Habitat (Sludge management atlas), FAO/IWMI (AQUASTAT: from wastewater generation to use), UNEP (Global water quality assessment), the Water and Sanitation Program (WSP) of the World Bank (IBNET: Water and sanitation utility performance), and Global Water Intelligence (Wastewater treatment and reuse market reports), are conducting several researches with the aim of selecting and harmonizing the best available data around water quality, wastewater and sludge production, treatment, and/or use (Drechsel et al., 2015b). The publication by these organizations has challenged developed and developing countries to assess their progress towards contributing to the Sustainable Development Goals (SDGs).

The uses of wastewater sludge mainly depend on the toxic characteristics. Drechsel et al., (2015) reported that almost 100% of biosolids generated in Spain are used for agriculture whereas Netherlands incinerates almost 100%. They further stated that industrial economies like Spain opt for energy resource recovery. However, several studies reviewed indicate that the use of wastewater sludge globally as soil amendment is steadily decreasing due to restrictions on heavy metals in sludge (Snyman & Herselman, 2009; Mateo-Sagasta et al., 2015; Zhang et al., 2017).

2.4.2 Sludge Re-use for Agriculture in Africa

The Water Research Commission in South Africa funded a project to develop a series of guidelines for the utilization and disposal of wastewater sludge for South Africa (Snyman & Herselman, 2009). These guidelines compel South African wastewater treatment plants to classify their sludge in accordance with its characteristics (see Table 2.2) which could be used as a guideline for sludge re-use.

Table 2. 2:The South African wastewater sludge classification system as found in volume 3 of 5 of the utilization and disposal of wastewater (Snyman & Herselman, 2009).

Classification class	**Best quality**	**Intermediate quality**	**Worse quality**
Microbiological class	A	B	C
Stability class	1	2	3
Pollutant class	a	B	c

Wastewater sludge classified under "A1a" would be the best quality and could easily be used as soil amendment or fertilizer. Class "A1b" sludge could require treatment before use for agriculture or be recovered as per the recommendations of the published series of sludge management volumes. However, due to the presence of microbiological class, instability and pollutant of class "B2B"and C3C" sludge, agricultural use is demotivated. Volume 2 of the publication series describes the requirements for the agricultural use of sludge. It also takes into consideration that the soils to be amended might be contaminated and the classification of those soils must be categorized to minimize for appropriate application of sludge.

2.4.3 Sustainability Impacts in Re-Using Wastewater Sludge as Fertilizer

Adoption of the South African guidelines (Snyman & Herselman, 2009) for treatment of sludge in Eswatini would result in a significant positive impact economically, socially, environmentally, and ultimately human health.

Environmental Impact: The biggest concern with sludge treatment processes and re-use for agricultural purposes is the fundamental environmental impacts. The gases produced during sludge digestion treatment process (Jiménez et al., 2009b) have a long-term global warming effect. Also, most toxicity (including heavy metals) found in wastewater is treated through sludge removal which can be viewed as a hazard transfer. Therefore, recovery and treatment of these wastewater by-products to acceptable standards is essential. The environmental impacts of re-using treated sludge as fertilizer can then be quantified by less or no degradation of soil such that it requires rehabilitation. Even though the long-term effect of immobilized heavy metals is not known (Zhang et al., 2017), immobilizing heavy metals in sludge would prevent surface water contamination and minimize the plant uptake of heavy metals, thereby reducing environment and human health risk (Babel & Kurniawan, 2003).

Social Impacts: Eswatini is known to be one of the African countries that has many people living below poverty line and largely depends on agriculture for food. Using nutrients found in wastewater sludge as fertilizer increases the crop yield and thus can ensure food security (Jiménez, 2006). Equally, health risks associated with the consumption of heavy metals within allowable safe limits should be considered (Babel & Kurniawan, 2003). In as much as the public and political pressures coupled with opposition from the media may have serious reservations on the re-use of wastewater sludge, extensive awareness and environmental auditing needs to be undertaken to curb the possible barriers.

The re-use of sludge for agricultural purposes increases potential for job creation. Snyman, (2018) reported that six (6) small enterprises created 36 semi-skilled and skilled jobs often for sole breadwinners. It is evident that if more enterprises could take this advantage for sludge re-use, the social impact would be substantial.

Economic Impact: Farmers either complain about the availability of fertilizer which meet the health and safety requirements or the cost versus production (Snyman, 2018). The search for alternative fertilizer sources is a common subject aimed at reducing the current cost of fertilizer for growing crops which are ultimately consumed by human beings (Snyman, 2018). Avoidance of the deterioration of land indirectly eliminates litigation costs by local environmental authority.

2.5 Other Wastewater Recovery Potential

The concept of looking at wastewater as a resource requires a shift from today's paradigm, which puts emphasis on what must be removed from wastewater to a new paradigm which puts emphasis on what can be recovered. From this perspective, wastewater facilities can be viewed as part of the circular economy.

2.5.1 Water Recovery and Reuse as Treated Wastewater

The primary purpose of treating wastewater is "resource recovery" which for many years has been mostly focusing on the availability of fresh or drinking water. Global trends of freshwater availability experienced a drastic water depletion between 2002 and 2016 (Crellin, 2018). In response to freshwater depletion concerns, researchers have put more efforts into sourcing solutions for treating different residues of wastewater treatment processes in quest to curb global freshwater challenge. One which is the removal of heavy metals using different methods such as chemical precipitation, coagulation and flocculation, electrochemical treatment, ion exchange, membrane filtration, electrodialysis and biological methods proved to be effective (Gunatilake, 2015). However, most of these wastewater treatment methods remove heavy metals through sludge discharge. The onus then remains with the wastewater treatment operators to safely dispose of the generated sludge. Landfilling wastewater sludge has been the most preferred solution from the management and handling perspective (Gupta et al., 2020; Snyman, 2018), which is not a favorable disposal method in the waste hierarchy.

2.5.2 Biogas Recovery and Possibilities for Use

Biogas is a by-product of the anaerobic digestion process of wastewater sludge. There are several ways in which biogas can be generated and collected, either in controlled tanks (biodigesters) or engineered lined landfills. Dissolved oxygen is not present in this process and gases like hydrogen sulfide (H_2S), methane (CH_4), Carbon Dioxide (CO_2), and other gases are produced, and some are characterized by bad odour. Some of these gases are classified as greenhouse gases (GHG) and have a negative effect on global warming. (Gupta et al., 2020) reported that the recovery of biogas and nutrients can be one of the most valuable resources that can be recovered during wastewater treatment. Biogas contains roughly 50 – 70% percent methane, and 30 – 40% carbon dioxide. Other gases are later removed leaving only the methane which is the primary component of natural gas (Tanigawa, 2017). The following possibilities can be considered for utilizing and treatment of the digester gas.

Biogas for combined heat and power – Damiam, (2022) records that one cubic meter of biogas at 60% methane content converts into 6.7kWh energy. Biogas is captured to produce heat and electricity for use in engines, microturbines and fuel cells (Kozak & Majchrzycka, 2009). The electricity produced can either be used for aeration, pumping systems, and equipment for the dewatering, and drying of sewage sludge. Advanced wastewater treatment plants, e.g., for nutrient removal, require more energy than plants that only achieve primary or secondary treatment. Alternatively, it can be diverted into the local electricity company grid.

Biofuel Recovery – One very interesting organic waste recovery, which has attracted researchers for improvement is through a biorefinery. According to the American National Renewable Energy Laboratory (NREL), biorefinery can be defined as a facility that integrates biomass conversion process and equipment to produce fuels, power, and chemicals (Mumtha et al., 2022). Wastewater sludge is considered the popular inoculum for optimizing the production processes because sewerage has a versatile microbial community (Moodley et al., 2020). Biogas, biohydrogen, bioethanol, biobutanol are some of the examples of new forms of energy that are produced through biological routes. Amongst all of them biohydrogen has been shown to be a very promising alternative to carbon base fuel compared to other options because it is a clean renewable energy (Moodley et al., 2020). It has a very high calorific value of approximately 120 MJ/kg (SFC Energy AG, 2022) and its combustion only produces water as a byproduct. Biohydrogen is produced through digestion of organic matter under dark fermentation and photo fermentation conditions where microbes can be employed to make biohydrogen (Mumtha et al., 2022). The substrates can be used for agricultural purposes as the sewerage content is rich in nutrients. This recovery method may not be feasible for Eswatini due to lack of capacity and that the substrate or sludge will require disposal thereafter, which could be limited by its contaminants.

2.6 Risks of Heavy Metals in Agriculture

Heavy metals are natural but harmful when in excess (Ali et al., 2019). Many countries and organizations have investigated toxicity of heavy metals and published legal threshold guidelines for heavy metals in soils, sludge intended for agriculture, crops, meat, wastewater effluent and drinking water. These guidelines are meant to preserve the environment and protect human and aquatic life. This research reviewed limits published by USEPA, China, European Commission and South Africa (see Table 2.3). The allowable limits of heavy metals in sludge and soils are almost similar for WHO, USEPA, South Africa and Europe. China seems more tolerant on Cu, Ni, Zn compared to the other organizations / countries.

Table 2. 3: Acceptable limits of Heavy metals in Soil, Sludge, and Crops for use in agriculture in milligrams per kilogram (mg/kg)

Organisation/Country		**Elements (mg/kg)**								**Reference**
		Arsenic (As)	**Cadmium (Cd)**	**Chromium (Cr)**	**Copper (Cu)**	**Lead (Pb)**	**Mercury (Hg)**	**Nickel (Ni)**	**Zinc (Zn)**	
USEPA	Sludge	41	39	-	1500	300	17	420	2800	USEPA, 1994
WHO	soil	-	0.8	100	36	85	-	35	50	WHO, 1996
	Plant	-	0.02	1.3	10	2	-	10	0.6	WHO, 1996
China	soil	30	0.6	250	100	350	-	60	300	Wang et al., 2008
	Sludge	75	20	1200	1500	1000	-	200	3000	Wang et al., 2008
	Leafy vegetables	0.05	0.2	0.5	10	0.3	-	-	20	Wang *et al.*, 2008
Europe	soil	-	1.00	-	50-140	50-300	1-1.5	30-75	150-300	(EC. European Commission, 2018)
	Sludge	-	20-40	-	1000-1750	750-1200	16-25	300-400	2500-4000	(EC. European Commission, 2018)
South Africa	soil	2	3	350	120	100	1	150	200	(Snyman, 2018)
	Sludge (a)	<40	< 40	< 1200	< 1500	< 300	< 15	< 420	< 2800	(Snyman, 2018)
	Sludge (b)	40-75	40-85	1200-3000	1500-4300	300-840	15-55	420	2800-7500	(Snyman, 2018)

USEPA, WHO, China, Europe, and South Africa have almost similar thresholds for heavy metals in sludge. South Africa as the closest country to Eswatini with similar environmental conditions provide classification for intermediate quality sludge. This presents an opportunity to users to pre-treat WWTP sludge before application in agriculture. This study will use the threshold in Table 2.3 to determine if the Eswatini wastewater sludge complies with the regional and international standards.

2.6.2 Effects of Heavy Metals in Humans

Eswatini has a few to no practices of minimizing heavy metals in sludge and is currently stockpiled onsite to prevent unforeseen contamination from entering food chain. USEPA published maximum contaminated level (MCL) standards for heavy metals as shown in Table 2.4 (Babel & Kurniawan, 2003).When ingested to excess limits, humans may develop chronic diseases.

Table 2. 4: The Maximum Contaminated Levels (MCL) for the most hazardous heavy metals (Babel & Kurniawan, 2003)

Heavy Metal	**Origin**	**Limits (mg/L)**	**Toxicities for humans**
Arsenic (As)	Coal, limestone, sandstone, anthropogenic sources.	0.05	Skin manifestation, visceral cancers, vascular disease
Cadmium (Cd)	P fertilizers, phosphate rocks	0.01	Kidney damage, renal disorder, human carcinogenic
Chromium Cr)	Tannery and timber treatment effluents	0.05	Headache, diarrhea, nausea, vomiting, carcinogenic.
Copper (Cu)	Chalcopyrite, bornite,	0.25	Liver damage, Wilson disease, insomnia
Nickel (Ni)	Rocks weathering, combustion of coal, fuel oil, incineration of waste	0.20	Dermatitis, nausea, chronic asthma, coughing, human carcinogen.
Zinc (Zn)	Galvanizing industries	0.80	Depression, lethargy, neurological signs, and increased thirst
Lead (Pb)	Pb petrol, glazed ceramic ware.	0.006	Damage the fetal brain, disease of the kidney, circulatory system, and nervous system.
Mercury (Hg)	Volcanic and geological activities	0.00003	Rheumatoid arthritis, and disease of the kidney, circulatory system, and nervous system

2.7 Methods of Treating Heavy Metals in Sludge

About 80% to 90% of heavy metals in wastewater influent accumulate in the sludge (Agoro et al., 2020) and would contaminate natural water bodies, sediments, and soils when release from both natural (e.g., volcanic eruption, weathering of metal containing rocks) and anthropogenic (e.g., industries, mining and smelting, phosphate fertilizers, combustion of fossil fuel, metallo-pesticides,) sources (Ali et al., 2019). This has challenged environmental engineers and scientists to look into effective and sustainable treatment of wastewater sludge to meet disposal requirements.

Zhang et al., (2017) published an article on the remediation of soils contaminated with heavy metals, comparing mobilization and immobilization methods. The findings from Zhang et al., (2017) concluded that chemical immobilization can successfully fixing heavy metals in sewage sludge, making it safe for land application and cost-effective alternative for sewage sludge disposal. Mobilizing agents enhances solubility or bioavailability of heavy metals (Ali et al., 2019), meaning the heavy metals present in soils can easily be absorbed by plant or leach into the ground water. This practice could lead to transference of heavy metals from source which threatens the environment and cause accumulation in the food chain. On the other hand, immobilizing or stabilizing agents reduce solubility or mobility of heavy metals such that the plant uptake and leaching is minimal (Zhang et al., 2017). The immobilized heavy metals are retained in soils and there has been minimal to no research done to analyze the long-term effects.

2.7.1 Immobilizing or Stabilization Agents for Heavy Metals

Immobilization of heavy metals in sludge can either be achieved through sludge composting or chemical immobilization (Zhang et al., 2017). Sludge composting is one of the commonly used treatment methods. The challenges with this method include the longer period of time needed for the largest proportions of metals to significantly reduce or transform such that the bioavailability of heavy metals is minimal. Also, the volume of the wastewater sludge increases as a result of co-composting with bulking agents such as wood chips and sawdust. This could be feasible for the purpose of selling the treated wastewater sludge to agricultural industries. It should be noted that the bioavailability of heavy metals at the end of the composting process depends on many mobilizing factors including the pH. The more acidic the final composted product is, the higher the probability for some heavy metals distribution and mobilization which could lead to leaching into the ground water or plant uptake (Lake, 2000).

The alternative chemical immobilization includes precipitation, chelation, adsorption, and ion exchange and is considered as a cheaper method since the processes have no or minimal effects on the wastewater sludge volume (Zhang et al., 2017). Many studies have been conducted using this type of treatment methods, which could be motivated by the fact that it is less cost prohibitive, and it has more scientific backup (Kazem Hashemimajd, 2012; Wyciszkiewicz et al., 2017). Most researched chemical additives which could be explored in Eswatini are lime, phosphate-bearing materials, red mud, and sulfide.

a) Lime

Lime is a basic compound that is widely known for increasing sludge pH which results with the heavy metals precipitating into hydroxide form (Zhang et al., 2017) and decreasing electrical conductivity (EC) through precipitation of soluble ions. It can also be considered as a co-amendment solution to reduce the availability of heavy metals in soil amendments. Application of 5%, 7%, 10%, 12%, and 15% of lime into dewatered sludge at 86.0% moisture content indicated that metals such as Cadmium (Cd), Copper (Cu), and zinc (Zn) in acid-extractable form were significantly reduced, with the reduction optimum at 7%. Since the application ultimate application of lime treated wastewater sludge will be on soils, assessment of the soil's pH will be necessary to prevent reaction with the immobilized heavy metals and potentially harm the environment (Ali et al., 2019).

b) Phosphate-bearing materials

Mostly used phosphorus-bearing materials can be: (1) chemical materials, such as H_3PO_4, $(NH_4)_2HPO_4$, or KH_2PO_4; (2) fertilizer, such as calcium phosphate; (3) biological materials, such as crushed bones and (3) mineral materials, such as hydroxyapatite and phosphate rocks (Wyciszkiewicz et al., 2017). The use of bones as immobilizing agent is viewed as a useful waste recovery as it not widely re-used in Eswatini and most bones end up in sanitary landfills or dumps. Zhang et al., (2017) revealed that the phosphorus treatment method has no influence on pH. The benefits of using phosphate-bearing materials includes the release of phosphate nutrients (Wyciszkiewicz et al., 2017) which are valuable for plant growth. However, the application of excess phosphate material can be a threat to the environment if enters the waterway leading to algae blooms that produce algal toxins (USEPA, 2022). Wyciszkiewicz et al., (2017) further discovered that a mix molar ratio of H_3PO_4: hydroxyapatite for soils soil with phosphorus was optimum at 0.75:1 to minimize phosphorus leaching. However, the immobilization of Zn in the soil using phosphorus has minimal effects (Yao et al., 2011).

c) Red mud

Eswatini has plenty of land with red mud which could be rich in iron and thus yield high crops. Zhang et al., (2017) defines red mud as the alumina production by-product that leaches strong alkali and increased quantity can immobilize effectiveness of (Pb), zinc (Zn) and cadmium (Cd) to 82%, 92%, and 100% respectively. Liang et al. (2012) reported that the immobilization effectiveness of lead (Pb), zinc (Zn) and cadmium (Cd) was 62.2%, 85.7% and 100% respectively, when the wastewater sludge was mixed with 5% red mud. These analyses indicate that bioavailability of heavy metals is further reduced with more red mud due to its iron oxide content. Therefore, it would be beneficial and interesting to explore how the red mud reacts with other heavy metals that are not mentioned in this study.

2.8 Nutrients Required by Plants

Plants need both macro and micro-nutrients to survive (see table 2.5). Macro nutrients are divided into primary macronutrients (i.e., Nitrogen, Phosphorus and Potassium) which are needed in large amounts by plants and secondary macro nutrients (i.e., Sulphur, Calcium and Magnesium) (Johnson & Mirza, 2020). If these nutrients are absorbed in excess, they cause stress to plants which expose them to pest, diseases and can cause abiotic stress (Johnson & Mirza, 2020). Micronutrients include Chlorine, Iron, Boron, Manganese, Zinc, Copper, Molybdenum and Nickel (Epstein, 1965).

Table 2. 5: Nutrients Concentrations sufficient for plant growth (Epstein, 1965;Johnson & Mirza, 2020).

Elements	**Symbol**	**Concentration (mg/kg)**	**Role in Plants**
Nitrogen	N	15000	Increases the vegetation crop, leaves sizes, production of seeds and fruit growth.
Potassium	K	10000	Supports disease resistance and plant hardiness
Calcium	Ca	5000	Essential for cell wall formation and maintains the permeability of cell wall
Magnesium	Mg	2000	Constitutes about 15-0% of the plant and is essential for production of ATP which is key for energy production.
Phosphorus	P	2000	Supports roots growth
Sulfur	S	1000	Essential for protein and amino acid activity which improves quality of crops
Chlorine	Cl	100	Essential for photosynthesis and leaf turgor in plants
Iron	Fe	100	Essential for photosynthesis and respiration of the plant
Boron	B	20	Essential for reproductive tissue and cell wall formation
Manganese	Mn	50	Activates nitrogen assimilation enzyme
Zinc	Zn	6	Essential for internode elongation and production of hormones in plants.
Copper	Cu	6	Essential for protein synthesis, respiration, and chlorophyll production
Molybdenum	Mo	0.1	Serves as a catalyst that fixes nitrogen and enzymatic activity in pant
Nickel	Ni	0.1	Essential for the germination of seed

2.9 Conclusion

The review confirms that wastewater sludge contains essential nutrients that are needed for agricultural practices. However, treatment must first be conducted to meet a country's regulatory requirements. More research has focused on leaching heavy metals with the aim of improving technologies to minimize associated risks on the environment and human beings (Zhang et al., 2017). Immobilization methods have also been extensively researched but the long-term effects cannot be ascertained. Therefore, the next chapter will provide details of materials and methods employed for this study to determine the effectiveness of treating wastewater sludge with phosphorus.

CHAPTER 3: Materials and Methods

3.1 Introduction

This chapter describes the collection of data, resources used and gives an account of study analysis procedures followed in completing experiments. These will provide a basis of understanding heavy metals contamination and concentrations in Matsapha and Nhlambeni Wastewater Treatment Plant sludge before and after treatment with phosphorus.

3.2 Study Location

Eswatini, formerly known as Swaziland, is a small country with a population of about 1,2 million population which is surrounded by South Africa and Mozambique. It has four regions, namely: Manzini, Hhohho, Shiselweni and Lubombo. This study focused on one region, Manzini of Eswatini which is the most populated and has both industrial and domestic wastewater. This region has a population of 355,945 which is about 30% of the total population (UNFPA, 2017). Temperatures in this region range from approximately 10ºC to 27ºC, rarely below 7ºC or above 32ºC. Treatment chemical used contained Phosphorus which is a nutrient needed by plants and it is mostly use in industry fertilisers.

Figure 3.1 shows the Eswatini Map with locations of the two-wastewater treatment plant used to sample sludge, the University of Eswatini (UNESWA) campus where most of the practical experiments were conducted and the Eswatini Water Services Corporation (EWSC) laboratory where the ICP-OES tests were conducted.

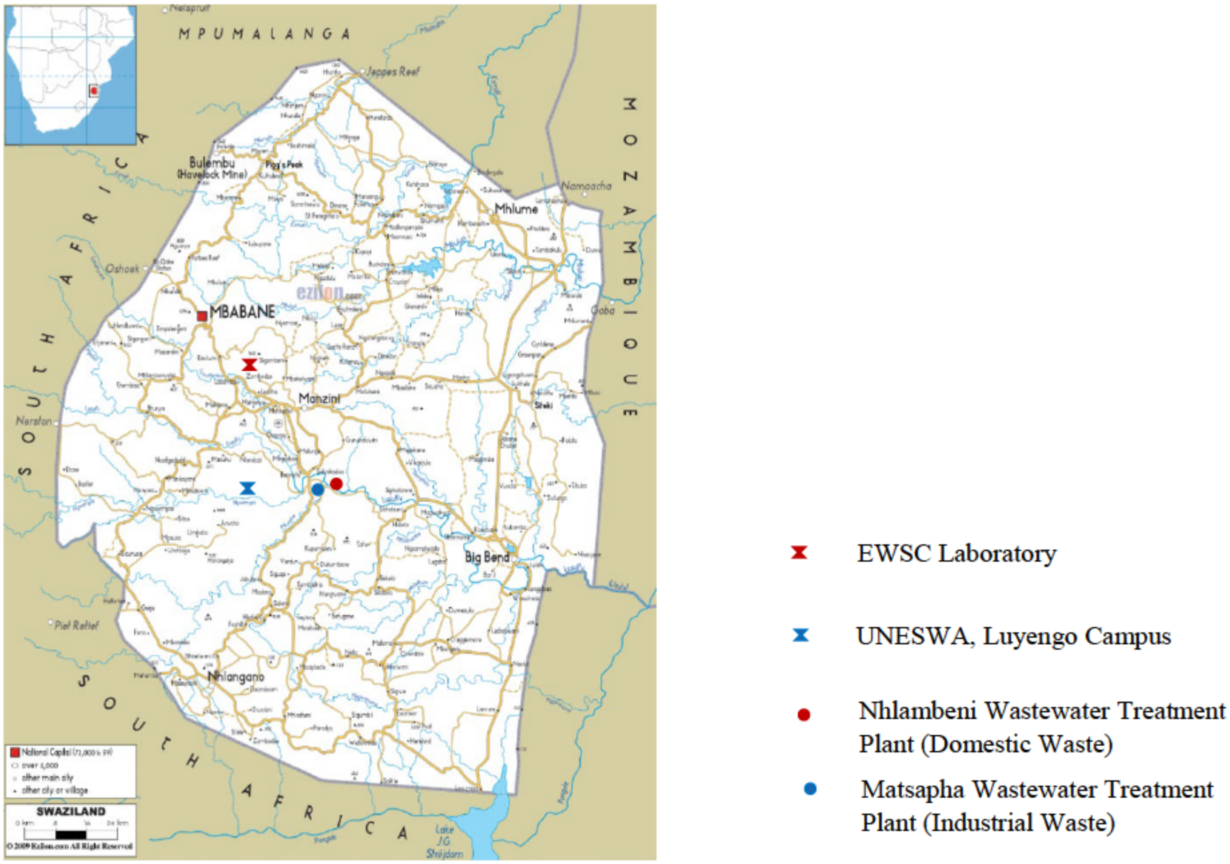

Figure 3.1: Map of Eswatini showing the sampling points and laboratories (Ezilon Map, 2009)

3.3 The Different Methodologies Used

This research required the use of a quantitative experimental approach to select the most appropriate quantities of phosphorus required to immobilise heavy metals that are present in wastewater sludge. Industrial Wastewater sludge is not recommended for treatment or use for soil amendment in most countries. However, this study considered that the Matsapha Wastewater sludge has less industrial effluent that could lead to excessive release of heavy metals when compared to most countries and that the treatment could be a possibility. Also, the study considered that as much as Nhlambeni Wastewater Plant is designed to receive domestic water, it could possibly have some heavy metals.

An extensive study was conducted including analysis of a 33-month aqueous solution archival data; 18 samples for sludge and soil properties (moisture content (MC), pH, Electrical Conductivity (EC)); 42 samples for Adsorption of phosphorus (P) by sludge analysis; 330 samples analysed through ICP-OES; and 228 samples analysed for plant nutrients. Materials and methods covered in this section are summarised in the schematic diagram shown in Figure 3.2.

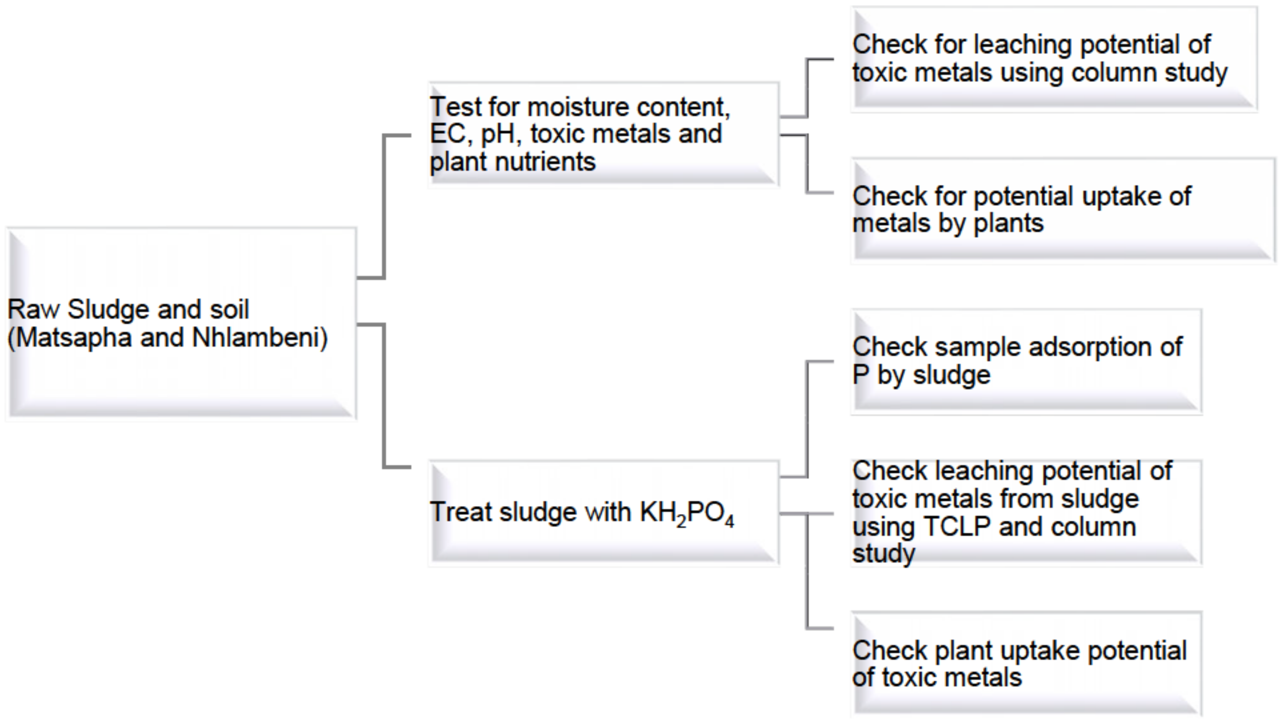

Figure 3. 1:Schematic diagram showing the summary of checking and testing methods used for the study.

3.3.1 Wastewater Treatment Processes for Sampled Sludge

Domestic Wastewater Sludge equivalent to a 25L bucket was sampled randomly from Nhlambeni Wastewater Treatment Plant drying beds. The sample was considered enough for both analysis and further investigations. The

Nhlambeni wastewater treatment plant was commissioned in 2005 and has a capacity of 10ML/day. It has a system that involves screening of solid materials through automated mechanical coarse and fine screens, primary settlement tanks (PSTs) primary biological filters, intermediate settlement tanks (ISTs), secondary biological filters, final settlement tanks (FSTs) and chlorination before release into the environment. The sludge collected from the settlement tanks is transferred to the sludge mixing tank, then to biological digesters where it undergoes anaerobic treatment before being discharged to the drying beds, where filtrate is pumped back to PSTs. Dried sludge is stockpiled in a concrete lined area.

Industrial (Matsapha) Wastewater Sludge was sampled at the discharge point of the belt-press dewatering plant using a clean 25Lplastic bucket. The wastewater treatment process of this plant involves screening of solids through fixed coarse screens and automated mechanical fine screens, biological reactor (with anaerobic, anoxic, and aerobic zones), settlement tanks and chlorination of treated water before release onto the nearby watercourse. Sludge harvested from the biological reactor is transferred to the sludge thickener tank, then to biological digesters to undergo anaerobic treatment. The treated sludge is then transferred to a sludge holding tank where it is pumped to the dewatering plant that uses a belt press system. Discharged sludge is dried and stockpiled on the concrete lined surface.

Four (4) of 25kg sacks were used for collection of soil that was sampled from the EWSC farm. Analysis done in soil are Moisture Content (MC), Electrical conductivity (EC), Heavy metals (HM), and potential of Hydrogen (pH). Analysis done in wastewater sludge are Moisture Content (MC), Electrical conductivity (EC), Heavy metals (HM), and potential of Hydrogen (pH), phosphate sorption capacity, and Toxicity Characteristic Leaching Procedure (TCLP). Further investigations were done through column study, and growing spinach and grass on soil mixed with sludge.

3.4 Description of Data Collection Methods and Analysis

3.4.1 Wastewater (aqueous solution) data

Wastewater effluent data was sourced from the Eswatini Water Services Corporation (EWSC) laboratory archives, from January 2019 to May 2022. In a quest to ensure quality of the wastewater effluent, EWSC takes representative samples daily for quality compliance analysis and keeps monthly records for research development purposes. The 33 months archival data was the only available data considered recent enough to provide sufficient information on the development of heavy metals within the treatment plant. The assumptions considered when collecting this form of data is that the heavy metals present in the untreated wastewater would be transferred to the sludge. The sludge could also present heavy metals that were not detected in the untreated wastewater.

3.4.2 Sampling and analysis of sludge and soil for heavy metals

Soil was sampled from 3 locations of the Eswatini Water Services Corporation (EWSC) farm, using a tractor-loader-backhoe (TLB) back bucket. The samples were mixed onsite to get the representative sample using the TLB bucket.

Industrial sludge (from Matsapha Wastewater) was sampled (in August 2021) fresh from the belt press sludge discharge (SEE Figure 3.3 A and B). The sludge was spread on the floor for a week for air drying (see Figure 3.3E). Two more sludge samples that were discharged and airdried on concrete lined sludge drying bed in January 2021 (see Figure 3.3D) and June 2021 (see Figure 3.3C) respectively. Triplicate samples for each sludge were used for analysis and further investigations.

Figure 3. 2: A: Pressed sludge; B: Pressed wet sludge (August 2021); C: Air dried Sludge (June 2021); D: Air dried sludge (January 2021); E: Air dried sludge (August 2021)

Domestic sludge (from Nhlambeni Wastewater) was also sampled from the dried heap of sludge from sludge drying beds (see Figure 3.4A and 3.4B). The sludge was crushed with car tyres, removed bidum and other dirt and further air dried for heavy metals analysis. All sludge samples were analysed for moisture content, pH, EC, micro and macro nutrients such as Magnesium (Mg), Manganese (Mn), Iron (Fe), Aluminium (Al), as well as for heavy metals such as Zinc (Zn), Arsenic (As), Lead (Pb), Cadmium (Cd), Copper (Cu), Selenium (Se), and Chromium (Cr), among others.

Figure 3. 3: A: Sampled domestic sludge – Nhlambeni WWTP; B: Sampled industrial sludge - Matsapha WTP

3.4.3 Analysis of Wastewater Sludge and Soil Properties (Moisture content, pH, EC, and heavy metals)

Both the sludge extracted direct from the belt press discharge point (Industrial from Matsapha WWTP) and from the drying beds (Domestic from Nhlambeni WTTP) was analysed for moisture content (MC), Potential of hydrogen (PH), Electrical Conductivity (EC) and Heavy Metals.

a) Moisture Content

Extracted moist samples were properly sealed with a lid to prevent any evaporation of moisture and were taken to the University of Eswatini, Luyengo Campus Chemistry laboratory for analysis. Triplicate samples were extracted and weighed, then dried in the oven (at 25ºC) until the dry weight remained constant (which took at most 2 weeks). Moisture Content (MC) was calculated by dividing mass of water with mass of dry sludge using the following equation by Craig, (1983).

$$\% MC = \frac{M_W - M_D}{M_D} x\ 100 \text{ ………………………………………………….. (Equation 3.1)}$$

b) Potential of Hydrogen (pH)

Triplicate sets of samples were analysed for pH in distilled water (H_2O), calcium chloride ($CaCl_2$), and in potassium chloride (KCl). The ratio of soil to waste and soil to both electrolytes was 1:2. The test was conducted with a $CaCl_2$ concentration of 0.01 moles per litre and 1 mole per litre of KCl. The solution was shaken thoroughly for an hour and the pH was measured using an electrode after simmering for 30 minutes (Lake, 2000) Conducting this test was considered essential for this study since the soil pH determines the availability of key nutrients and toxicity of some elements. These solutions were used for determination of the change in pH, which indicates the nutrients that will be absorbed by soils and that available for plant uptake. If negatively charged, it absorbs positively charged nutrients and visa versa.

c) Electrical Conductivity (EC)

Electrical conductivity is one of the critical elements in wastewater. It helps to determine the salinity of the wastewater solution and correlates with the concentration of metal ions in solution (Prieto et al, 2000). The experimental procedure involved a set up light bulb conductivity apparatus (i.e., electrodes, light bulb, electricity plug and a 50 ml beaker where acid digested sample was tested). The electrodes were rinsed thoroughly using distilled water before testing was conducted. The test required the use of rubber gloves as part of the PPE to prevent electricity shocks as the electrodes are plugged into the 100 volts of electricity plug.

d) Heavy Metals and Plant Nutrients

Wastewater sludge was airdried and put in the oven at 25°C temperature overnight for analysis, sieved through a 2mm sieve and digested using sulphuric acid and hydrogen peroxide until all the solids were dissolved. The dissolved sampled was diluted with distilled water up to 250ml, filtered through watman No. 42 filter paper and was taken to EWSC ISO 17025 certified laboratory to determine elements contained through ICP-OES. The method employed for the Model 4300DV ICP-OES tests are extracted from the ISO 11885:2007. ICP-OES is calibrated using multi-elements standards solutions, and the calibration is accepted if the correlation coefficient is greater than 0.995. The accuracy of the equipment is verified using 2mg/L analytical quality control standard which should have concentrations not exceeding ±5%. Triplicate samples of one solution were tested and the results were checked for consistency, odd results were taken out. Elements tested on these samples included Arsenic, Cadmium, Selenium, Aluminium, Chromium, Iron, Lead, Calcium, Magnesium, Manganese, Potassium, and Zinc. The detection limits of the tested elements were taken from American Public Health Association (2005) Standard Methods for the examination of water & wastewater (21st Edition). The ICP-OES equipment is commonly known to have problems such as precision, sample drift, no-ideal detection limits and inaccurate identification (Merson & Avans, 2003; Nizio &Harynuk, 2012; and Jantzi et al., 2016).

3.5 Phosphorus Treatment Analysis

3.5.1 Phosphate sorption capacity

Phosphate sorption analysis was conducted on both Nhlambeni and Matsapha Wastewater sludge (see Figure 3.4). Each sludge sample was air dried, crushed and filtered through a 2mm sieve. Triplicate samples, each weighing six (6) grams were put into a 50ml centrifuge tubes and suspended in 10ml of 2 mmol $CaCl_2$, 10 ml of 1 mmol

MgCl and 10ml of 0.5 mmol of $NaCl_2$ of supporting electrolyte containing 10ml of 0, 50, 100, 250, 500, 1000, and 2000 mg of phosphorus (P) per litre prepared from KH_2PO_4. The tubes were sealed and shaken horizontally end to end at 180 oscillations per minute for 2 hours which was repeated after 24 hours and placed in the oven set at constant temperature (25°C). After 48hours the samples were centrifuged at 2500 revolution per minute for 10 minutes and filtered through Watman No. 42 watman filter paper. Standard P Solutions: 0, 5, 10, 50, 100, 250 mg phosphorus per litre were prepared, read through the spectrophotometer and plotted on the graph. The filtered solutions were then analysed for P using the calibrated spectrophotometer. The amount of P sorbed was calculated as the difference between the amount of P added and the remaining in the solution. The sorption data was then fitted to a linearized form of Langmuir equation. The methos used that described by Essington, (2004).

Figure 3. 4: sludge samples suspended in sorption solution, being shaken and filtered for analysis.

a) Calculations of stock solutions chemicals

Salts solutions elements were read from the periodic table, each element was multiplied by its number of atoms in the molecule. The sum of each element multiplied by its number of atoms in the molecule was also multiplied by the number of moles specified in the phosphate sorption analysis method. For example;

$CaCl_2$

40.08 + (35.453 x 2) = 110.986

2 mmol required, ∴ 110.986 x 2 = 221.97

$MgCl_2$

24.305 + (35.453x2) = 95.211

1 mmol required, ∴ 95.211 x 1 = 95.21

NaCl

22.98977 + 35.453 = 58.44277

0.5 mmol required, ∴ 58.44277 x 0.5 = 29.22

Potassium dihydrogen phosphate (KH_2PO_4) solution was prepared similar to the salts, except that only phosphorus was required in the chemical concentration. Therefore, the stock solution was determined using the following equation by Aryangat, (2012).

$$stock = stock\ concentration\ \left(\frac{g}{L}\right) x\ [\frac{molar\ mass\ \left(\frac{g}{mol}\right)}{n\ x\ atomic\ mass\ \left(\frac{g}{mol}\right)}] \text{ ………………… (Equation 3.2)}$$

Where molar mass is the sum of atomic mass of the chemical, n is the number of moles of phosphorus (P) in a chemical and atomic mass refers to atomic mass of P as per the periodic table.

The stock solution was then diluted using the standard dilution formula as shown Equation 3.3 to determine the volume of chemical concentration that needed to be extracted from the prepared different concentration of P from 0g, 50g, 100g, 250g, 500g, 1000g and 2000g in a 50 ml tube for treatment. These concentrations were used to determine the sorption of P in each sample which indicated the possibility of immobilisation of heavy metal.

$$C_1V_1 = C_2V_2 \text{ ……………………………………………………………… (Equation 3.3)}$$

Where C_1 represents the concentration of phosphorus used on stock solution, V_1 represents the volume of distilled water for dilution on stock solution, C_2 represents the concentration of phosphorus required for treatment, and V_2 represents the volume of distilled water for dilution of required treatment.

3.5.2 Toxicity Characteristic Leaching Procedure (TCLP) and Analysis

This procedure was used as an analysis to simulate the leaching of the elements in the sludge samples by following the State of Connecticut Department of Environmental Protection TCLP, using the sw-846 method 1311 (Connecticut DEP QA/QC Workgroup, 2006). Two (2) grams wastewater solid extracts from the sorption analysis samples were suspended in 40ml of extraction fluid diluted to a volume of 1 litre, consisting of 5.7 ml glacial CH_3CH_2OOH added to reagent water, 64.3 ml of NaOH, with a pH of 4.93±0.05 (Figure 3.6). The tubes were sealed tightly and shaken horizontally at 30 ramps per minutes for 2 hours and stored in the oven set at constant temperature ($25^{0}C$). After 20 hours the samples were filtered through Whatman No. 42 filter paper and analysed for heavy metals using ICP-OES testing equipment.

Figure 3. 5: TCLP samples ready for heavy metals analysis using ICP-OES

3.6 Determination of Heavy Metals Mobility

A greyish sandy loam soil from the EWSC farm was used for this study. A total of 31 hand mixed samples for each analysis were prepared using recommendations by the South African Sludge Management Guidelines, which stipulates maximum application of 10-ton sludge per hectare of soil. This soil was used to plant both spinach and grass.

Mobility of heavy metals was assessed through planting of spinach and grass as well as through leaching on the soil-sludge mixtures representing 5ton, 10ton, 15 ton, and 20 ton of sludge per hectare of soil. Plant uptake through planting spinach This was believed to yield absolute maximum results because leafy vegetables are considered to absorb and accumulate high heavy metals compared to other vegetables (Zhou et al., 2016). Furthermore, bare soil with no plantation is likely to leach more heavy metals.

Soil quantities were determined by the size of the pot or column container. The required sludge was then calculated using the following method;

- The area (A) of sludge application was converted from hectares to square meters, which became 10000 m^2.
- Volume of the soil was calculated using 15cm depth (D), which is a normally estimated ploughing depth. Based on this the volume was calculated using the following equation by Jakins and Yeo, (2013).

$Volume\ =\ A\,x\,D$ (m^3) ……………………………………………………… (Equation 3.4)

Where A is the area and D is the depth

- 10 ton of sludge was converted to kilograms (kgs) by multiplying with 907.185, which became 9072 kgs.
- Volumes of pots and column containers were calculated using the following equation by Jakins and Yeo, (2013).
- .

$$Volume = \pi r^2 h \text{ (m}^3\text{)} \quad \text{(Equation 3.5)}$$

Where r is the radius and h is the height

- Samples were packed in triplicate to represent 0, 5, 10, 15 and 20 sludge per hector. Representative quantities of sludge were interpolated using the following density equation by Craig, (1983).

$$M_{RQS} = \frac{M_{RS}\ x\ V_{RQS}}{V_{RS}} \text{ (grams)} \quad \text{(Equation 3.6)}$$

Where M_{RQS} and V_{RQS} are mass and volume of the representative quantities of sludge and M_{RS} and V_{RS} are mass and volume of recommended sludge per hector.

3.6.1 Plant Uptake Analysis

In general, the pots were packed as per Figure 3.7 to 3.9 below. The spinach was planted in bigger pots which took about 4000 grams of soil whereas the grass was planted in a smaller pot with capacity of 1500 grams of soil. There were 11 samples in total for both spinach and grass cultivation whereby pots were packed with triplicate samples of soil only, sludge only, and 5,10,15,20 tons per hector of soil sludge representative. However, due to financial constrains the treated sludge was only analysed in 6 samples which included both spinach and grass in sludge only, 10 and 20 ton per hector of soil sludge representative (see Figure 3.9).

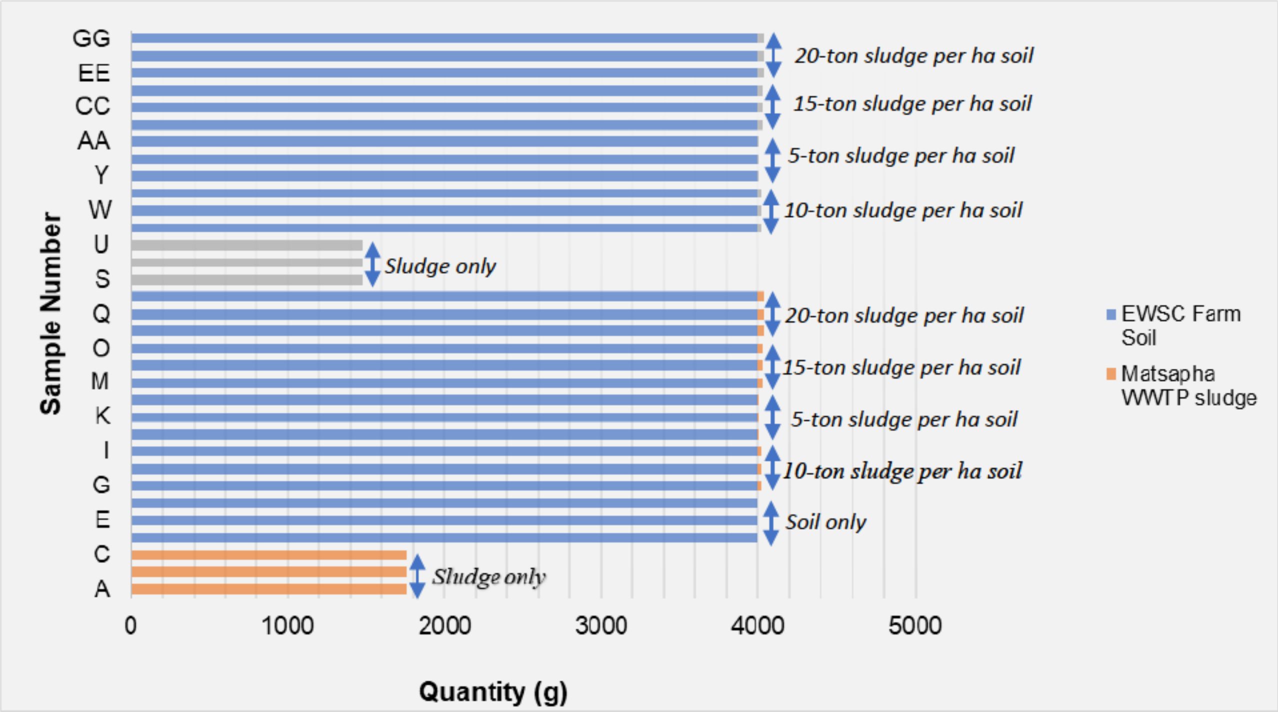

Figure 3. 6: Packing of untreated sludge and soil as per the South African Sludge Management Guidelines for growing spinach.

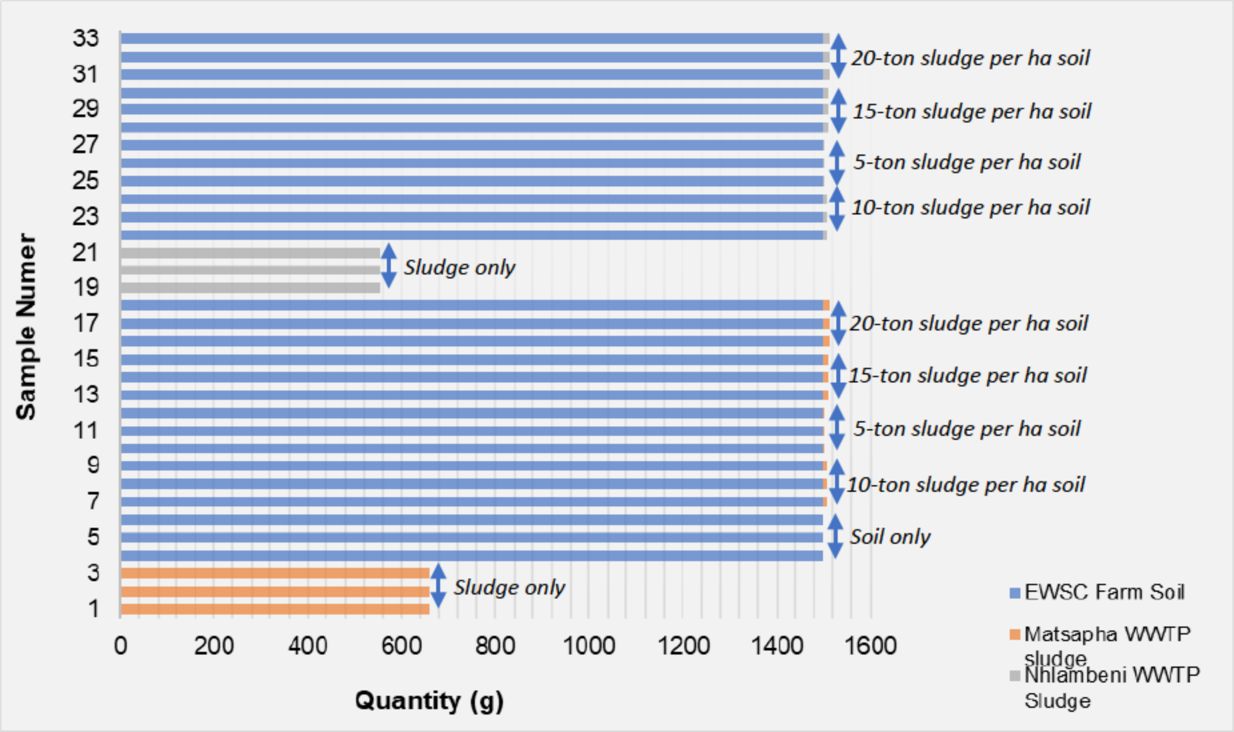

Figure 3. 7: Packing of untreated sludge and soil as per the South African Sludge Management Guidelines for growing grass.

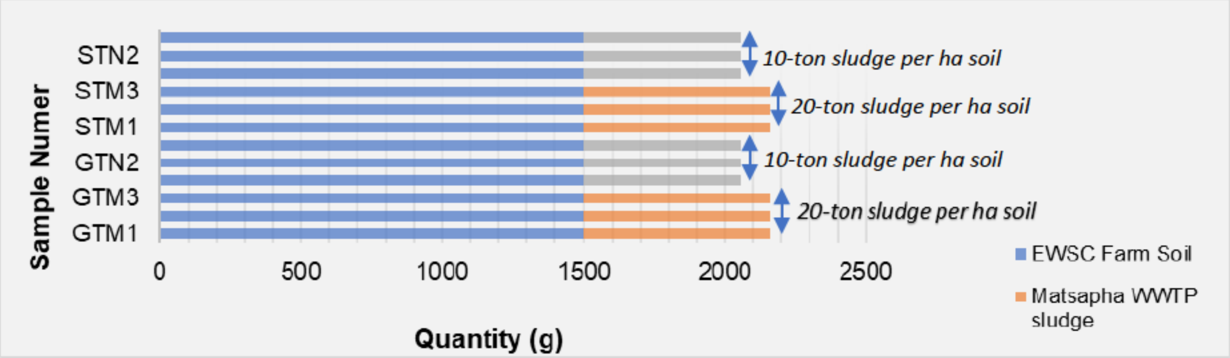

Figure 3. 8: Packing of treated sludge and soil as per the South African Sludge Management Guidelines for growing spinach and grass.

In the absence of a proper green house, the study was conducted in a closed shelter to prevent contamination by rainwater and insects (Figure 3.10). Both the spinach and the grass were measured for growth on weekly basis to determine the most effective treatment for agriculture application. After the spinach and grass stopped growing, they were harvested, dried in the oven, ground into a powder and acid digested (Figure 3.10) for heavy metal analysis using ICP-OES. The results in mg/L were converted to dry mg/kg of plant material.

Figure 3. 9: Spinach and grass and grass being digested using sulphuric acid and hydrogen peroxide grown in a closed shelter.

3.6.2 Leaching Analysis

Packing and leaching of columns containing soil and sludge (treated and untreated) was done as per Figure 3.11. However, only 6 samples which included both spinach and grass with sludge only were used together with mixtures of sludge and soil. Sludge of 10 and 20 ton per hectare of soil sludge representative were analysed for treated sludge. About 2000g of soil was used for each column with corresponding sludge quantities to represent sludge only, 10 and 20 ton per hectare of soil sludge (see Figure 3.12).

The study utilised recycled 2 litre bottles, cut at the bottom and placed in an inverted position (see Figure 3.13). A Whatman No. 42 filter paper was placed at the cone of the bottle to allow filtration through a wire size hole on the lid. In the absence of a proper column study set up, a platform made out of a steel frame and timber surface was built. The timber was drilled with holes of about 10cm diameter to hold the 2L inverted bottles. Another surface below was prepared to place leachate collection bottles, which were taken to EWSC laboratory for heavy metals analysis using ICP-OES.

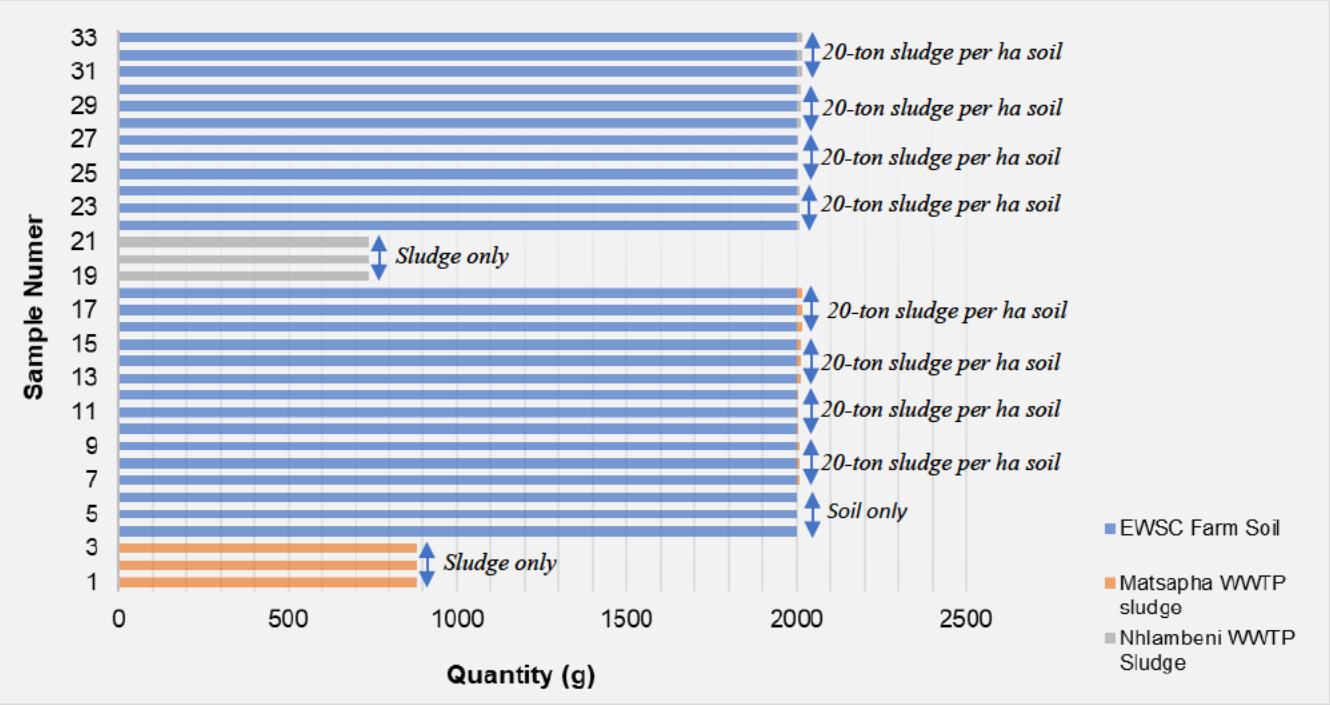

Figure 3. 10: Packing of untreated sludge and soil as per the South African Sludge Management Guidelines for leaching.

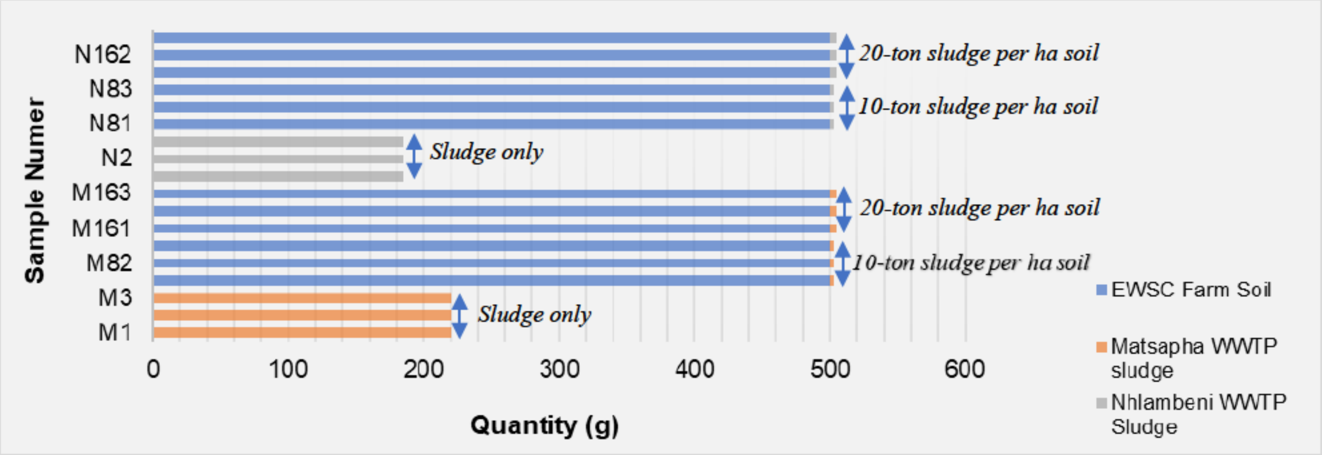

Figure 3. 11: Packing of treated sludge and soil as per the South African Sludge Management Guidelines for leaching.

This test was conducted at the belt-press dewatering plant room where room temperature of 25ºC was maintained. This was done to maintain the pH of the sludge in the mixture, thereby controlling the solubility effect to sensitive elements such as iron (Fe), Aluminium (Al) and Zinc (Zn). The leachate concentration of elements from these samples were compared to acceptable limits published by organisations and countries such as WHO, China, Europe and South African (see Table 2.3).

Figure 3. 12: Column Study Set Up Using Cut 2L Bottles in An Inverted Position.

3.7 Research Limitations

Several limitations were encountered during this study such as ongoing political unrests in Eswatini, financial constraints (to procure chemicals and transport the samples), as well as unavailability of resources. The study area was in Eswatini during the COVID 19 pandemic, where the environmental and cross boarder requirements were almost impossible given the research period. This resulted in using enclosed shelter with clear corrugated iron sheets and a net around to prevent insects for growing on spinach and grass. Column study was conducted using a manmade timber table with holes enough to hold an inverted 2L bottle. This study was conducted in an enclosed dewatering plant house which has a controlled room temperature. Several chemicals were needed to treat the sludge and digesting soil, sludge, grass and spinach as well as for the ICP-OES and plant nutrients analysis. These chemicals procurement took at least 3 weeks as the suppliers were importing them outside the country. Furthermore, the study was labour intensive and mostly clashed with the implementation of capital projects which required more discipline and reprioritisation. Lastly, the study areas were about 20kms apart and the ICP samples were transported from the University of Eswatini to EWSC laboratory which is about 40km travel. Also gaps in data for December 2020, December 2021 for the Matsapha WWTP and December 2020, July-August 2021, December 2021 and April 2021 for Nhlambeni WWTP.

3.8 Conclusion

This chapter started by describing several theoretical procedures that were adopted, which led to the research methodological approach. Raw sludge from Nhlambeni and Matsapha WWTP was sampled, dried, tested for moisture content, pH, EC, nutrients and heavy metals. Both sludge samples were treated with phosphorus (P) from the KH_2PO_4 and the sieved solution tested for adsorption. The treated samples with P were tested for TCLP. Furthermore, the untreated and treated sludge and soil mixture was tested for leaching via column study as well as plant uptake through growing spinach and grass. In consideration of the research question, aims and objectives, the rationale of the research was elucidated. These methods helped to answer the objectives of the study with the aim of establishing the concentration of heavy metals in the local sludge and to improve its potential use in agriculture as a soil amendment.

CHAPTER 4: Results and Discussions

4.1 Introduction

This chapter presents and discusses the results in line with the aim and objectives of the study. It starts with graphical representation of toxic and non-toxic elements as found in the EWSC archival data, the EC, pH, MC and change in pH for both Nhlambeni and Mtsapha WWTP samples, as well as presentation and analysis of toxic and non-toxic metal elements and nutrients.

4.2 Wastewater (effluent) data

The graphic presentation of heavy metals and other chemical elements in the data received from Eswatini Water Services Corporation (EWSC) archives is showing trends of different elements over the period of 33 months as shown in Figure 4.1 to 4.4 below.

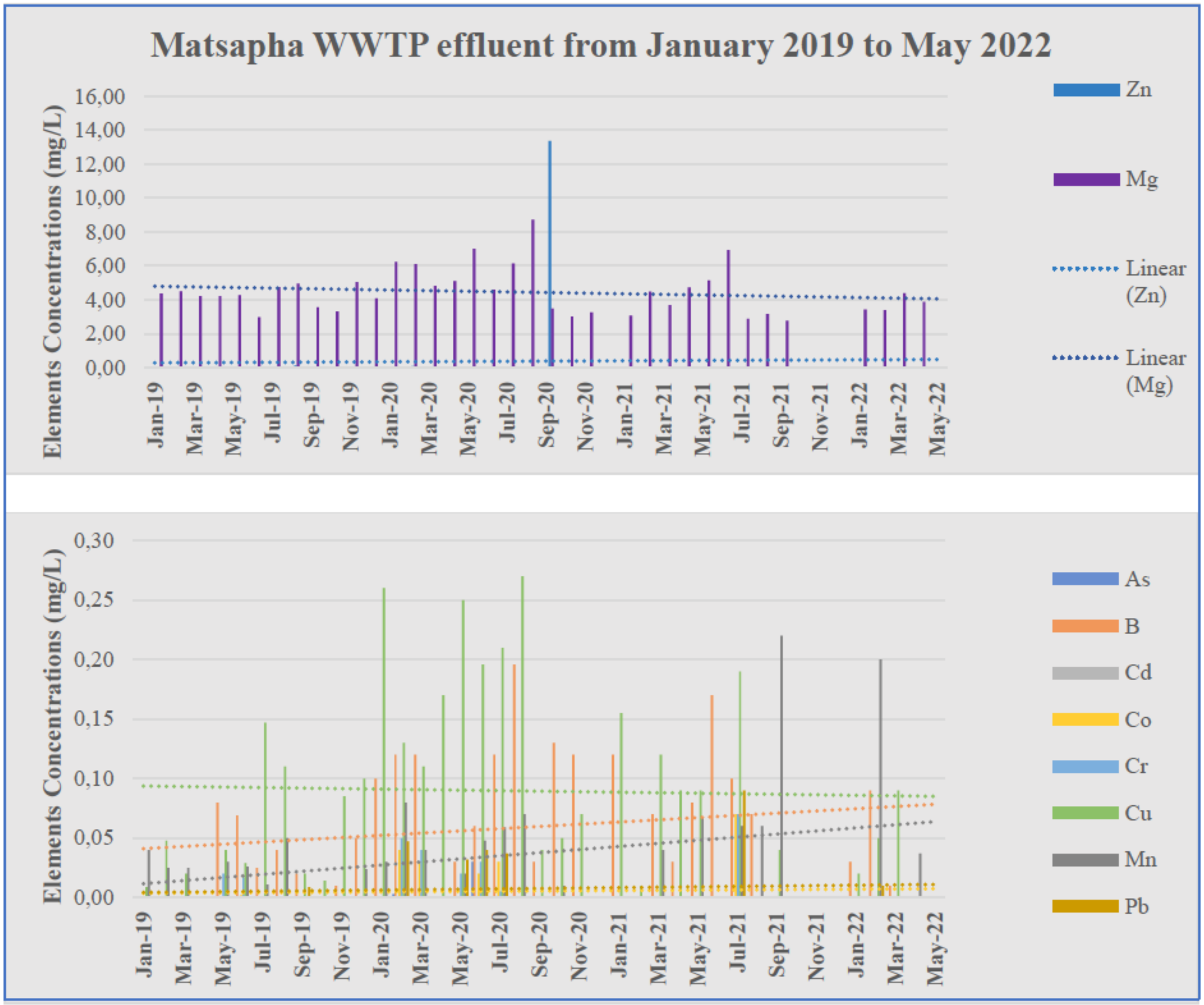

Figure 4. 1: Matsapha WWTP Effluent trends for toxic and nontoxic elements from archival data

This historical data of Matsapha WWTP archives data for key toxic metals indicate that Arsenic (As), Chromium (Cr) and Cadmium (Cd) have been below detection level from January 2019 to May 2022. Other toxic elements like Copper (Cu), Zinc (Zn), Boron (B) and Cobalt (Co) were detected to be at most 1mg/L with a slightly increasing average as shown by linear graph over the 33 months period. However, Zn was detected at about 13.5 mg/L in September 2020 which is above acceptable contamination level of 0.8mg/L (see table 2.4). This could have resulted from an unusual activity from the industries that discharge their water into the Matsapha WWTP.

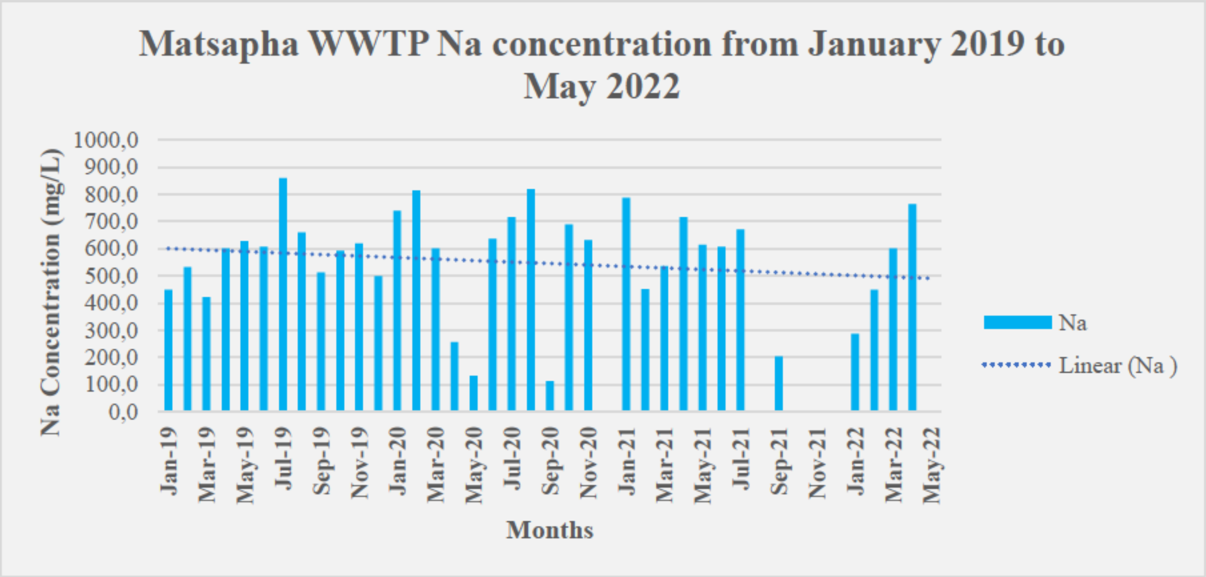

Figure 4. 2: Matsapha WWTP Effluent trends for Na nutrient

Sodium (Na) concentrations ranging between 110 to 850 mg/L were detected between January 2019 to May 2022. However, its overall concentration indicated a decline over the 33-month monitoring period as shown by the linear graph. Sodium (Na) is not a toxic metal however it helps in the concentrate carbon dioxide (CO_2) and some plants use it to promote metabolism (Lake, 2000). Therefore, it is considered as one of the essential nutrients for plants. However, historical data for December 2020, August 2021, October to December 2021, and May 2022 was not available for the Matsapha WWTP. This could mean the tests were not conducted during these months or poor record keeping.

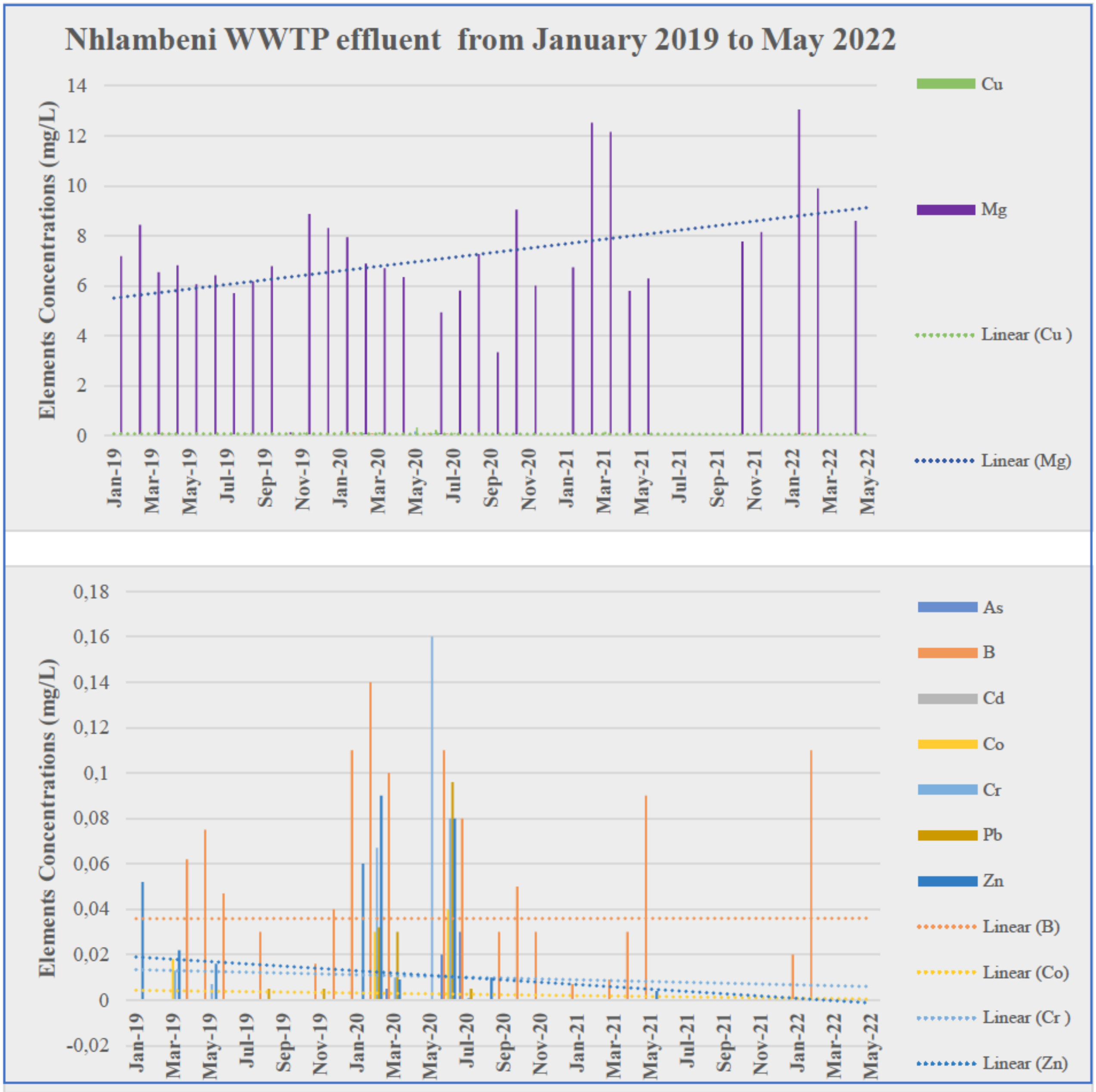

Figure 4. 3: Nhlambeni WWTP Effluent for toxic and nontoxic elements

Like in Matsapha WWTP, Arsenic (As) and Cadmium (Cd) were below detection level from January 2019 to May 2022 for Nhlambeni WWTP. Magnesium (Mg) was detected to a maximum of 13mg/L. Other elements were below 1mg/L, except Zinc (Zn) and Manganese (Mn) that shot up to 0.09 and 6.8 mg/L respectively. This could be resulted from unusual activities from the communities and commercial areas that discharge their wastewater to Nhlambeni WWTP. Zn was within acceptable contamination level of 0.8mg/L as stated in table 2.4 of this study. Mn is a micronutrient required by plants.

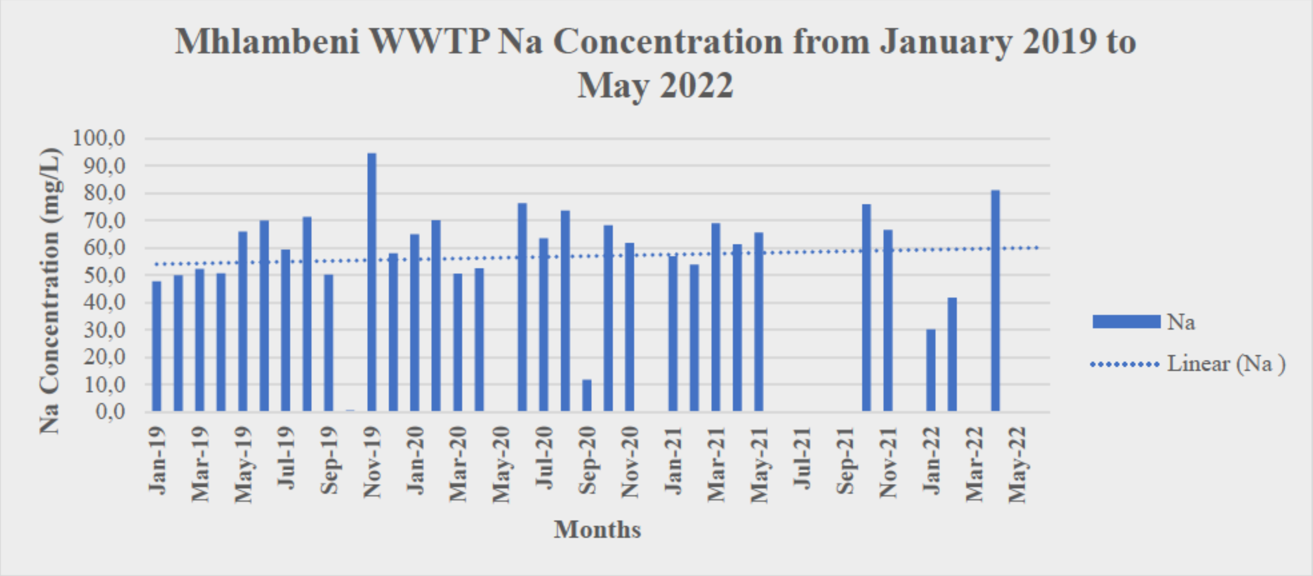

Figure 4. 4: Nhlambeni WWTP Effluent trends for Na element

Sodium (Na) Concentration for Nhlambeni WWTP was almost 10% of the concentrations found in Matsapha WWTP and indicated a linear progression over the 33 months monitoring period. The gaps in the graphs represent missing information in the archives for the months of October 2019; May and December 2020; June, July, August, September and December 2021; and March and May 2022. Like in Matsapha WWTP, the concentrations of Na in the effluent do not indicate a clear trend of concentration.

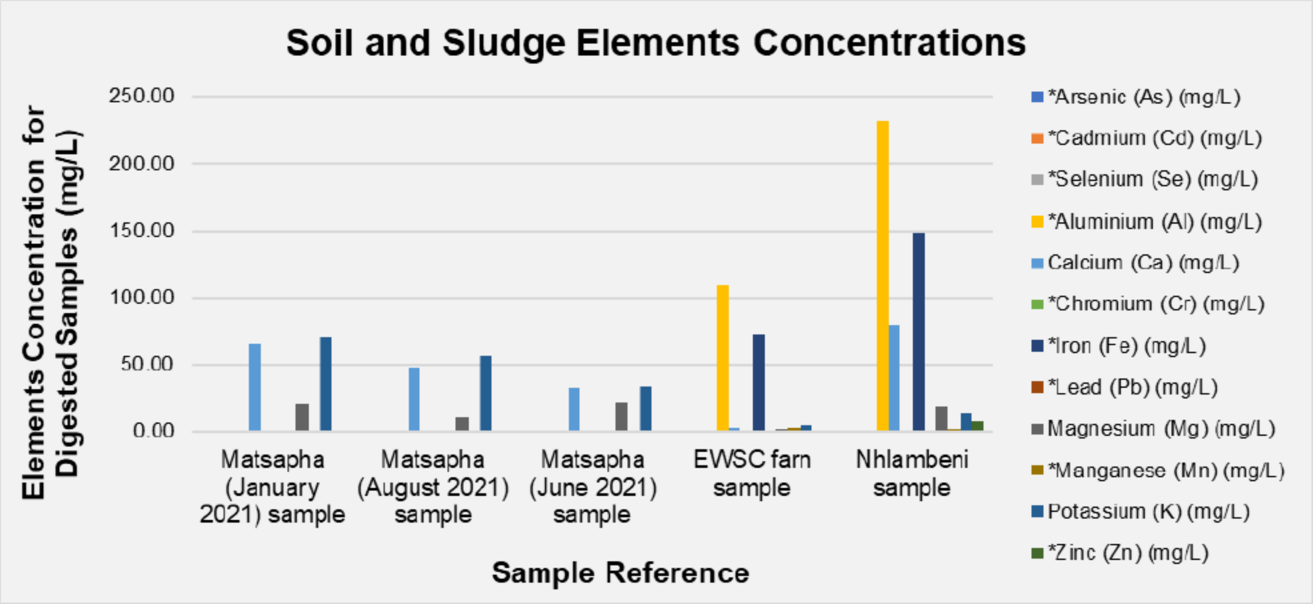

Figure 4. 5: Elements found in Soil, Matsapha and Nhlambeni WWTP Sludge Samples.

The graph (see Figure 4.5) presents total elemental content detected through acid digestion of the EWSC farm soil and sludge from Matsapha and Nhlambeni WWTPs. The results confirmed the finding by (Gupta et al., 2020b) that the wastewater sludge has more concentration of contaminants. Figures 4.1 and 4.3 indicate that Zn, Pb, As, Cd, B, Cr, Cu, Co elements, and nutrients such as Fe, Mg, Mn were detected to be below 14mg/L for both Matsapha and Nhlambeni WWTPs aqueous solutions. However, the same elements and nutrients appear to be higher in concentration with Fe detection of almost 150mg/L for Nhlambeni WWTP sludge. Lake, (2000) reported that at low pH (from 1 to 4) elements such as Fe, Al and Mn strive with a possibility of becoming toxic to plants when exceeding limits as shown in Table 2.5. However, it should be noted that such increase from micro-nutrients (i.e., Fe, Al, Mn) cannot be attributed by acid used to digest samples since the blank was included to eliminate all contributions by the chemicals used.

4.2.1 Wastewater Sludge and Soil Properties (Moisture content, pH, EC, and heavy metals)

The soil and sludge properties, i.e., pH, Electrical Conductivity (EC) and Moisture Content (MC) from Eswatini Water Services (EWSC) Farm (Located in Matsapha) and Nhlambeni and Matsapha Wastewater Treatment Plants were computed from the experimental data conducted in the laboratory (see Table 4.1). The pH data conducted in salts (i.e., Calcium Chloride and Potassium Chloride) and in water indicated all samples to be acidic. Preferable pH for optimum crop productivity is between 5.5 and 7.5 (Oshunsanya, 2018). In accordance with the United States Department of Agricultural National Resources Conservation Service, the soil samples are classified as having a very strong acidity (i.e., pH range from 4.5 to 5.0), Nhlambeni Wastewater sludge being extremely acidity (i.e., pH range from 3.5 to 4.4), and Matsapha Wastewater sludge ranging from very strong acid to strong acid (i.e., pH range from 5.1 to 5.5). Therefore, all samples have high potential to impede nutrients availability for plants and provoke excessive increase in other elements such as Al and Mn to toxic levels.

The change in pH (ΔpH) determined for soil and Nhlambeni Wastewater indicate negative charge of the oxide system, whereas the Matsapha Wastewater sludge indicated positive charge on the surface of the oxide system. If negative then it will adsorb positively charged nutrients (Ca, K, Mg) and if positively charged then it will adsorb negatively charged nutrients (N, P). This means the Nhlambeni WWTP sludge, and farm soil as shown in Table 4.1 has the potential to absorb and retain macro nutrients such as Ca, K and Mg against leaching to the environment and will be available for plant uptake since they are exchanged with those in the soil solution taken up by plant roots (Ukiwe, 2008). Matsapha WWTP sludge and Soil have the potential to adsorb macronutrients like N and P (see Table 4.1) and Matsapha WWTP sludge has a potential to adsorb macronutrients such as Ca, Mg and K.

Moisture content was only conducted on the Matsapha WWTP sludge which indicated approximately 31% for the sludge taken direct from the dewatering plant discharge system in August 2021, about 14% for the sludge that was discharged in June 2021 and about 6% moisture content for the sludge extracted in January 2021 (Table 4.1).

Table 4. 1: Properties of soil and sludge samples

Sample Reference	pH ($CaCl_2$)	pH (KCl)	pH (H_2O)	ΔpH	EC (mS/m)	MC (%)
Soil	4.96	4.25	4.87	-0.63	24.90	
Nhlambeni WWTP Sludge	4.25	4.16	4.39	-0.23	24.23	
Matsapha WWTP Sludge (A)	5.13	4.85	4.66	0.18		5.92
Matsapha WWTP Sludge (B)	5.33	4.62	4.51	0.11		31.45
Matsapha WWTP Sludge (C)	5.82	4.13	4.03	0.10		14.35

Note: EC = electrical conductivity; MC = Moisture content, pH = Potential of Hydrogen

Other properties such as heavy metals for the soil and sludge samples from Matsapha and Nhlambeni Wastewater Treatments Plants are presented in Figure 4.6 to 4.8.

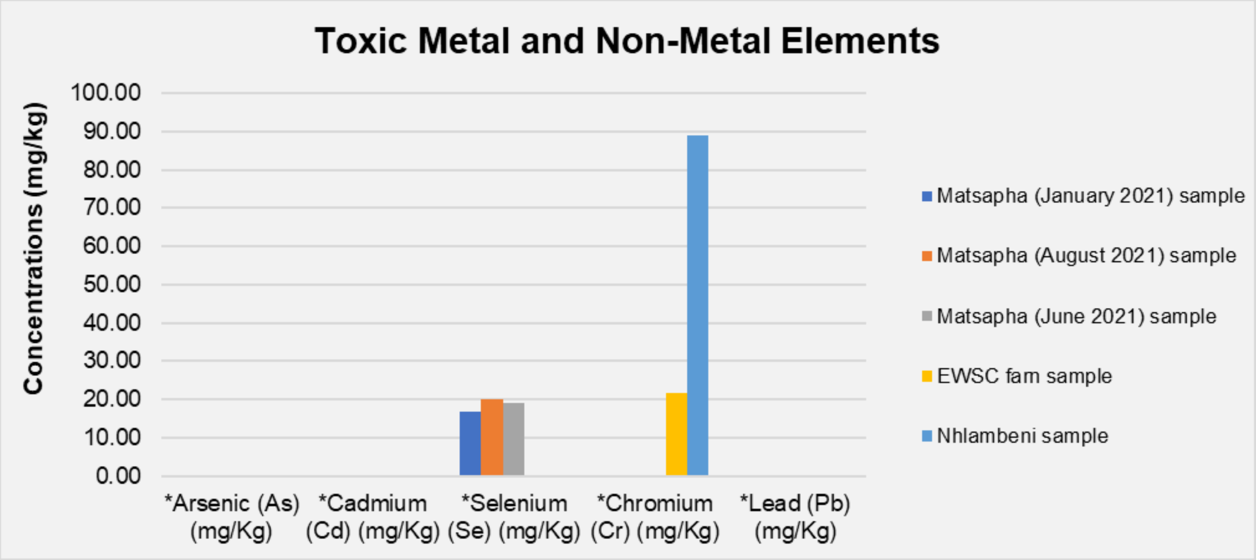

Figure 4.6: Toxic and non-metal elements found in digested sludge (from Matsapha and Nhlambeni WWTPs) and soil in mg/kg.

Acid digestion of the EWSC farm soil and sludge from Matsapha and Nhlambeni wastewater indicate that As, Cd and Pb were below detection level. Also, Cr indicated below detection for Matsapha WWTP sludge. Matsapha WWTP Se and Cr were detected at about 20mg/kg and 90mg/kg respectively. These detection levels are below WHO, China and South Africa legislated thresholds. However, their availability for plant update is not known. Therefore, treatment of the sludge samples was conducted to determine the effectiveness, considering that over time the detected elements may accumulate and increase concentrations to toxic levels.

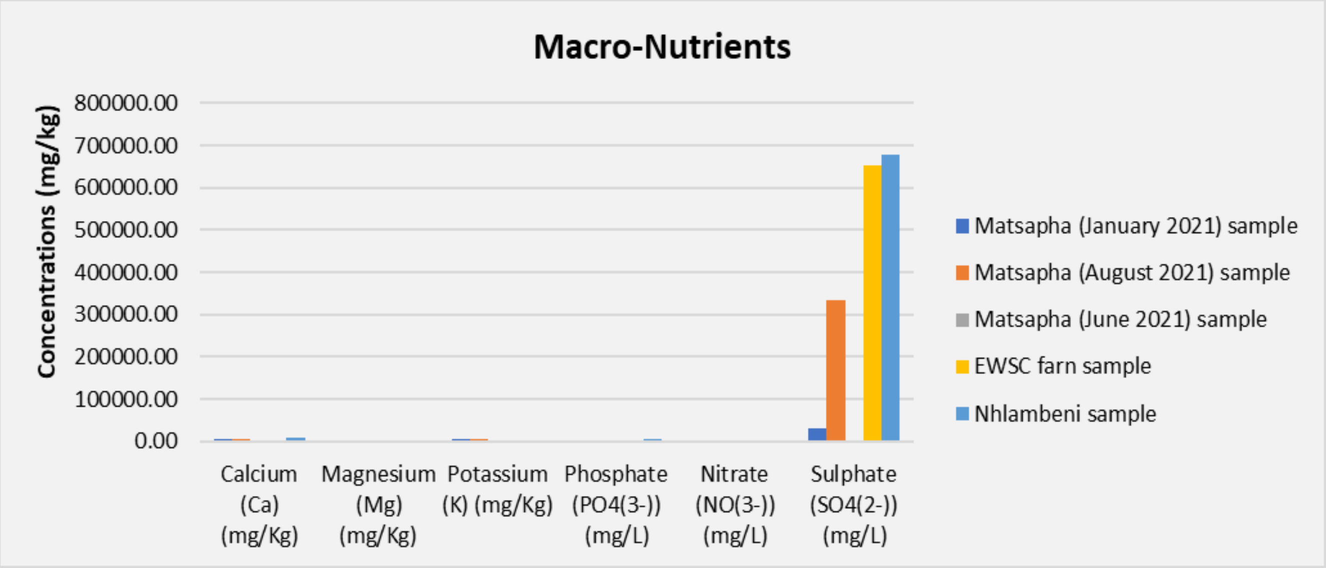

Figure 4. 7: Macro-Nutrients found in digested sludge (from Matsapha and Nhlambeni WWTPs) and soil in mg/kg.

Macro-nutrients were detected in sludge sampled in different periods from the Matsapha WWTP, Nhlabeni sludge and EWSC soil. It was therefore evident that the wastewater sludge had a potential to be used as soil amendment or fertiliser. However, the Suphate was found to be in excess compared to the required Sulfur concentration required to imrove the quality of crops (see table 2.5).

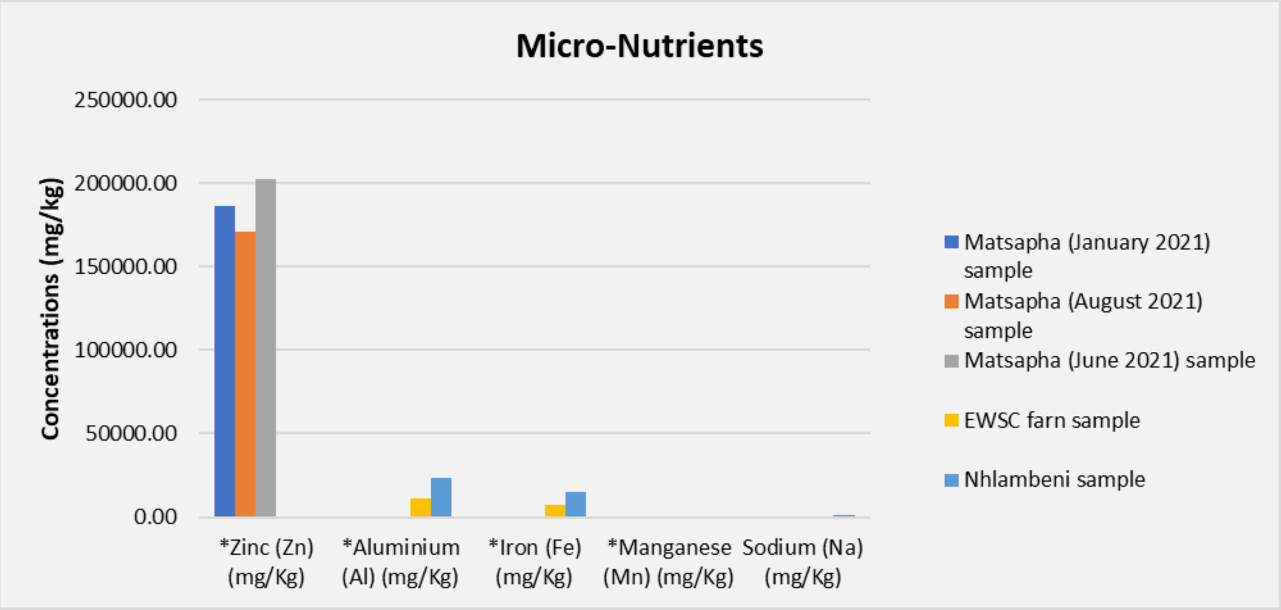

Figure 4. 8: Micro-Nutrients found in digested sludge (from Matsapha and Nhlambeni WWTPs) and soil in mg/kg.

Micro-nutrients were detected in all sludge samples and soil. This means the plants may thrive but would require careful monitoring of micro-nutrients increase in concentration since both the soil and the sludge samples from treatment plants indicated to be acidic in nature. Matsapha WWTP Zn was detected to be high and exceeds legislation thresholds set by China, Europe, USA and South Africa in table 2.3 of this study. As much as the legislation recommends other modes of disposal to agriculture, the sludge samples were treated with P to immobilize the availability of Zn which appears to be extreme compared to thresholds in table 2.3 of this study. The percentage of the available Zn for plant uptake and leaching is not known.

4.3 Phosphate Sorption Capacity Results

The graphical representations of Phosphate Sorption Capacity for phosphorus treated sludge samples at different concentrations for Nhlambeni and Matsapha Wastewater sludge samples used in the study is shown in Figure 4.9.

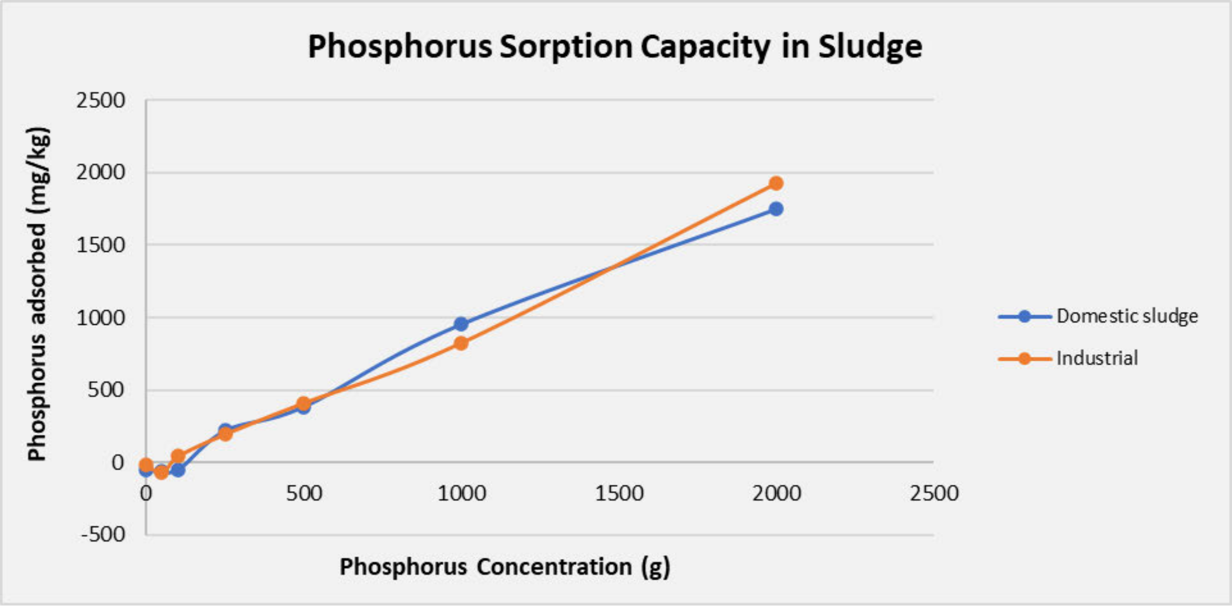

Figure 4. 9: Phosphorus Sorption Capacity in Matsapha and Nhlambeni Wastewater Treatment Plant

The treatment of sludge samples shows that the Matsapha WWTP sludge adsorbed phosphorus at 100-grams concentration, whereas Nhlambeni WWTP sludge adsorbed phosphorus at 250-grams. This indicates a high possibility of immobilization of heavy metals at the absorbance concentration.

4.4 Toxicity Characteristic Leaching Procedure (TCLP) and Analysis

Absorbance was further verified through a TCLP analysis and presented graphically in Figure 4.10. The TCLP results conducted on different concentrations of Phosphorus (P) indicated that the toxic metal and non-metal were immobile when acid washed with acetic acid. This procedure simulates the reactions of these elements on the ground.

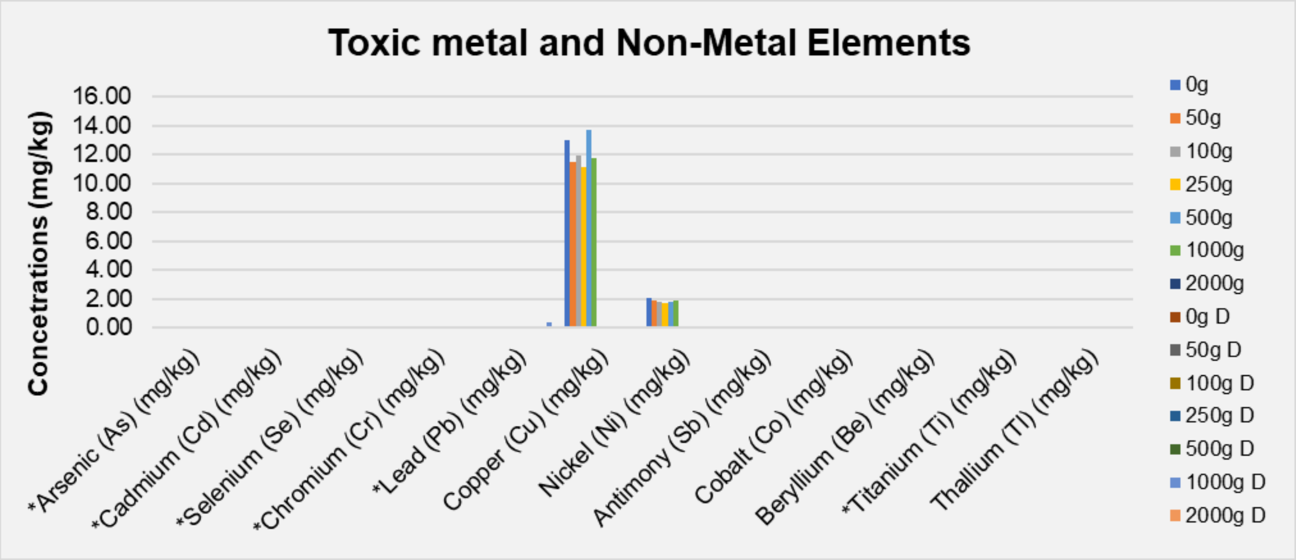

Figure 4. 10: Toxic metal and non-metal elements extracted using the TCLP for Matsapha and Nhlambeni WWTPs

It is worth mentioning that Cu was still detectible at between 11 and 13.8mg/kg and Ni was below 2mg/kg. Cu and Ni detection levels were significantly below threshold set out by USEPA, WHO, China, Europe, and South Africa. However, the availability for plant uptake is not ascertained by the proceedure. Therefore, acid digested grass and spinach planted on untreated and treated sludge was analyzed (see Figure 4.14, 4.17 and 4.20).

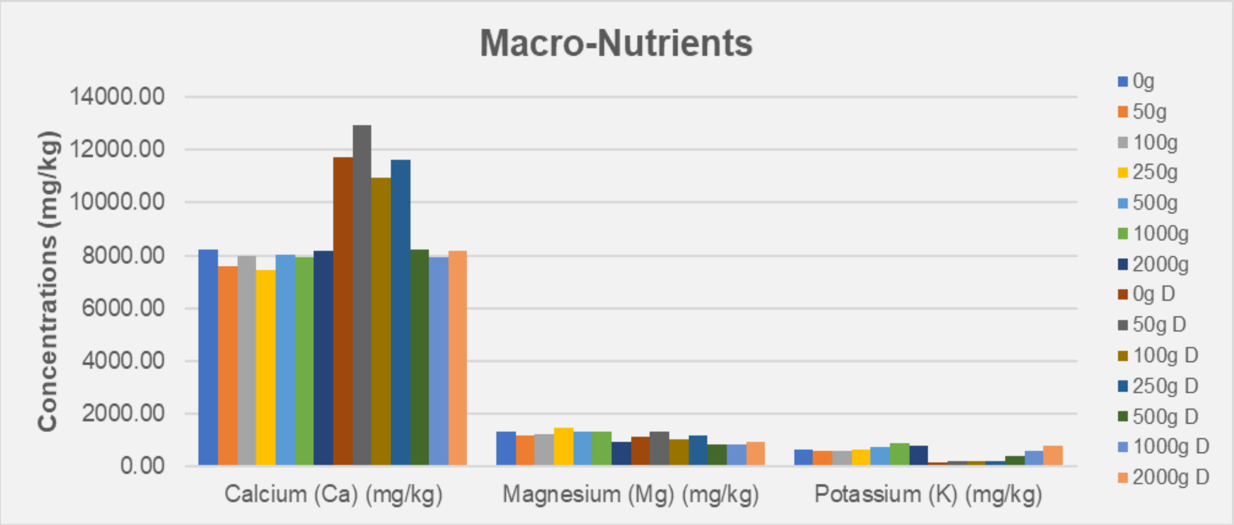

Figure 4. 11: Macro-nutrients extracted using the TCLP for Matsapha and Nhlambeni WWTPs

Calcium (Ca) concentrations ranged from about 7500 to 12900mg/kg which is above 5000mg/kg required for plant growth (see Figure 4.11). Both magnesium (Mg) and Potassium (K) were detected below 2000mg/kg, which is below 2000mg/kg and 10000mg/kg required for plant growth respectively (Johnson & Mirza, 2020). It is noted that the concentrations of macro-nutrients under TCLP analysis increased compared to acid digested samples.

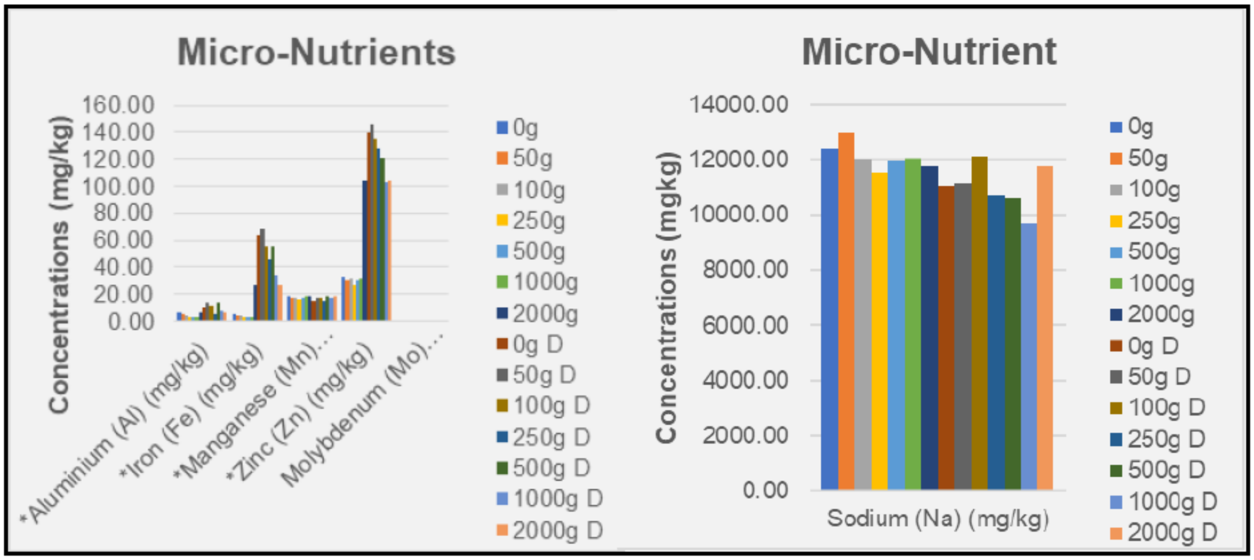

Figure 4. 12: Micro-nutrients extracted using the TCLP for Matsapha and Nhlambeni WWTPs

Micro-nutrients indicate that the availability of Zn ranges from 29.71mg/kg to 104.73mg/kg for Matsapha WWTP treated sludge and from 134.80mg/kg to 103.29mg/kg for Nhlambeni WWTP P sludge (see Figure 4.12). These concentrations are above 20mg/kg required for plant growth and below sludge toxicity thresholds set up by USEPA, WHO, China, Europe and South Africa. When comparing the Zn TCLP results with the original acid digested samples, Matsapha WWTP sludge shows optimum treatment at 250g of P, with 89.00%, 88.57%, 90.33%, 88.74%, 88.44%, 61.21% immobilization on samples treated with 50g, 100g, 250g, 500g, 1000g, and 2000g of P respectively. Nhlambeni WWTP sludge indicated optimum treatment at 1000g of P, with 98.19%, 98.34%, 98.42%, 98.52%, 98.73, and 98.71% immobilization on samples treated with 50g, 100g, 250g, 500g, 1000g, and 2000g of P respectively. Other micro-nutrients such as Al, Fe, Mg, Mo and Na were detected at values not exceeding 17, 67,19, 0 and 12900 mg/kg. This confirmed that the treatment does not negatively affect availability of plant nutrients.

4.5 Plant Uptake Analysis

Determination of plant uptake was measured by the growth of spinach and grass planted on the untreated sludge mixed with farm soil. The height of the grass and spinach were measured weekly, recorded and presented graphically (see Figure 4.13).

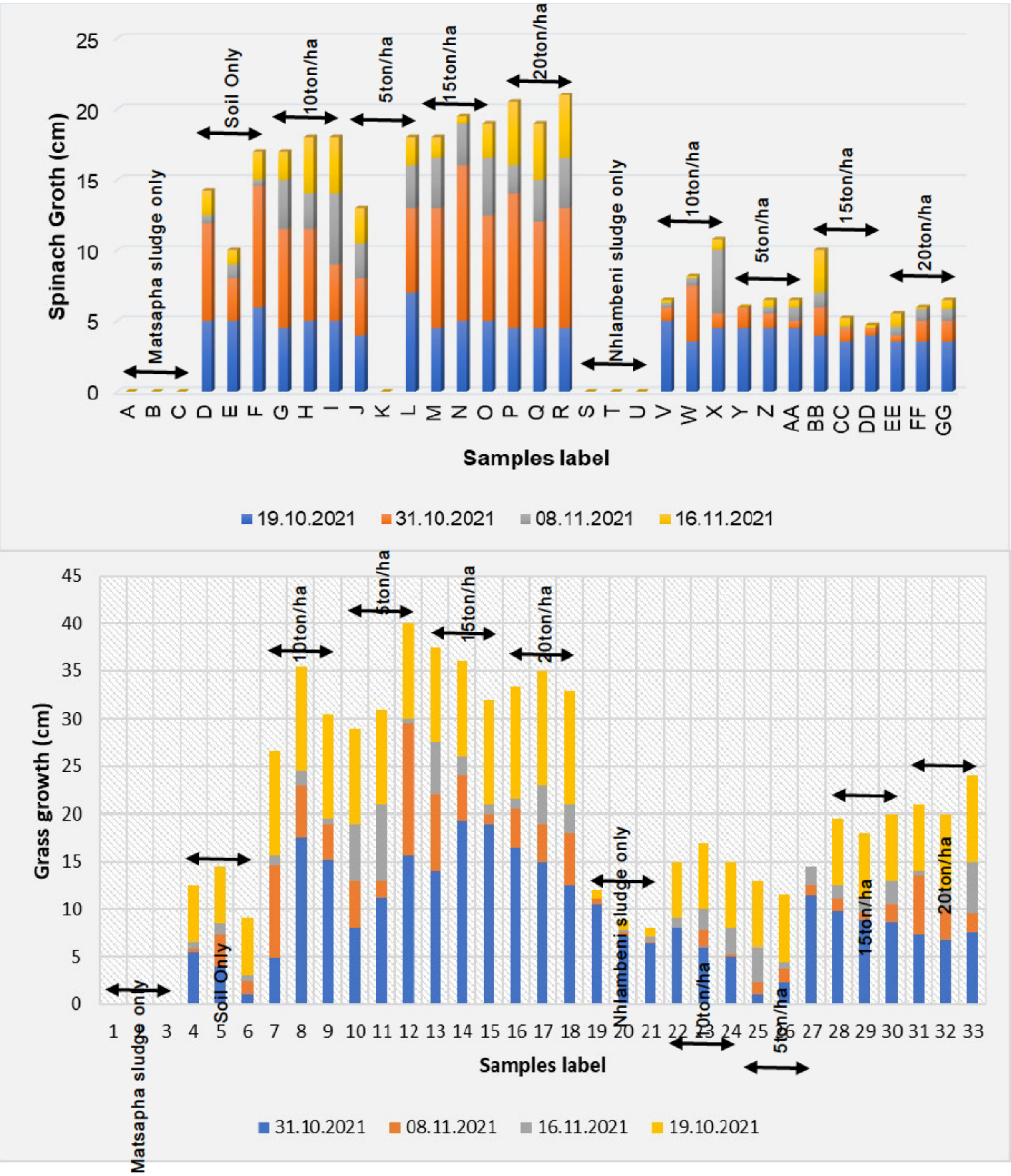

Figure 4. 13: Graphical presentation of spinach and grass grown on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) at different quantities.

The spinach and the grass seeds planted on Nhlambeni WWTP sludge only took about 2 weeks to geminate and dried out after a few days. The spinach and the grass seeds planted on Matsapha WWTP sludge only did not grow at all. This means that as much as both treatment plants sludge samples have nutrients, the acidic nature of the sludge samples defeats the purpose of growing plants on sludge only. Spinach samples grown on soil and sludge mixture indicated to be more productive at 20 tons of sludge per hectare soil for Matsapha WWTP sludge and more productive at 10 tons of sludge per hectare soil for Nhlambeni WWTP. Growing grass on soil and sludge mixture proved to be more productive on 15tons of sludge per hectare soil for Mtsapha WWTP and 20 tons of sludge per hectare soil for Nhlambeni WWTP. Further toxicity uptake analyses of spinach and grass planted on the mixture of soil and sludge are presented in Figure 4.14 to 4.19.

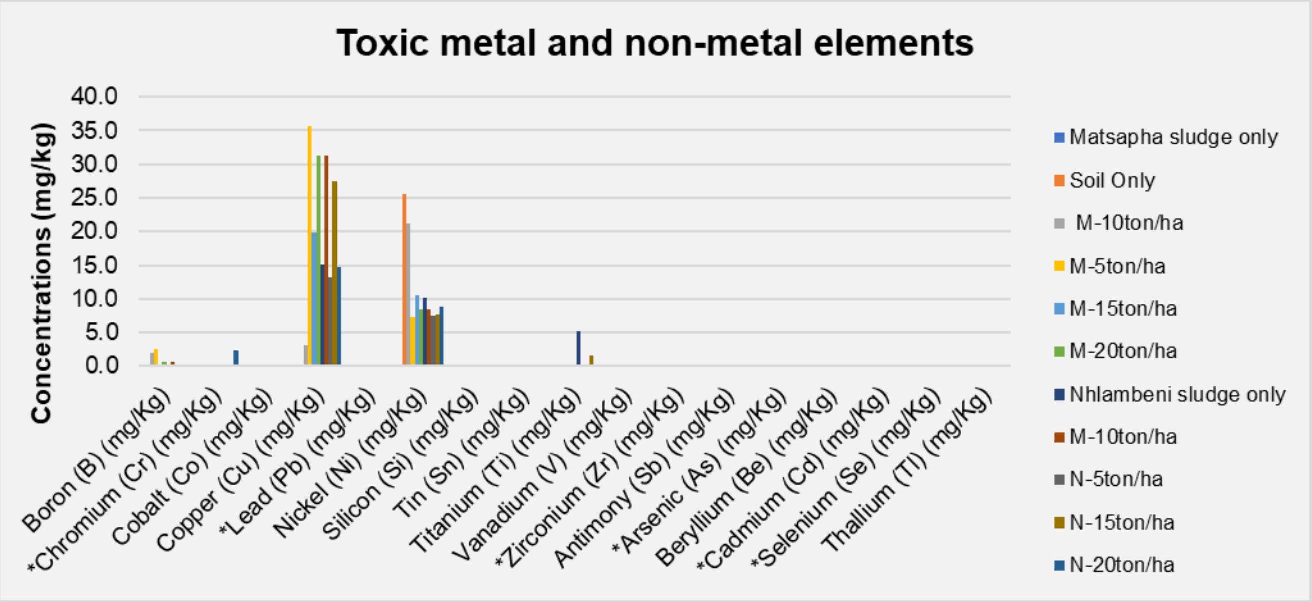

Figure 4. 14: Toxic metal and non-metal elements found in digested spinach planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

Mixture of soil and untreated sludge indicated an uptake of some metals. Availability of key elements indicated Cr at about 2.4mg/kg for Nhlambeni sludge only, Copper (Cu) between about 2.5 and 35.5 mg/kg and Ni between about 7.4 and 25.5mg/kg for both Matsapha and Nhlambeni at different soil-sludge mixture. Chromium detected at Nhlambeni WWTP spinach sample exceeded the legislated 1.3 mg/kg by WHO on plants and 0.5mg/kg by China on leafy vegatables. Chromium exceeded 10 mg/kg thresholds by WHO and China for plants and leafy vegetables respetively, except Mastapha sample of 10ton of sludge per hactare soil mixture which was withing limits. Nickel detection at Matsapha spinach sample met the legislated requirements by WHO of 10mg/kg for plants whereas Nhlambeni Ni detection exceeds the WHO legislated limits. This expresses the need for treatment of sludge before use for agricultural purposes. Other elements of not importance as produced by the ICP-OES were presented to indicate their concentrations.

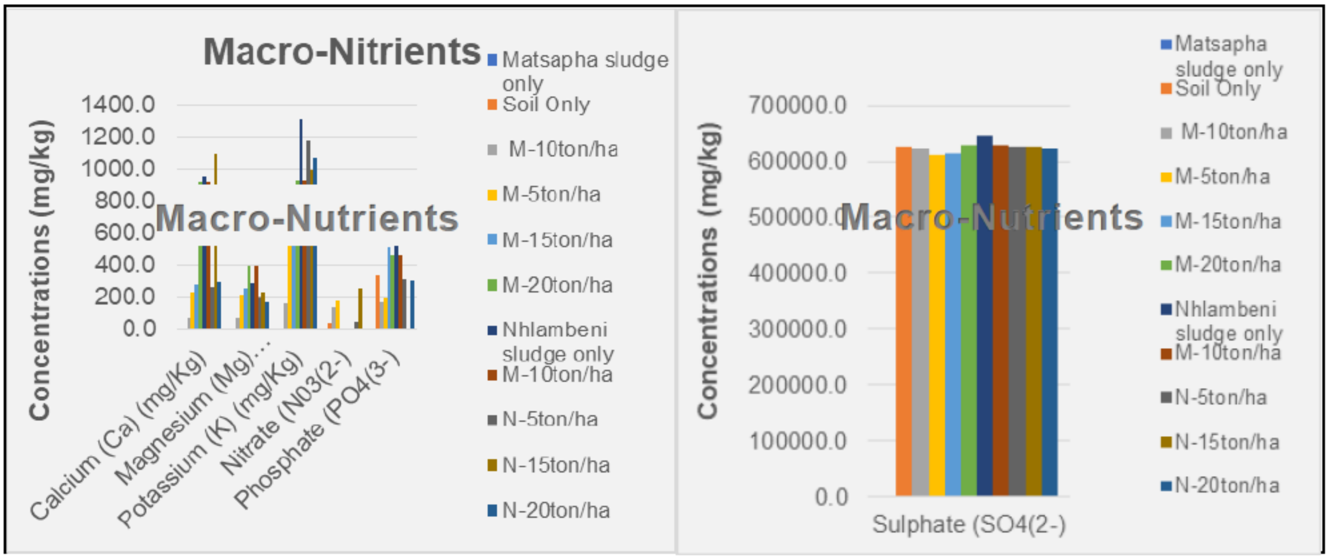

Figure 4. 15: Macro-Nutrients found in digested spinach planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

Macro-nutrients which are essential for plant growth and were detected in acid digested spinach (see Figure 4.15). This meant that the macro-ntrients on the solid mixture were sufficient for spinach growth and available for uptake. Moreover, sulphate detection exceeded requirements of 1000mg/kg of Sulphur (S) for plant frowth.

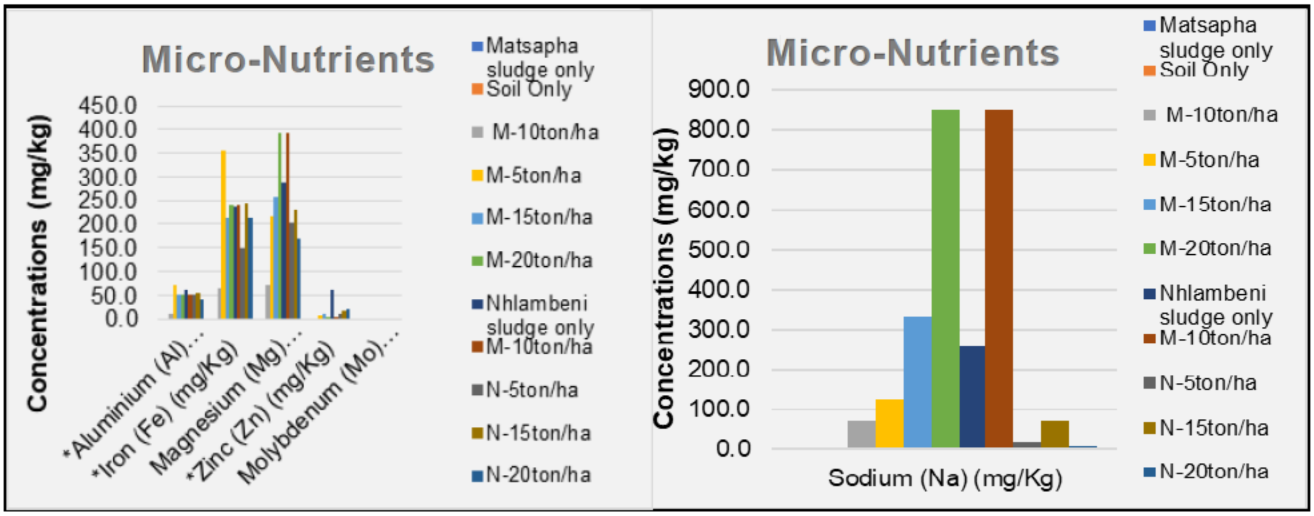

Figure 4. 16: Micro-Nutrients found in digested spinach planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

The micro-nutrients graphs indicate that the spinach absorbed the nutrients (see Figure 4.16). However, Zn detection for Nhlambeni WWTP sludge only exceeded legislated limits for WHO and China of 0.6 and 20 mg/kg respectively. Zinc detected on all other mixtures only WHO threshold. As much as it is needed for plant growth (see Table 2.5), it could also cause damage to fetal brain, disease of the kidney, circulatory system, and nervous system (see table 2.4).

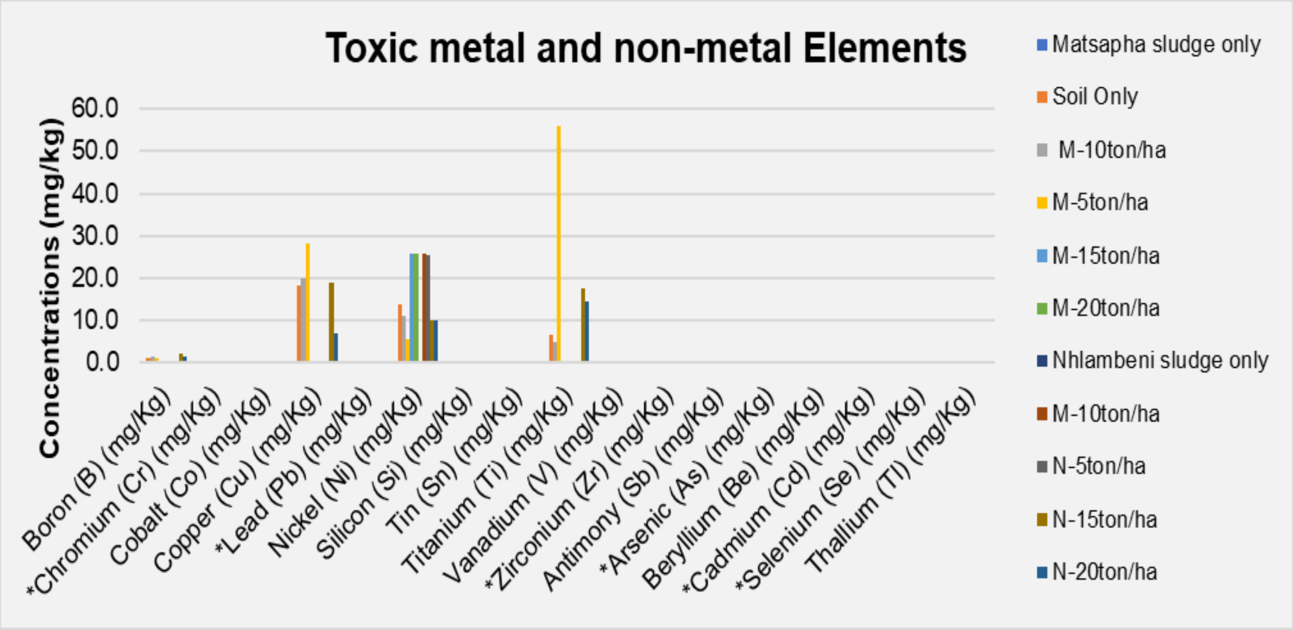

Figure 4. 17: Toxic metal and non-metal elements found in digested grass planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

Availability of key elements in grass indicated Cu to be between 6.5 and 28 mg/kg and Ni to be between 5 and 25 mg/kg for both Matsapha and Nhlambeni in different soil-sludge mixtures. Cu exceeds 10 mg/kg thresholds by WHO and China for plants and leafy vegetables respetively, except Nhlambeni sludge only sample which was withing threshold limits. Ni detection on acid digested grass for Matsapha indicated only 5 ton of sludge per hactare soil sample that meets the legislated requirements by WHO of 10 for plants whereas Nhlambeni Ni detection only meets legislated limits by WHO on 15 and 20 tons of sludge per hectare soils samples.

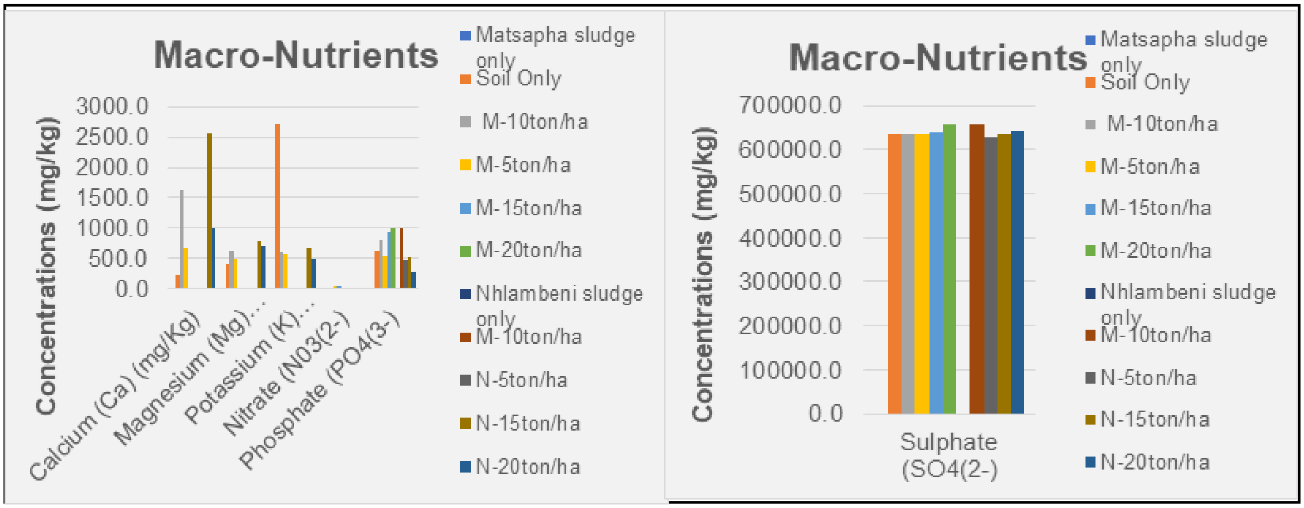

Figure 4. 18: Macro-Nutrients found in digested grass planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

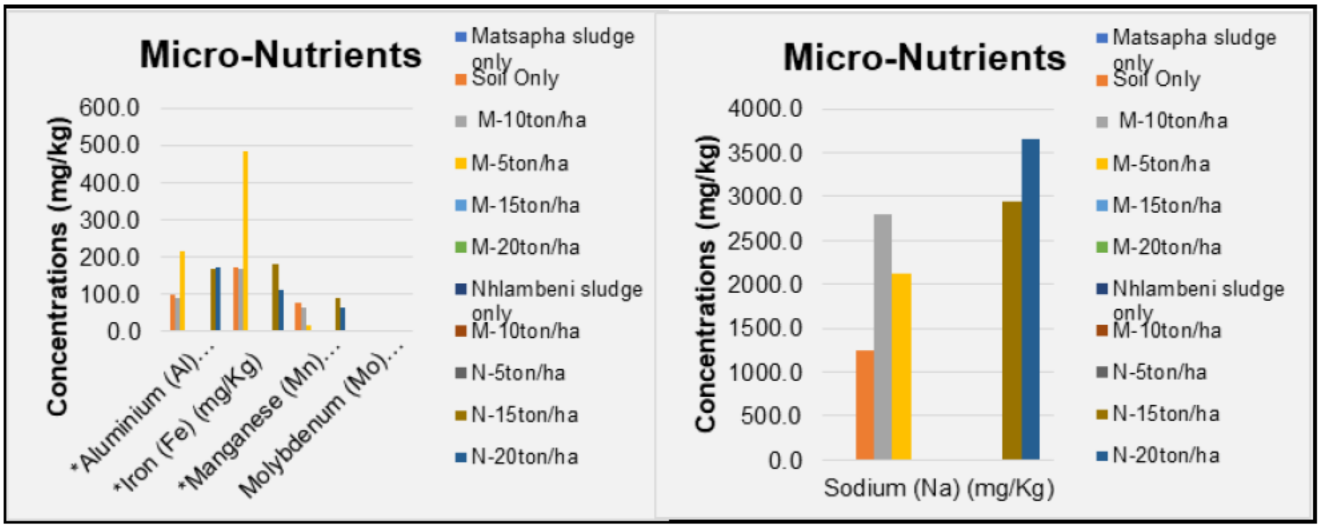

Figure 4. 19: Micro-Nutrients found in digested spinach planted on soil mixed with untreated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

Macro and micro-nutrients were detected in acid digested grass (see Figure 4.18 to 4.19). It is noted that soil only samples have the least nutrients. The soil samples mixed with different wastewater sludge rates show an increase in nutrients, even though the percentage is minimal. However, Fe detection levels were found to exceed the threshold of 100mg/kg required for plant growth. This may require further assessment to determine the availability of Fe for plant uptake.

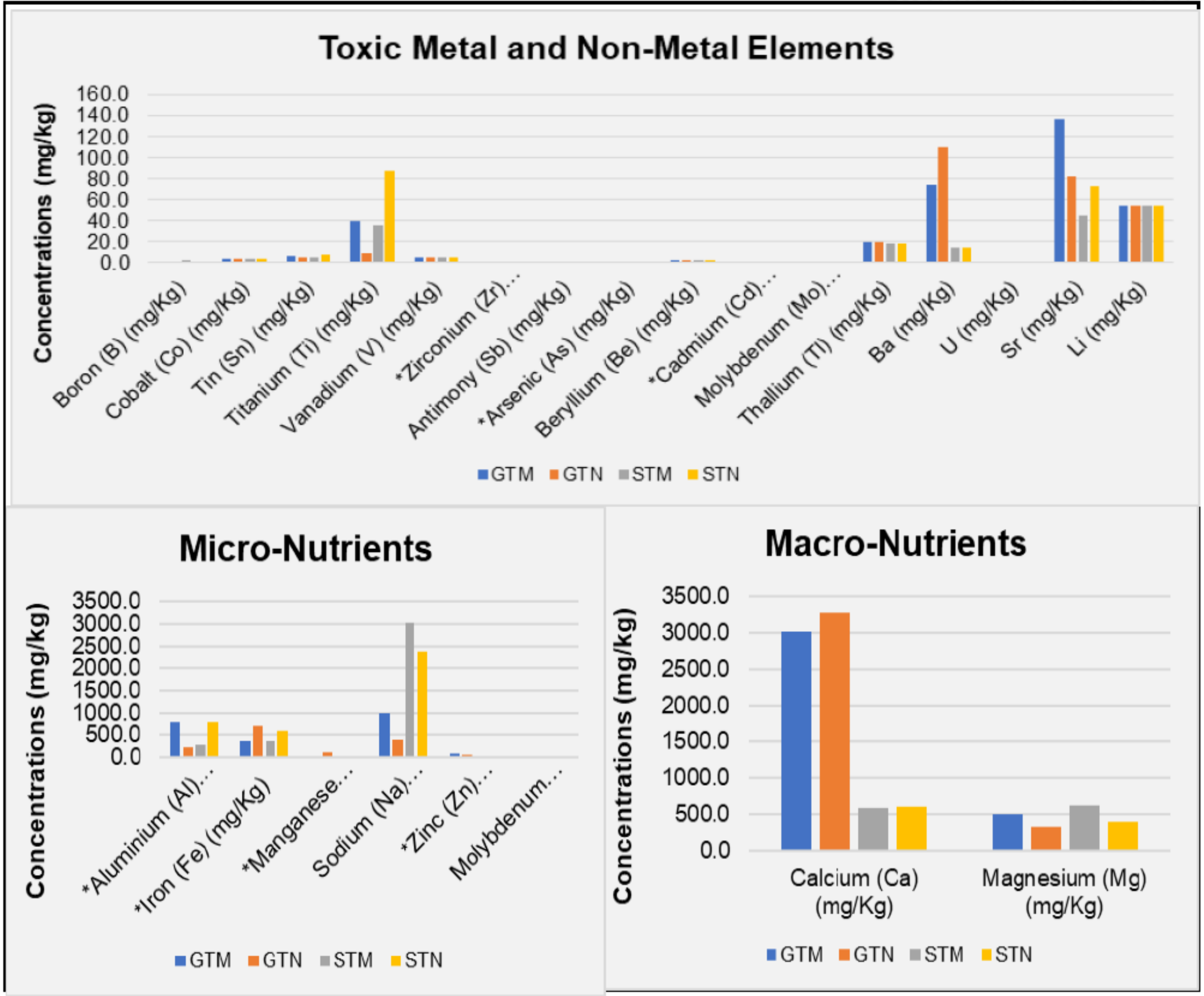

Figure 4. 20: Toxic metal and non-metal elements, Macro and Micro-Nutrients found in digested grass and spinach planted on soil mixed with treated sludge (from Matsapha and Nhlambeni WWTPs) in mg/kg.

The results of both spinach and grass planted on treated sludge (see Figure 4.20) indicated increase in macro-nutrients and significant immobilisation of heavy metals. Zinc was immobilised to acceptable limits for consumption. Micro-nutients like Fe and Al indicated an increase which could require more monitoring and modification of treatment. Soil and sludge used to plant spinach and grass have shown to be acidic. The reaction of micro-nutrients (such as Al, Mn and Fe) with acid could result in increased concentrations to toxic levels.

4.6 Column Study Analysis

The leachate from the column study indicated that elements such as Cr, As, Cd, Co, Pb, Ni, Se, Sn, Sb Ti, V and Zr were below detection level. This section reports about the detected elements regarded and macro and micro-nutrients, toxic and non-toxic metals.

Potassium is an essential macro-nutrient for agriculture for plant growth. This essential nutient was not determined for the Matsapha untreated sludge only due to the saturated concentration of the sample. The other untreated 30 samples leached on soil only, Nhlambeni sludge only and soil-sludge mix at different rates of sludge indicates presence of this essesntia nutirent, with soil only sample having the least concentration (see Figure 4.21 left graph). Also, treated samples (see Figure 4.21 right graph) leachate indicated presence of potassium at higher concentrations compared to leached samples on untreated sludge. This is a clear indication that the Potasium dihydrogen phosphate (KH_2PO_4) does not have negative impact on the presence of essential macro-nutrients.

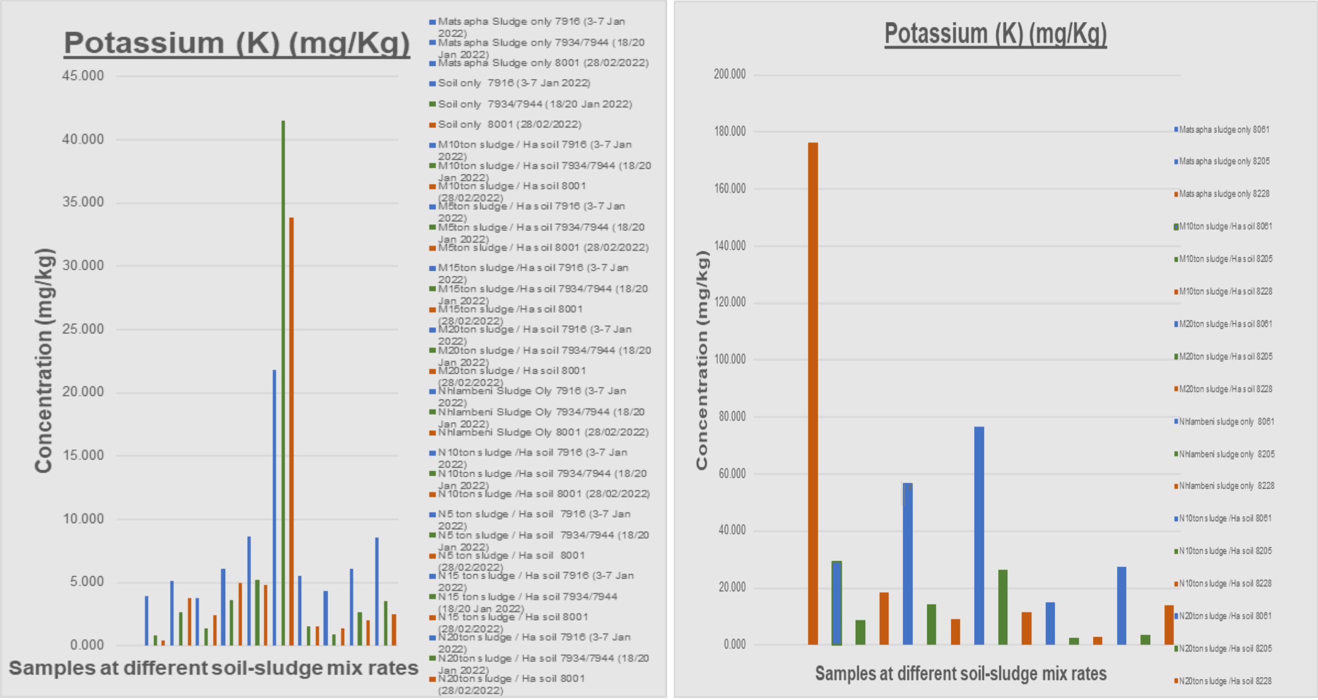

Figure 4. 21: Potassium (K) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates

Calcium is also amoungst the essential macro-nutrients. Both treated and untreated leached samples indicate presence of Calcium concentration (see Figure 4.22). However,like in Potassium concentration the treated leached samples show increased concentrations of Calcium.

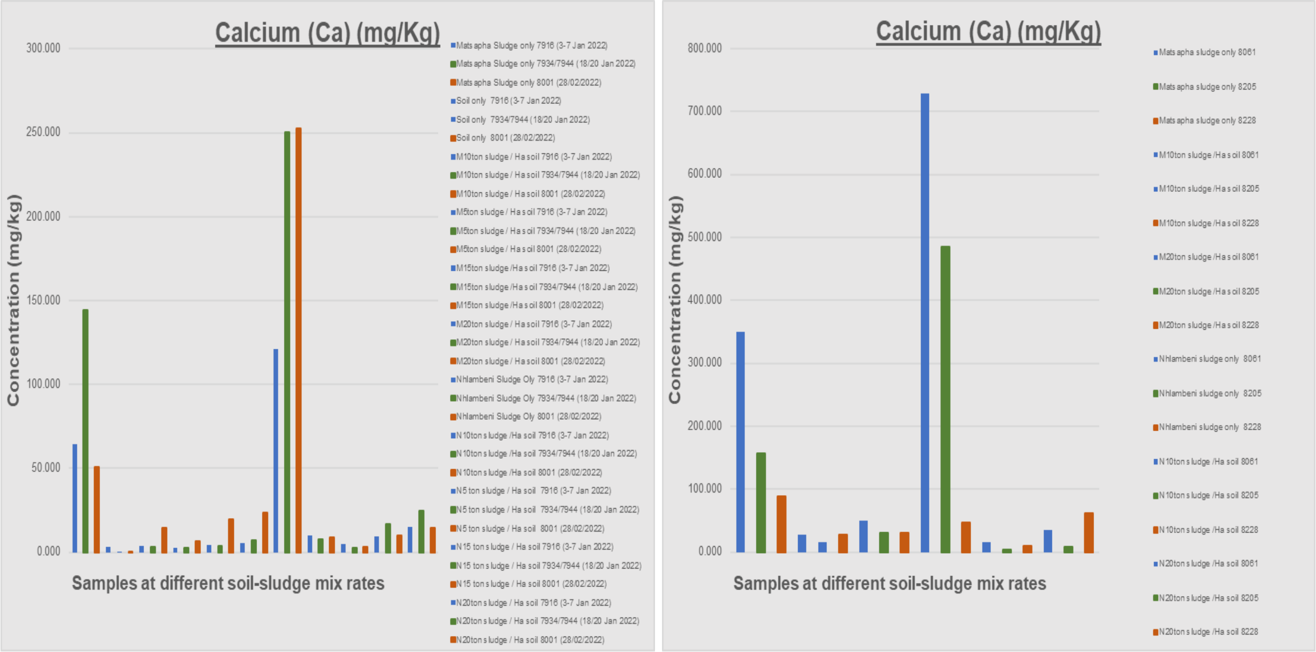

Figure 4. 22: Calcium (Ca) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

Magnesium is also regarded as an essential macro-nutrients. Both treated and untreated leached samples indicate presence of Magnesium concentration (see Figure 4.23), with treated leached samples showing increased concentrations of Magnesium.

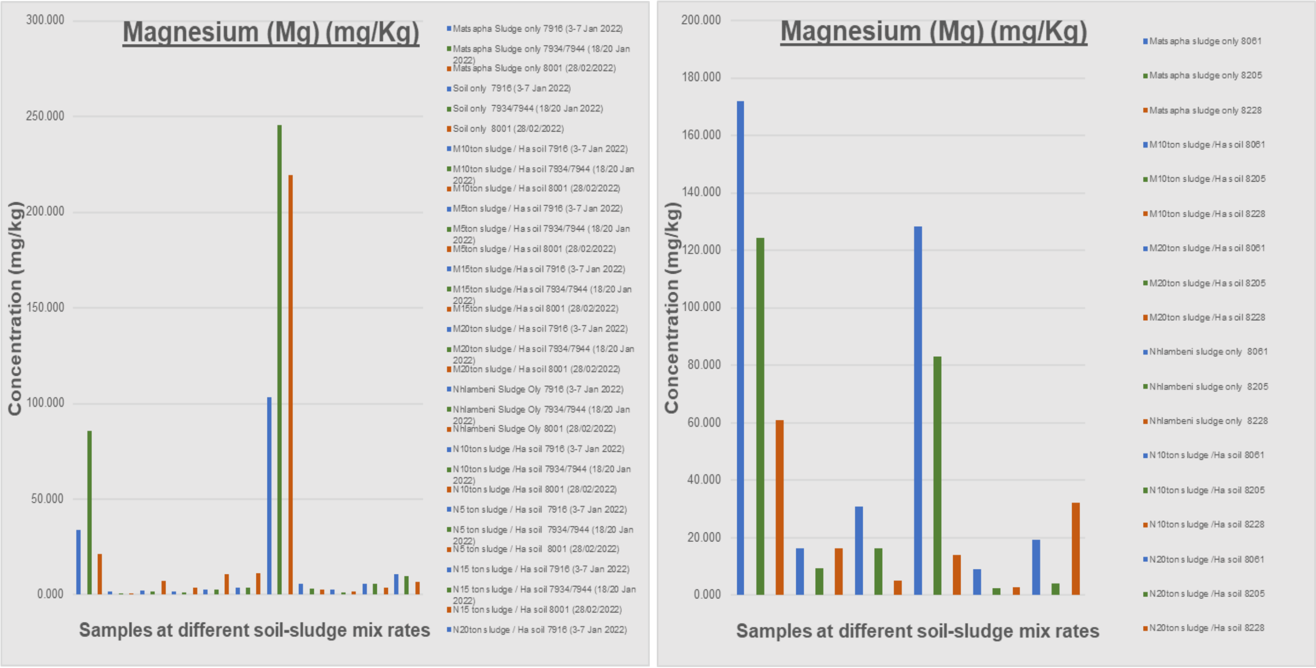

Figure 4. 23: Magnesium (Mg) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

Manganese is one of the essential micro-nutrients that can be toxic at higher concentration. Both treated and untreated leached samples indicate presence of Manganese concentration (see Figure 4.24), with treated leached samples showing increased concentrations of Manganese.

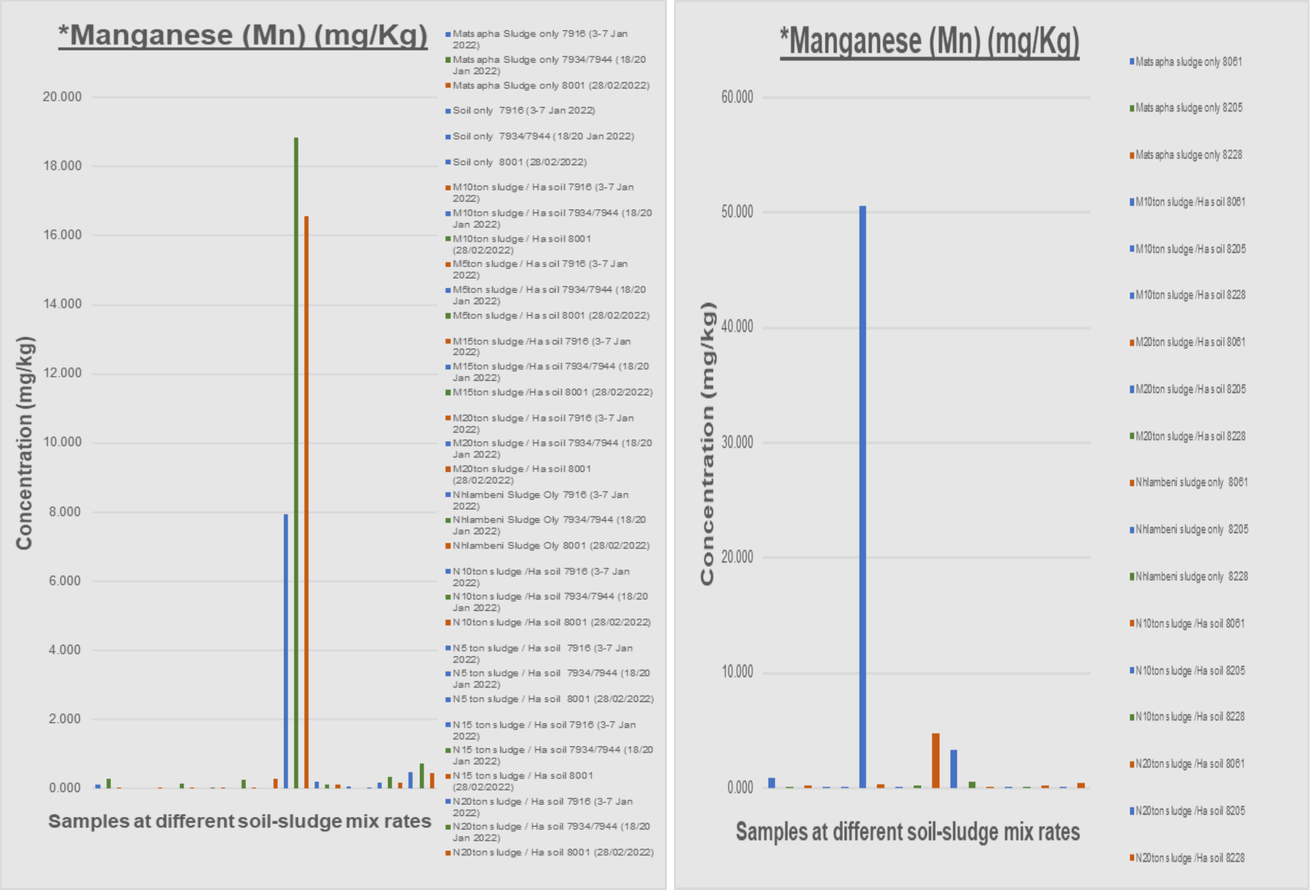

Figure 4. 24: Manganese (Mn) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates

Sodium was detected on both untreated and treated leached samples (see Figure 4.25). Treated sample indicate an increase in concrentration (see Figure 4:25 right graph).

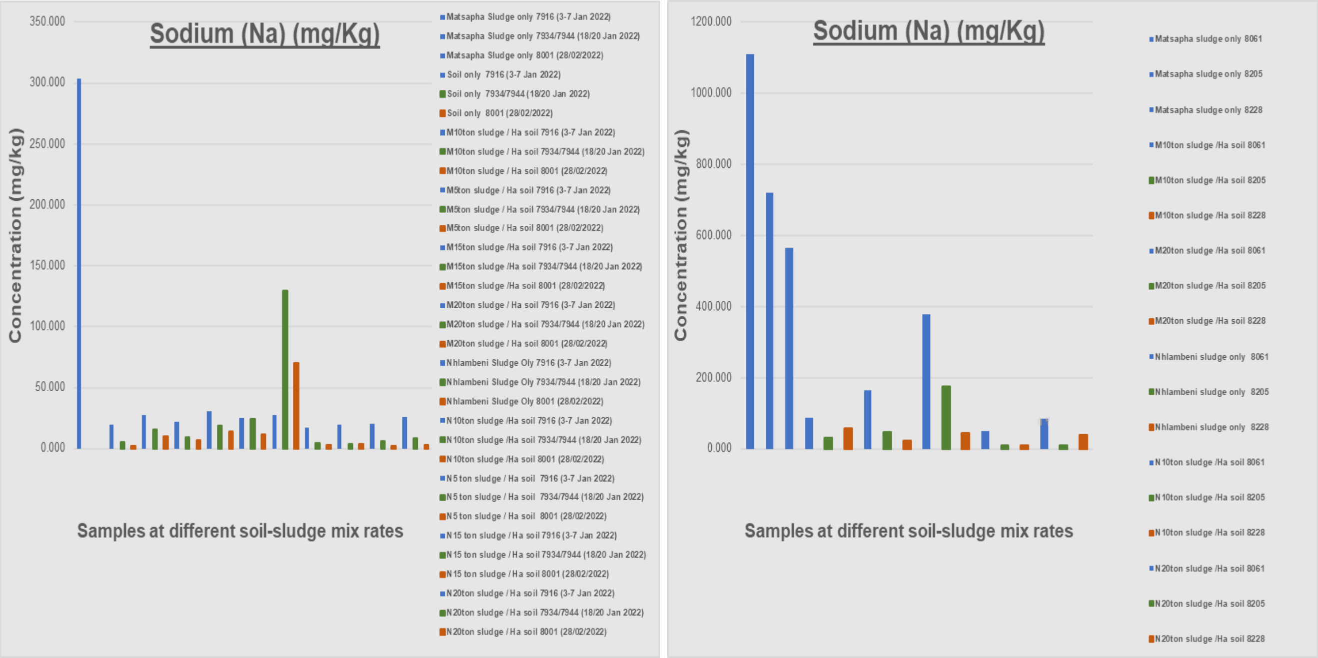

Figure 4. 25: Sodium (Na) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

Silicon is a non-toxic element which was detected more in the Nhlambeni wastewaetr sludge than in the Matsapha wastewater sludge. Concentrations increased on treated sludge (see Figure 4.26).

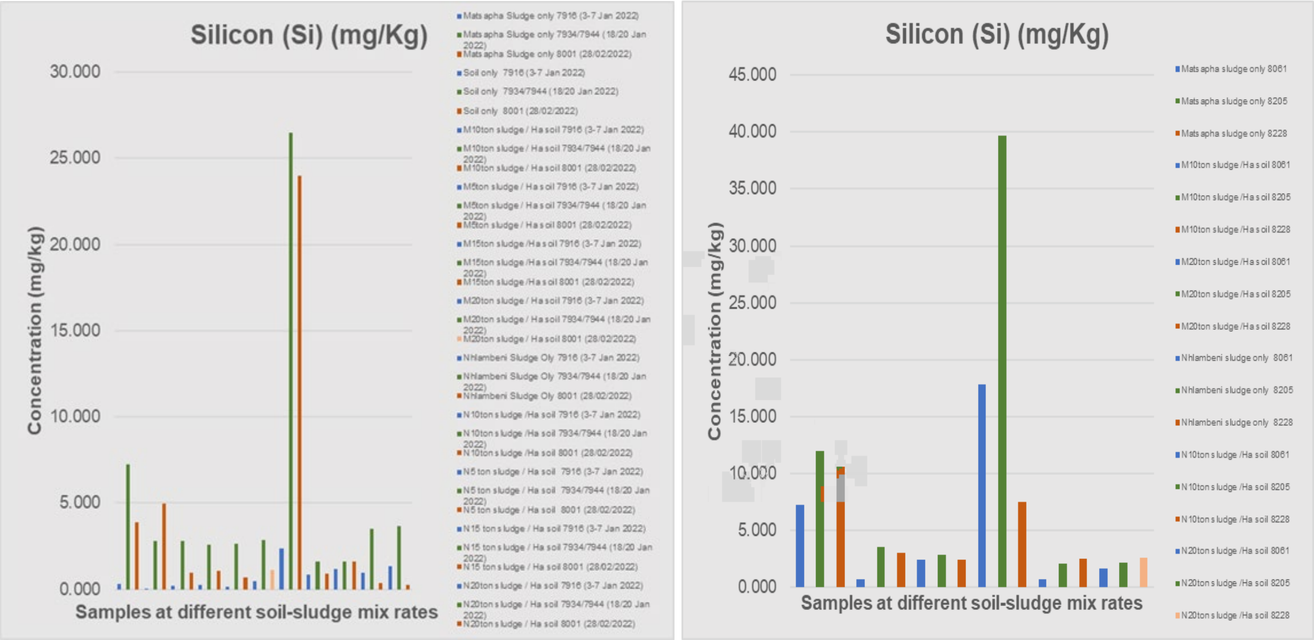

Figure 4.26: Silicon (Si) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates

Zinc (Zn) is one of the non-essential micro-nutrient but it is toxic at concenration exceeding 2800 mg/kg (see Table 2.3). Figure 4.27 shows the graphs of both untreated and treated leached samples. Both graphs indicate concentrations less than thresholds by different organisation as stated in Table 2.3. Nhlambeni wastewater shows concenrations of Zn to be almost 30mg/kg and the rest of leached samples were below 2mg/kg. It was noted that treatment with KH_2PO_4 immobilised Zn element and reduced its concentration for Nhlambeni WWTP sludge to less than a 3rd of its original concentrations. Unfotunately, the reduced concentrations are below 6mg/kg of Zn required by plant for elongation and production of hormone in plant(Johnson & Mirza, 2020).

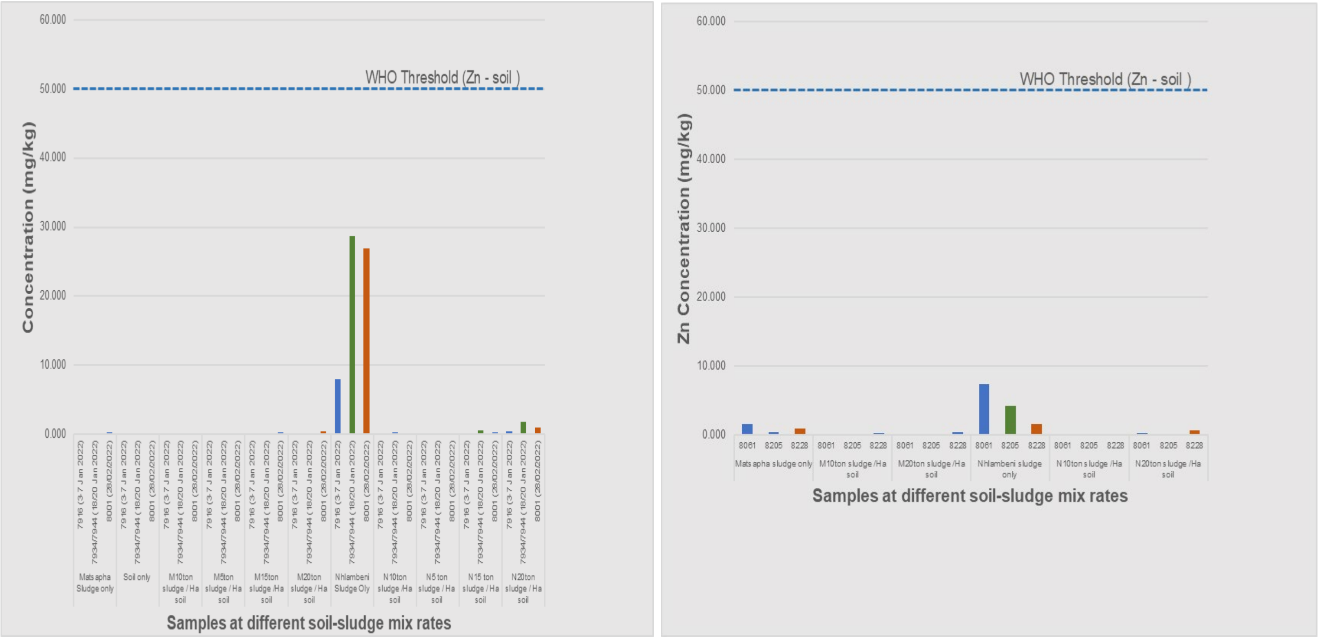

Figure 4. 27: Zinc (Zn) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

Copper (Cu) is an essential nutrient but also a toxic metal which was detected more in the Matsapha wastewater sludge (see Figure 4.28). Both treated and untreated leached samples had concentrations below thresholds OF 1500 mg/kg set by different organizations and countries as stated in Table 2.3. However, treated samples indicate a slight increase which may indicate the need for monitoring although Cu has a high range before becoming toxic.

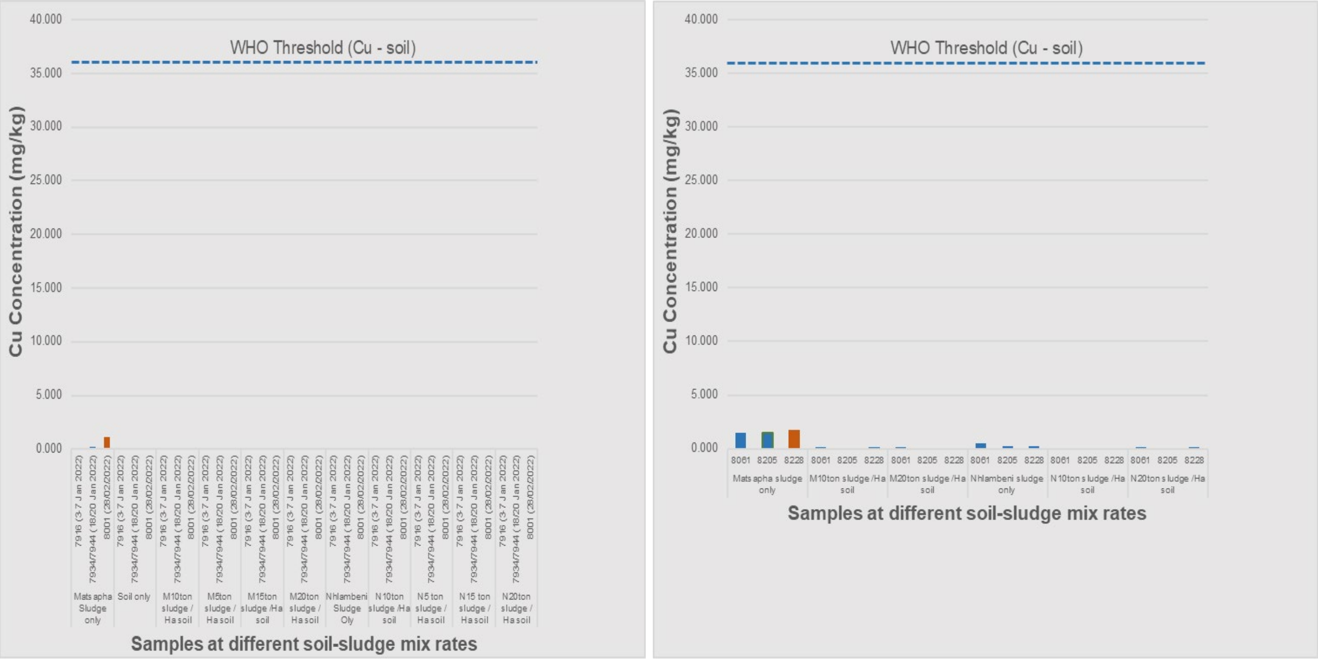

Figure 4. 28: Copper (Cu) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates

Boron (B), Iron (Fe) and Aluminum (Al) were detected below standard thresholds of 0.5, 4.5 and 15mg/kg respectively, except one treated leached sample tested for B from Matsapha wastewater sludge. Treatment with P immobilised B on soil-sludge leached samples slightly reduced concentraction of B sludge only leached samples (see Figure 4.29).

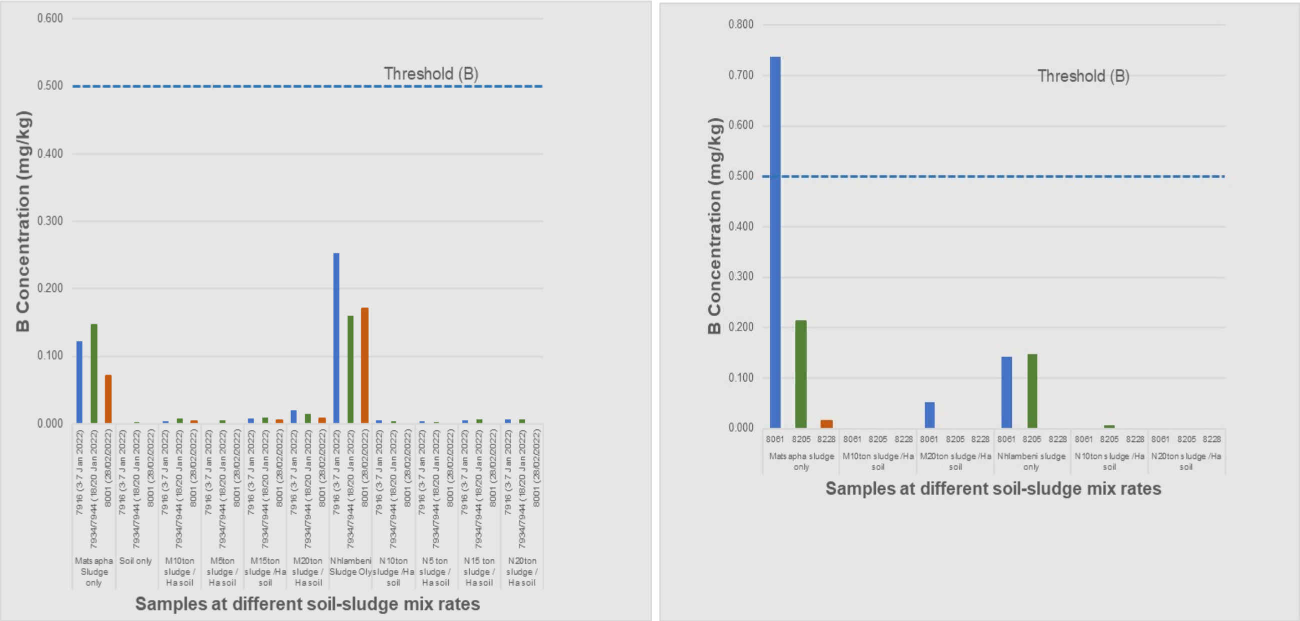

Figure 4. 29: Boron (B) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates

Iron (Fe) increased slighly from the original concentrations and Al remained almost the same (see Figure 4.30 and 4.31).

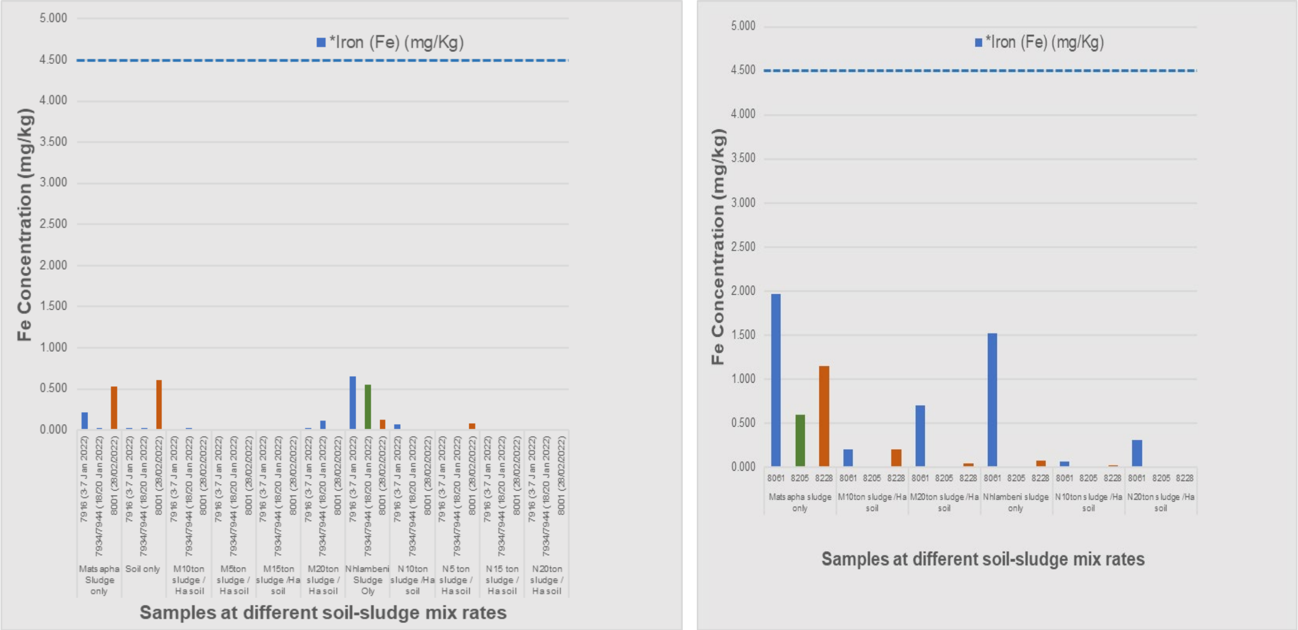

Figure 4. 30: Iron (Fe) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

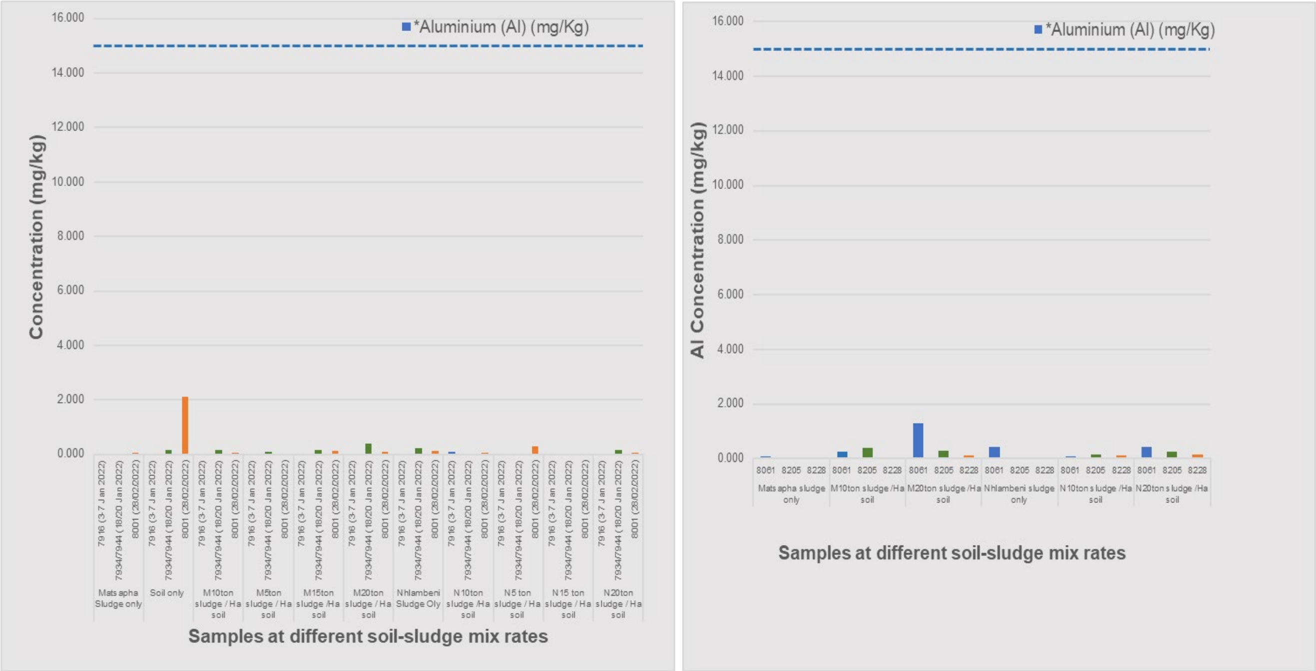

Figure 4. 31: Aluminum (Al) concentration for untreated (left graph) and treated (right graph) sludge at different soil-sludge mix rates.

4.7 Overall interpretation and discussions

This chapter discussed toxic metals and non-metal elements, macro and micronutrients as found the EWSC farm and sludge from Matsapha and Nhlambeni wastewater treatment plants. Determination of heavy metals by acid digestion proved that the soil and sludge samples had some toxic elements that are regulated globally. Experimental data showed that P extracted from potassium dihydrogen phosphate (KH_2PO_4) chemical has a potential to immobilize Toxic metal components. This was first indicated by the TCLP results and further confirmed by leached samples from column study as well as acid digested samples for grass and spinach that was planted on soil mixed with different quantities of KH_2PO_4 treated sludge. However, the tests conducted did not stipulate how much of the elements would be available for plant uptake, but only leachate tests were done. Considering the seriousness associated with toxic metals consumptions, further assessment of treated sludge was conducted which proved significant immobilisation of the present toxic metals. The presence of heavy metals at low concentration on the leached samples indicate that the sludge can be used without treatment. The next chapter concludes the entire study and provides recommendations for further research.

CHAPTER 5: Conclusion and Recommendations

5.1 Conclusion

Wastewater sludge offers several recovery potentials which are of benefit for sustainable development. While one of the potential uses is in agriculture as soil amendment or fertiliser, the heavy metals treatment gaps prevent the full realisation of its benefits. This research aimed to improve the wastewater potential for use in agriculture by treating it with phosphorus from the KH_2PO_4 chemical to reduce metal solubility.

This study established the presence and concentration of heavy metals (i.e., Zn, As, Pb, Cr, Cu, and Cd) in Matsapha and Nhlambeni Wastewater Treatment Plants sludge, compared them with their effluent concentration, treated the samples with P and determined its immobility effectiveness. Other non-toxic elements as produced by the ICP-OES were also reported. The laboratory experimental analysis helped determine the sorption effectiveness sludge when treated with P. The TCLP analysis was conducted on the P treated samples to simulate the leaching of the elements in sludge samples. Furthermore, acid digestion of grass and spinach to determine plant uptake and leaching of sludge and soil mixture analysis were conducted to verify the sorption and TCLP results.

The wastewater sludge samples tested for heavy metals indicated to be mostly in compliance with concentration threshold set by USA, China, Europe, and South Africa. The results analysis for the Matsapha Wastewater sludge indicated that toxic elements such as As, Cd, Cr, and Pb were below detection level. The Nhlambeni Wastewater sludge detected Cr up to 90 mg/ kg which is about 7.5% of the 1200mg/kg threshold stipulated by China and South African guidelines. By contrast Zn absorbed by spinach on untreated sludge was found to be in excess compared to the limits set by WHO. The results of the acid digested spinach which was planted on treated sludge at 250g P concentration indicated that heavy metals are absorbed to acceptable limits by WHO. Also, the detected macro and micro-nutrients in both treated and non-treated samples were sufficient for plant growth at the rate of 10 ton of sludge per hectare soil as recommended by the South African guidelines.

5.2 Recommendations

The study was conducted on acidic soil with acidic sludge. Proper monitoring of the micro-nutrients with toxicity potential at high concentration will be required. Availability of the detected elements such as Zn and Cr require attention to understand the impact, even though the toxic elements are mostly withing the global legislation guidelines. Further assessment at 500g concentration of P is needed for complete mobilization of heavy metals, though they were detected at low concentrations. Lastly, a column study for a period not less than 6 months would be required to understand the long-term effects of the immobilized toxic elements.

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