DETERMINATION OF THE LEVELS OF HEAVY METALS IN WATER, PASTURES AND MEAT TISSUES OF PEDI GOATS ACROSS TWO RIVERS IN LIMPOPO PROVINCE, SOUTH AFRICA

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DECLARATION

I declare that the dissertation hereby submitted to the University of Limpopo for the degree of Master of Science in Agriculture (Animal Production) has not previously been submitted by me for a degree at this or any other University. I, also, confirm that it is my independent work in design and execution, and that all materials contained therein have been duly acknowledged.

Signature………………………………..……   Date…………………………………

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DEDICATION

I dedicate this study to my late beloved uncle, Mr Selomane Noko Walter. “I have achieved your dreams.” May your soul rest in everlasting peace.

ABSTRACT

The study was carried out to determine the concentration levels of mercury (Hg), lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni) and zinc (Zn) in water, soil, witbuffels grass and meat of goats reared along the river banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers. The samples were collected from the river water, soils along the river banks, grass grown along the river banks and male Pedi goats reared in Mogalatsana and Papegaai villages. The samples were analysed for the selected heavy metals with an inductively coupled plasma mass spectroscopy (ICP-MS). Data was analysed as in a complete randomised design. The results of selected heavy metals in water of both rivers ranged from 0.00 mg/litre of water (Ni and Cr) to 0.04 mg/litre of water (Hg). The concentration levels of selected heavy metals in water were similar (P>0.05) for Middle Olifants and Mogalakwena rivers. The concentration levels of selected heavy metals in the soils along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM soil (Hg and Cd) to 63.70 mg/kg DM soil (Cr). There were similar (P>0.05) concentration levels of selected heavy metals in the soils along the banks of Middle Olifants and Mogalakwena rivers. Heavy metal concentration levels in the witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM of grass (Hg and Cd) to 5.05 mg/kg DM of grass (Zn). Similar (P>0.05) concentrations of selected heavy metals were observed in witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers. However, the concentration levels of Zn, Pb and Cd in water from both sites were above internationally maximum permissible levels, indicating that the water from these rivers was not safe for drinking by humans and animals. The concentration levels of Ni and Pb in soils from both sites were above internationally recommended maximum permissible limits. Similarly, chromium concentration levels in witbuffels grass from both sites were above the recommended maximum permissible limits for livestock, indicating that the grass was not safe for consumption by livestock. It is recommended that further studies be conducted to ascertain these findings.

Blood, liver, kidney and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) had similar (P>0.05) Cr, Cd, Hg, Ni and Pb concentration levels, respectively. However, goat liver samples had higher (P<0.05) Zn concentrations than meat, kidney and blood samples. Samples of goat

meat contained higher (P<0.05) Zn concentrations than those of kidneys and blood. Similarly, goat kidney samples contained more (P<0.05) Zn than blood samples. Blood, liver, kidney and meat samples of Pedi goats grazing along the banks of Mogalakwena river (Papegaai village) contained similar (P>0.05) concentration levels of Cr, Cd, Hg, Ni and Pb, respectively. However, goat meat samples contained higher (P<0.05) Zn concentrations than liver, kidney and blood samples. Samples of goat liver contained higher (P<0.05) Zn concentration levels than kidney and blood samples. Similarly, goat kidney samples contained more (P<0.05) Zn than blood samples.

Meat, blood, liver and kidney samples of male Pedi goats raised in Mogalatsana and Papegaai villages had similar (P>0.05) chromium, cadmium, mercury, nickel and lead concentrations, respectively. However, liver and kidney samples of goats from Mogalatsana village had higher (P<0.05) zinc levels than those from Papegaai village. Blood and meat samples of goats from Papegaai village had higher (P<0.05) zinc levels than those from Mogalatsana village. The concentration levels of Zn, Ni, Pb, Cr and Cd in the blood, liver, kidney and meat samples of male Pedi goats reared along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels for human consumption. Mercury concentration levels in liver, kidney and meat samples of the goats were within the maximum permissible levels for human consumption. However, mercury concentration levels in the blood of goats grazing along the banks of Middle Olifants and Mogalakwena rivers were above the maximum permissible limit of 0.2 mg/litre of blood. It was concluded that meat, livers and kidneys of the goats were fit for human consumption. However, blood from these goats was not fit for human consumption.

TABLE OF CONTENTS

Content **Page**

LIST OF ABBREVAITIONS

ATSDR	Agency for Toxic Substances and Disease Registry
Cd	Cadmium
Cr	Chromium
DAFF	Department of Agriculture, Forestry and Fisheries
DAGRIS	Domestic Animal Genetic Resources Information Systems
DWAF	Department of Water Affairs and Forestry
EDTA	Ethylene Diamine Tetraacetic Acid
FAO/WHO	Food and Agricultre Organization/World Health Organization
g/cm^3	Gram to cubic centimeter
Hg	Mercury
ICP-MS	Inductively Coupled Plasma- Mass Spetrometry
IARC	International Agency for Research on Cancer
LATS	Limpopo Agro-Food Technology Station
mg/kg	Milligrams per kilogram
MPL	Maximum Permissible Limits
Ni	Nickel
NRC	National Research Council
Pb	Lead
SACRM	South African Coal Road Map
TWQR	Total Water Quality Range
USEPA	United State of Environmental Protection Administration
WRC	Water Research Council
Zn	Zinc

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background

Goat production plays a valuable role in poverty alleviation, empowerment, cultural purposes and food security in small-holder households in rural areas of Limpopo province (Ng'ambi *et al*., 2013; Dasbasi *et al*., 2016). Many of these goats in Limpopo province are of Pedi breed. Many of these goats depend on water and communal natural pastures along the Middle Olifants basin for their nutrient requirements (Ng'ambi *et al*., 2013). Unfortunately, the Olifants river is one of the most polluted river systems in South Africa (Heath *et al*., 2010; Ashton and Dabrowski, 2011; Oberholster *et al*., 2012). The river receives wastes from anthropogenic activities such as mines, industries, and agriculture (Oberholster *et al*., 2010; Ashton and Dabrowski, 2011). Thus, animals depending on this polluted water system may end up being polluted with the heavy metals found in the water and pastures (Alonso *et al*., 2002; Alexandre *et al*., 2010).

1.2 Problem statement

Limpopo province is one of the provinces in South Africa with high percentage of mining, industrial and agricultural activities which are major sources of heavy metal pollution (Hobbs *et al*., 2008; Dabrowski *et al*., 2008; Ashton and Dabrowski, 2011). Most heavy metals constitute serious environmental problems. Animals that graze on such contaminated pastures and drink such polluted water accumulate metals in their bodies (Jabeen *et al*., 2012). These elements tend to bio-accumulative, increasingly in meat tissues and organs of animals, especially the liver and kidneys (Adelekon and Abegunde, 2011). People eating contaminated meat may have higher levels of heavy metals in their bodies (Harmanescu *et al*., 2011). Thus, consumption of such meat may lead to lung cancer, high blood pressure, gastrointestinal cancer, and kidney and bone problems in humans (Demirezen and Uruç, 2006). Heavy metals are poorly lost in the food chain, which enables them to settle down, transferred and magnified (Mann *et al*., 2011). High levels of metals such as lead (Pb), zinc (Zn), mercury (Hg) and chromium (Cr) have been found in Olifants river water (Grobler *et al*., 1994; Dabrowski *et al*., 2008). Studies of the Olifants river water indicate heavy metal accumulation (Coetzee *et al.,* 2002; Jooste *et al*., 2014). However, information on the levels of heavy metals in meat tissues of yearling Pedi goats reared along Middle Olifants river catchment area is unknown. Thus, there is a need to determine their levels in meat tissues from such goats. There is also needed to determine heavy metal levels in pastures grown along the river.

1.3 Justification

This study will provide useful information on the levels of selected metals in water, soil, pastures, and meat tissues of yearling Pedi goats reared along the banks of Middle Olifants river. Such information on Pedi goats reared along the Middle Olifants river catchment is unknown. There is a need to monitor the levels of heavy metals in meat tissues of Pedi goats to ensure that levels do not reach fatal points in tissues and organs of the goats. Pedi goats are the common sources of meat and milk for small-holder farmers in rural areas. Data from this study will help the government of South Africa and other stakeholders to develop strategies for reducing wastes from anthropogenic activities. It will, also, help in environmental assessment and monitoring of pollutants. There are health issues associated with consumption of meat high in heavy metals (Mitsch and Wise, 1998). It is, therefore, important to determine heavy metal levels in Pedi goats grazing along Middle Olifants river catchment area.

1.4 Aim

The study aimed at assessing the levels of heavy metals in water, soil, pastures, and meat tissues of yearling Pedi goats reared along the Middle Olifants and Mogalakwena riverbanks.

1.5 Objectives

The objectives of this study were to determine:

i. the levels of lead, mercury, zinc, cadmium, nickel and chromium in water, soil and pastures growing along the Middle Olifants and Mogalakwena riverbanks.
ii. the levels of lead, mercury, zinc, cadmium, nickel, and chromium in meat tissues of yearling Pedi goats reared along the Middle Olifants and Mogalakwena riverbanks

1.6 Hypotheses

The hypotheses of the study were as follows:

i. There are low levels of Pb, Hg, Zn, Cd, Ni and Cr in water, soil and pastures growing along the Middle Olifants and Mogalakwena riverbanks.

ii. There are low levels of Pb, Hg, Zn, Cd, Ni and Cr in meat tissues of yearling Pedi goats reared along the Middle Olifants and Mogalakwena riverbanks.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Goats (*Capra hircus*) are widely distributed around the world (Devendra, 2010). Goats represent one of the earliest species to be domesticated by man (Casey *et al*., 2003; Aziz, 2010). They were originally domesticated in southwest Asia, thereafter, quickly moved into Africa (Devendra, 2006; 2010). Domesticated goats derived from wild goat (Devendra, 2006). There has been a rapid spread of domestic goats worldwide because of various activities and they are true friends to the rural families of Sub-Saharan Africa (Peacock, 1996; Clutton-Brock, 2000). They are known to be productive and resilient with wide ecological adaptation (Casey and Webb, 2010). Goats in rural areas depend on communal natural pastures and river or borehole water for their nutrient requirements (Ng'ambi *et al*., 2013). In South Africa, 50% of the indigenous goat population is kept under small-scale conditions (Ng'ambi *et al*., 2013). Hence, they are mostly found in the communal districts of the Limpopo, Eastern Cape, North West, and KwaZulu Natal provinces (Morrison, 2007; DAFF, 2012).

2.2 Indigenous goat production

Goats are multipurpose breeds, and their production systems differ in terms of feeding, breeding, and housing due to factors such as climate, needs of the owner, standard of living and the level of infrastructure or technology available (Peacock, 1996). Indigenous goats are commonly found in small-scale production systems in the communal areas (Lebbie and Ramsay, 1999). Most of the communal goats are kept under the extensive system of management with free-ranging and herding as the main management system (Rumosa Gwaze, 2009). Keeping of goats plays a significant role in poverty alleviation, ensuring food security and economic status of rural dwellers and they used in controlling bush encroachment (Ng'ambi *et al*., 2013; Dasbasi *et al*., 2016). They are herded or set free during the day and penned at night. These animals utilize feedstuffs from natural pastures like *Urochloa mosambecencis* and drink water from river basins or boreholes (Ng'ambi *et al*., 2013). Indigenous goats are drought tolerant and can withstand and adapt well to adverse harsh conditions with nutritional constraints (Morand-Fehr *et al*., 2004).

Pedi goats play an important role in the livelihood of rural people in communal areas of Limpopo province (Ng'ambi *et al*., 2013). The name Pedi goat breed is derived from Bapedi people of South Africa (Dagris, 2007). Goats support subsistence farming because they supply meat, milk, skin, horns, and cash to the farmers (Ng'ambi *et al*., 2013). They, also, provide an additional broad range of socio-economic services such as dowry and used in cultural benefits (Peacock, 1996). Shackleton *et al*. (2001) found that 61.5% of households in communal areas used goats in ceremonies, mostly in Eastern Cape and Limpopo provinces of South Africa. However, goats are regularly discriminated against and neglected by a large part of the human population for their destructive behaviour with regards to forestry care (Devendra, 2006).

2.3 Indigenous Pedi goats of South Africa

South African indigenous goats are of three distinct types, namely, Pedi goats, Nguni goats and Xhosa lop ear ecotypes (DAFF, 2012). These types of goats are normally termed according to the tribe that owns them (Morrison, 2007). Hence, 83% of South African indigenous goats are mostly found in the regions of the Limpopo, Eastern Cape, Northwest, and KwaZulu Natal provinces. The remaining 17% are scattered among the remaining other five provinces (DAFF, 2012).

2.3.1 Phenotypic characteristics of Pedi goats

The physical appearance of the goat is a result of both genetic makeup and the environment (Hunter, 2009). Pedi goats are hollow-horned small ruminants. They have a small to medium frame size with short horns (Snyman, 2014). These animals are characterised by a variety of coat colour decorations and phenotypic traits such as small to medium-sized ears, hair type, horn length, and tail length (Snyman, 2014). According to Ben Salem and Smith (2008), their genetic separation has led to phenotypic variations, which can help in meeting future challenges in the environment. Pedi goats can efficiently survive on marginal land where crops don't do well.

2.3.2 Adaptive characteristics of Pedi goats

The indigenous goats are well adapted to the local extensive farming systems, generally characterised by a little standard of management such as low inputs of labour and easy to manage (Rumosa Gwaze, 2009). Pedi goats can adapt to extreme environments and possess some unique adaptation traits because of physiological, morphological, behavioural, and genetic bases (Peacock, 1996). They are the most adaptable and geographically widespread livestock species (Dagris, 2007). They serve as a genetic reservoir for the identification of genes necessary for environmental adaptation, improved productivity under local conditions and disease resistance (Peacock, 1996; Ben Salem and Smith, 2008). Their genes allow them to be hardy, survive difficult periods and tolerant to local parasites and diseases such as heart water (Miles, 2007). Their skin pigmentation and hooves had tolerated them to adapt well to harsh environments (Mohy El-Deen *et al*., 1985; Casey and Webb, 2010). Clutton-Brock (2000) observed that indigenous goats can walk for long distances in search of water and feed. Therefore, Pedi goats are easy to keep in comparison to other livestock species, hence, are well-adapted to limited forage and can utilize marginal land efficiently (Morand-Fehr *et al*., 2004). They are characterised by a unique adaptive mechanism which allows them to survive in different regions (Galal, 2005).

2.3.3 Reproductive characteristics of Pedi goats

Indigenous goat flocks from different households and villages forage together across the grazing land (Peacock, 2005). This allows them to breed freely without any controlled breeding. They interbreed as a single flock in the veld (Peacock, 2005). According to Miles (2007), they mate all year round, are very fertile and reach early sexual maturity compared to most other breeds. Indigenous Pedi goats attain sexual maturity at the age of 7 months with the live body weight around 14 to 15 kg (Lehloenya *et al*., 2005). Furthermore, their age at first kidding ranges between 16-18 months (Lehloenya *et al*., 2007). Pedi goats have shorter gestation length, on average of 5-9 months (Amoah *et al*., 1996). Webb and Mamabolo (2004) indicated that the average litter size of indigenous goats is twins per doe and two parturitions per year. Generally, inadequate nutrition adversely affects growth, age at puberty, oestrus, and prolonged parturition interval in goats (Stagg *et al*., 1995).

2.3.4 Growth characteristics of Pedi goats

Pedi goats have a small body frame and low meat yield with an average mature body weight of around 25-30 kg (Lehloenya *et al*., 2005). Their growth performance is generally slow because of poor genetic potential, disease and parasite challenges and low nutrition (Peacock, 1996; Miles, 2007). They grow slowly in nature (Lehloenya *et al*., 2007). Indigenous goats have a lower carcass weight (Webb and Mamabolo, 2004). Sex of the Pedi goats has a significant impact on the growth of body tissues, usually, males attain puberty earlier than females (Warmington and Kirton, 1990).

Thus, their poor genetic potential for growth results in low meat and milk yield compared to other goat breeds (Smith *et al*., 1978).

2.3.5 Carcass characteristics of Pedi goats

The phenotypic and genotypic traits of Pedi goats affect carcass and meat quality (Casey and Webb, 2010). Goat meat is regarded as lean red meat with a convenient source of nutritional characteristics (Webb *et al*., 2005). Normally, carcases are classified based on meat colour and fat content as a class of carcass weight (Babiker *et al*., 1990). Webb *et al.* (2005) demonstrated that the dressing percentage of goat carcasses is smaller than that of sheep, mainly, due to low carcass fat content. Goats have low subcutaneous fat content with more muscle component, and they deposit high amounts of polyunsaturated fatty acids (Babiker *et al*., 1990; Tshabalala *et al*., 2003). Casey *et al.* (2003) reported that the goat carcass fat deposit occurs later in the growth process. Ideal Pedi goat carcass weight varies between 12 and 15 kg, thus, older goats weigh more than 20 kg and are highly perceived as stingy, tough, and strongly flavoured (Webb *et al*., 2005; Casey and Webb, 2010). The goat meat has a rougher texture, darker red colour and different aroma and flavour (Simela *et al*., 2004a, b). Webb *et al*. (2005) confirmed that good tenderness, taste, and flavour are generally expected from carcasses of young goats.

2.4 Environmental consequences of mining on livestock production

In South Africa, the anthropogenic sources such as mines, industries, agriculture, and municipal waste have been reported as main sources of environmental contamination (Batchelor and Engelbrecht, 1992; Ashton and Dabrowski, 2011). Indigenous goats that forage on such contaminated environment may accumulate heavy metals in their bodies (Jabeen *et al*., 2012). Environmental contamination with heavy metals is a serious threat because of their toxicity, bioaccumulation, and non-biodegradability (El-Salam *et al*., 2013). To ascertain the safety of goat meat, it is important that the heavy metals concentration should not be above the acceptable levels (Table 2.1) for the animals (Jabeen *et al*., 2012).

Table 2.1 Maximum permissible levels of heavy metals in ruminants*

Tissue types	cadmium	chromium	lead	zinc	nickel	mercury
Blood (mg/L)	0.5	1.0	0.5	80	0.5	0.2
Liver (mg/kg)	0.5	1.0	0.5	80	2.0	0.2
Kidney (mg/kg)	1.0	1.0	0.5	80	2.0	0.2
Meat (mg/kg)	0.05	1.0	0.1	60	0.5	0.2

* : Maximum permissible limits (FAO/WHO, 2007)

The earth's crust is made of smaller quantities of rock-forming minerals (Lurie, 1977). Minerals have been used by humans for various purposes, for example, trading and economic purposes (Lurie, 1977). Minerals are extracted from the piles of earth crust through the surface and underground mining activities (Bloodworth *et al*., 2009). Mining is an activity with many conflicting issues. Its operations are normally recognised as environmentally and socially disruptive (Zhengfu *et al*., 2010). Mining and agriculture have been the key driving forces behind the South African economy (Masindi *et al*., 2015). Limpopo province is the largest mining province in South Africa because of its wide varieties of mineral deposits (Jeffrey, 2005a). The core mineral commodities exploited in Limpopo province are gold, diamonds, coal, iron, platinum, chromium, and copper (Peck and Sinding, 2003). The strength of the impact of mining depends on the commodity being mined and the mining methods (Bloodworth *et al*., 2009).

Despite the benefits of mining to the country’s economy, mining can have significant adverse environmental impacts (Hilson, 2006). Mining operations can result in the change of landscape, loss of biodiversity, and contamination of soil, groundwater, and surface water (Dudka and Adriano, 1997). Residents are, also, affected as the mining process is implemented, such as displacing them from their original locations (Mtegha *et al*., 2007). The effluents from mining harm surrounding human and livestock and crop production (Hilson, 2006). Thus, wastes from mining and industries persist in all parts of the environment.

Water quality and animal well-being are major concerns when mining occurs (Peck and Sinding, 2003). Plant habitats and communities along the river margins can be directly or indirectly affected by toxic withdrawals from mining operation (NRC, 1999).

The body tissues can control some of these quantities of metals, under normal circumstances (Salem *et al*., 2000). However, higher concentrations of metals cause adverse effects if exposed to human and animal population (Simate and Ndlovu, 2014). The impacts associated with mining has been a major concern over the years on livestock production and the destruction of livelihoods in Limpopo province (Peck and Sinding, 2003).

2.4.1 Environmental contamination

The surroundings within which humans live can be referred to as the environment (Dallas and Day, 2004). Contaminants can be naturally occurring compounds or foreign matter which when in contact with the environment cause adverse changes (Hobbs and Kennedy, 2011). These can be heavy metals, pesticides and effluents. The environment is comprised of the land, the water, the atmosphere, plant, and animal lives (Dallas and Day, 2004). Therefore, mining and urbanization have weakened the environment and their ability to foster life (Mosilova *et al*., 2016). The high levels of heavy metals in water, soil and pastures in Limpopo province have a significant impact on livestock production and crop production (Simate and Ndlovu, 2014). The most significant concern is the river systems and the impact of water quality flowing downstream for domestic and agricultural use (Mitsch and Wise, 1998). National Research Council (1999) showed that mining from the river basin causes long term alteration to water quality and quantity. The upper Olifants river catchment area in South Africa has been polluted by mining, industrial and agricultural effluents (Heath *et al*., 2010; Ashton and Dabrowski 2011). The widespread heavy metal contamination has elevated public and scientific interest due to their toxic effects even at low concentrations (Mitsch and Wise, 1998).

2.4.2 Land disturbance

Mining often competes with other types of land use such as agriculture and residential land use (Hilson, 2002). During the mining operation, the arable topsoil will be disturbed, even long after reclamation (Aken *et al*., 2012). Bian *et al*. (2010) found that mining changes the local landscape significantly through the destruction of land resources and delaying the growth of vegetation. According to Zhengfu *et al*. (2010), coal mining has caused the destruction of the land followed by land desertification. The land surface that is plain without plants is exposed to various agents of erosion

(Van der Burgh, 2012). Mining operations directly or indirectly affect land use such as the production of livestock and crops, encouraging the topography failure causing the loss of water and plants (Zhengfu *et al*., 2010). Mining has been found to cause flooding of contaminants into the water system in Limpopo province (Jeffrey, 2005a).

Mining can affect land use and become a danger to both animals and humans (Van der Burgh, 2012). Van der Burgh (2012) further reported a significant impact of mining on agricultural activities in general. Lin *et al.* (2010) indicated that the outflow of acid water from the mine can result in high levels of heavy metals in the soils and river water. These harm livestock and crop production. Contaminated soil results in pastures being contaminated with heavy metals (Zhengfu *et al*., 2010). This may result in animals being contaminated with heavy metals. Humans who consume such contaminated meat may, also, become contaminated with heavy metals (Lin *et al*., 2010).

2.4.3 Water quality

Mining requires a large amount of clean water to operate and harms the amount of drinking water for humans and animals (Howard, 2016). Water use in mining may differ according to operations (Mavis, 2003). Therefore, freshwater ecosystems are most threatened ecosystems with river systems being polluted because of increasing anthropogenic activities (Ashton and Dabrowski, 2011). Natural water bodies create an important part of the landscape (Zhengfu *et al*., 2010). They have a specific ecological and socio-economic function for plants, animals, and humans (Schultze *et al*., 2010). Mining operations apply their effects to cause environmental contamination to freshwater bodies (Oberholster *et al*., 2010). Zhengfu *et al.* (2010) showed that the anthropogenic activities discharge metal-containing pollutants into the environment, subsequently increasing metal levels in the surface and ground water.

South Africa's surface and groundwater display changes in water quality (WRC, 2017). Toxic metals from mining operations find their way into the rivers, streams, and vegetation (Netshitungulwana and Yibas, 2012). The Olifants river in South Africa is one of the most polluted river systems due to mining, industrial and agricultural activities (Oberholster *et al*. 2010; Ashton and Dabrowski 2011). In this river, there were large fish kills in 2007 along with many crocodile deaths associated with heavy metals (De Villiers and Mkwelo, 2009; Ashton, 2010). Therefore, the outflow of acid water from abandoned mines in the upper Olifants river catchment is resulting in the mobilization and accumulation of heavy metals in river systems (Netshitungulwana and Yibas, 2012).

Limpopo province is a low rainfall region with few perennial rivers and dams (Howard *et al*., 2013). Thus, most of the population is dependent upon surface and groundwater for their existence (Howard *et al*., 2013). Livestock and people living in rural areas near the rivers may be exposed to harmful heavy metals. Contamination of water sources with heavy metals results in bioaccumulation of toxic metals across the food chain (Adeleken and Abegunde, 2011).

2.4.4 Air quality

Air pollution is also one of the major environmental impacts associated with mining and industrial activities. Air pollution can spread a lot faster than polluted water and can cover a larger area (Zhengfu *et al*., 2010). The air pollution from mines is mainly due to the emission of solid and liquid particles such as dust suspended in air (particulate matter) and gases such as methane and sulphur dioxide (Munnick, 2010). Releases of gaseous pollutants from mining are associated with the processing of large quantities of sulphur-containing minerals (Kaonga and Kgabi, 2009). Therefore, air pollution has been enhanced by particulate matters which are released through natural and anthropogenic activities (Munnick, 2010).

In South Africa, thoughtless burning of coal is a problem where open-cast mining occurs (South African Coal Road Map, 2011). According to Aneja *et al.* (2012), surface mining generates air pollution, mainly through particulate matter and wind erosion of exposed areas. The coal of an abandoned mine in Witbank Coalfield has been undergoing spontaneous combustion over the years (SACRM, 2011). Thus, smoke released through unplanned burning is associated with negative effects on animals and human health through inhalation (Aneja *et al*., 2012). The inhalation of dirty dust consisting of a mixture of particles and droplets of heavy metals has been related to serious health problems in humans (Ventura *et al*., 2017). Heavy metal droplets in air can lead to health problems such as respiratory infections, premature mortality, cardiovascular diseases in animals and human beings (Ventura *et al*., 2017). Greenpeace (2008) found that air pollution caused by unplanned coal burnings contributes to climate change and may cause acid rain. Thus, acid rain causes soil acidification and thereby contaminating water sources and plants (Greenpeace, 2008).

2.5 Heavy metals in water, pastures, and livestock meat

2.5.1 Heavy metals

Living organisms are being exposed to various aspects and factors which hamper the habitat in which they live (Mosilova *et al*., 2016). Toxic heavy metals like Pb, Hg, Cd, Cr, Ni and Zn are an example. Heavy metals occur naturally in the crust of the earth having atomic weight and a high density greater than that of water (Zhang *et al*., 2011). These elements can conduct heat, electricity and are malleable, ductile, and even lustre in nature (Agency for Toxic Substances and Disease Registry, 2008). They are non-biodegradable and persistent in all parts of the environment (El-Salam *et al*., 2013). The build-up of heavy metals in different environmental compartments leads to undesirable consequences for live organisms (Hobbs and Kennedy, 2011).

Metals with a density of 5 g/cm^3 cannot be destroyed, therefore, bioaccumulate in biological systems (Jabeen *et al.,* 2012). Heavy metals are grouped into three groups: A, B, and borderline (International Agency for Research on Cancer, 2014). Group A metals prefer ligands containing oxygen (e.g., manganese and uranium). Group B elements prefer to form ligands with sulphur and nitrogen (e.g., zinc, lead, chromium, and nickel). Borderline elements are middle between group A and group B (e.g., mercury and cadmium) (IARC, 2014). These elements can originate from both anthropogenic and natural processes. Heavy metals of a public health concern to living organisms include Hg, Cd, Pb, Ni, Cr and Zn (IARC, 2014). They occur naturally in the environment in small quantities (Hobbs and Kennedy, 2011). However, some of these metals in small amounts are nutritionally essential for a healthy life (Jabeen *et al.,* 2012).

2.5.2 Exposure pathways of heavy metals in the environment

Heavy metals accumulate in various environmental compartments (soil, water, plants, and air) originating from both natural and anthropogenic processes (El-Salam *et al*., 2013). Contamination of the environment with heavy metals poses a serious threat due to their toxicity, bioaccumulation and increasing in concentrations in the food chain (Mann *et al*., 2011). Food safety is an important public health concern. As indicated in the diagram below (Figure 2.1) the discharges of heavy metals into the ecosystem occur through the range of processes and pathways (Pollard *et al*., 2014). Heavy metals at concentrations exceeding the recommended limit pose serious risks to ecosystems and human health (World Health Organization, 2011). Man-made processes promote heavy metal contamination through various activities. These activities release metals into the environment. Heavy metals cannot be destroyed, and they persist in the environment for years (El-Salam *et al*., 2013). Heavy metals in nature have a unique way of expressing themselves and follow definite pathways in the ecosystem as given in Fig.2.1 (Correll *et al*., 2004).

People and animals are more susceptible to exposure of possibly harmful heavy metals in food, air, soil, and water (Zhang *et al*., 2011). The contact between the heavy metal, the animal and human body has caused increasing concern (Mosilova *et al*., 2016). These elements can cause various biological and biochemical disorders (Hobbs and Kennedy, 2011). Water is an important resource for the sustainability of life and any pollution of water sources can be located to the environmental components (Schultze *et al*., 2010). Pastures take up heavy metals from contaminated soil and water. Leaves of plants serve as a diet for goats and other organisms. However, the effects of contaminants on the environment depend on the mobility and availability of each metal through environmental compartments and pathways (Grobler *et al.,* 1994).

2.5.3 Heavy metals in water

Water is a vital medium for the transport of metals. Heavy metals are natural constituents of the piles of earth crust and are normally found at low concentrations in surface and groundwater (Zhang *et al*., 2011). Heavy metals are transported by runoff from man-made activities. These elements end up accumulating in the water and sediments (Oberholster *et al*., 2012). The presence of heavy metals in water degrades their quality, which affects all live organisms (Department of Water Affairs and Forestry, 1996). Goats are prone to hazards of contamination originating from man-made activities (Correll *et al*., 2004). Humans eating such contaminated meat are liable to severe health problems due to increasing concentrations of heavy metals in their bodies (Du Preez *et al*., 2003). The Olifants river, a tributary of the Limpopo river, is one of the most polluted river systems in South Africa (Oberholster *et al*., 2010). This river passes through the urban and rural areas until it joins the Limpopo river.

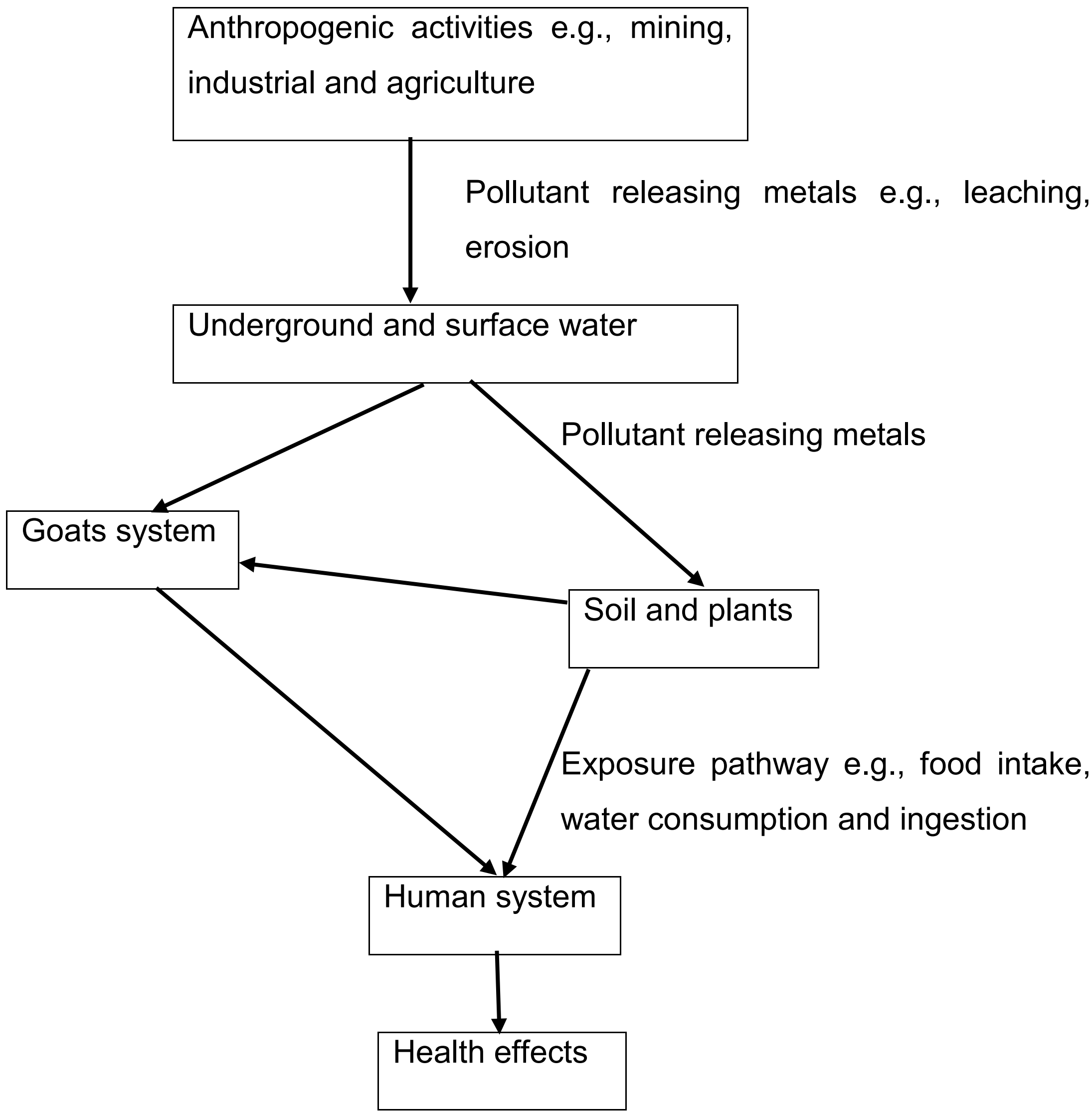

Fig.2.1 Simplified diagrammatic representative pathways of heavy metals in the food chain (Source: Correll *et al*., 2004)

All species have tolerance limits which vary from one species to another (du Preez *et al*., 2003). DWAF (1996) reported that the recommended limits of heavy metals should not overdo tolerable limits. Metals such as Zn, Cu and Fe are needed at low concentrations as catalysts for enzyme activities (WHO, 1991). However, at high levels they may cause acute or chronic illnesses in animals and humans (Correll *et al*., 2004). According to Dallas and Day (2004), increasing heavy metal concentrations in water result in adverse effects on fish and animals drinking the water. The Loskop and Flag Boshielo dams have been a storehouse for contaminants from the upper catchments of the Olifants River system (Oberholster *et al*., 2010). Studies from the Loskop, Flag Boshielo and Phalaborwa Barrage impoundments on the main stem of

Olifants River have revealed higher levels of metals in fish (Addo-Bediako *et al*., 2014a, 2014b; Jooste *et al*., 2014, 2015). Okonkwo and Mothiba (2005) found high levels of Cd and Pb contaminants in the Dzindi, Madazhe and Mvudi rivers of Thohoyandou in Limpopo province. Lebepe *et al.* (2016) reported the Zn levels ranged between 0.0003 and 0.003 mg/L in the Loskop dam and that ranged between 0.002 and 0.003 mg/L in the Flag Boshielo dam, respectively.

Zinc is a chemical element with atomic number 30 (IARC, 2014). Zinc has a shining bluish-white appearance and occurs naturally in water (DWAF, 1996). Mining and industries increase zinc concentrations in water bodies (Mohod and Dhote, 2013). The toxicity of zinc occurs in various forms either in an acute or chronic form (WHO, 2011). Acute effects include nausea, loss of appetite, diarrhoea, and metabolic defects (WHO, 2011). Chronic effects include immunity declines, copper deficiency and organ damage (WHO, 2011). Zinc in low concentrations is an essential element for animals and humans in forming connective tissues like ligaments and tendons (Mohod and Dhote, 2013). However, excess Zn is toxic to pastures, animals, and humans.

Lead is a chemical element with atomic number 82 (IARC, 2014). Lead is a bluish or silvery grey, soft and malleable metal present in the environment and occurs naturally in rocks, soils, and the water (IARC, 2014). It has no nutritional value and there is no confirmed safe level of lead exposure (WHO, 2011). The anthropogenic activities such as mining, metallurgical industry, motor oil and storage battery production are the major discharges of lead particulate into the environment (DWAF, 1996). Lead is an abundant metal that poses a threat to animal and human health (Mohod and Dhote, 2013). It adversely affects the formation of haemoglobin, gastro internal tract, central nervous system, kidneys and may cause liver damage (WHO, 2011). Lead can be transferred to the goats through drinking contaminated water and eating contaminated pastures. Lead is among the most deleterious metals that cause significant contamination of the earths water and soil (IARC, 2014).

Cadmium is a chemical element with an atomic number 48 (IARC, 2014). Cadmium is soft, silvery-white and a highly toxic metal in nature, even at low concentrations (DWAF, 1996). Cadmium has been used for pigments, coating, plating, stabilizers for plastics and in textile industry (Lopez *et al*., 2006; Mohod and Dhote, 2013). Naturally, a high level of cadmium is released into the environment, especially into rivers and soils through weathering of rocks and human activities such as textile industry and manufacturing (DWAF, 1996). Cadmium waste streams from human activities end up in water and soils. Cadmium is characterized by high mobility in the biological systems (Grobler *et al.,* 1994). High levels of Cadmium have no essential functions to the environment and pose harmful effects in animals and human beings (WHO, 2011). IARC (2014) indicated that cadmium is usually found as a compound combined with other elements like oxygen (cadmium oxide) or chlorine (cadmium chloride) in the ecosystem. Long-term exposure to Cd has been associated with lung cancer, kidney dysfunction, bone defects and renal dysfunction in live organisms (WHO, 2011).

Chromium is a naturally abundant heavy metal in the environment with an atomic number 24 (IARC, 2014). It is a steely grey, lustrous, hard, and brittle transitional metal (IARC, 2014). Chromium is naturally present in the environment in low levels but industrial use in stainless steel, chrome plating and dyes for textiles increase the levels of Cd in the environment (Lugueno *et al*., 2013). Chromium is mainly found in differing levels in the water, soil, and air (DWAF, 1991). However, different kinds of Cr differ in their effects upon organisms (WHO, 2011). Chromium enters the water, soil and pastures in the Cr (III) and Cr (VI) form through human and natural activities (Lugueno *et al*., 2013). Lugueno *et al.* (2013) found that the aqueous solubility of Cr (III) is a function of the pH of the water. WHO (2011) demonstrated that chromium is regarded as a carcinogenic agent to humans of which can result in ulceration of the skin, nose irritation and weak immunity. Long-term exposure to chromium can cause kidney and liver damages and nerve tissue damage in live organisms (IARC, 2014). In animals, it decreases longevity, impairs growth, and decreases reproductive functions (WHO, 2011).

Mercury is a chemical element with an atomic number 80 (IARC, 2014). Mercury occurs in the environment either in an organic or inorganic form (IARC, 2014). Mercury dissolves many metals such as gold and silver to form amalgams (Jeffrey, 2005a). Mining and smelting increase concentration of Hg in the environment (DWAF, 1996). According to WHO (2011), live organisms may be exposed to high concentration of Hg, either in acute or chronic exposure. Its toxicity poses many health problems and is very difficult for the body to eliminate it (Mohod and Dhote, 2013). Methylmercury is a non-essential and toxic metal which is usually associated with various diseases like nervous, digestive, and immune systems damage in animals, fish, and human beings (Chen *et al.,* 2012).

Nickel is a chemical element with an atomic number 28. It is a silver-white lustrous transitional metal (IARC, 2014). Nickel is found naturally in Earth's crust only in low levels usually in water and rocks (DWAF, 1991). Cempel and Nickel (2006) found that nickel is accumulative in water, but its presence is not magnified along the food chain. The man-made sources of Ni are mainly from mining, corroded metal pipes and containers (Cempel and Nickel, 2006). Animals and humans may absorb nickel toxicity from water and food. Nickel is not a cumulative poison, but high levels of exposure may be carcinogenic and cause damage to DNA and skin disorders (WHO, 2011). Nickel can replace essential metal ions in enzymes, proteins, and cellular compounds in animals, therefore, resulting in lethal effects (Cempel and Nickel, 2006).

2.5.4 Heavy metals in soils

Heavy metals occur naturally in soils at low levels because of weathering and formation of soil processes (Alloway, 2013). Kabata-Pendias and Pendias (2001) indicated that heavy metal levels in soils are likely to increase with growing mining, industrial and agricultural activities. Soil acts as a sink for heavy metal absorption. Similarly, Herselman *et al*. (2006) demonstrated that the soil is a crucial component to terrestrial ecosystems. Accumulation of heavy metals in soils depletes slowly by leaching, erosion, and pasture uptake (Kabata-Pendias and Pendias, 2001). However, soil pH, organic matter content, plants varieties and plant age influence the metals concentration in soil (Alloway, 2013). Adeleken and Abegunde (2011) indicated that the presence of heavy metals in the soil can adversely affect soil microbes. The toxicity and mobility of heavy metals in the soil depend on the metal properties, soil properties and environmental factors (Herselman and Steyn, 2001).

Heavy metals in the soil were studied in different parts of South Africa (Herselman *et al*., 2006). Soil contamination is of great concern throughout the world due to the potential risk of affecting food quality, pasture growth and environment (Herselman and Steyn, 2001). Heavy metals such as Pb, Zn, Cu, Cr, Cd, Cu and Ni are of most concern in a South African soils (Herselman *et al*., 2006). Zinc is an abundant metal in the crust of the earth and often found as ZnS in the natural ores (Kabata-Pendias and Pendias, 2001). High levels of zinc in the soil can be associated with anthropogenic activities such as mining and smelting operations, making it mobile and available to pastures (Herselman *et al*., 2006). Soil is the greatest reservoir of Zn concentration (Kabata-Pendias and Pendias, 2001). Herselman *et al*. (2006) reported that zinc is more mobile in soil and further available to pastures than other heavy metals. Excessive levels of Zn in the soil can change the activities of the soil microorganisms, which affect organic matter breakdown (Lokeshwari and Chandrappa, 2006). Lokeshwari and Chandrappa (2006) further indicated that high levels of Zn in soil interfere with the ability of pastures to absorb other essential metals.

Chromium is an abundant metal in the earth layer, and it occurs as chromite (Lugueno *et al*., 2013). It exists in several oxidation states in the soil such as the trivalent Cr (III) and hexavalent Cr (VI) (Dheeba and Sampathkumar, 2012). Chromium enters the soil and water in the form of Cr (III) and Cr (VI). Lugueno *et al*. (2013) indicated that through waste disposal Cr will end up in soils. Chromium in soils attaches to soil particles and as a result, it will not move towards groundwater (Dheeba and Sampathkumar, 2012). The levels of Cr in the soil may increase mainly through anthropogenic activities (Herselman *et al*., 2006). The Cr (III) is an essential nutrient for animals and humans and shortages may cause health effects (WHO, 2011). Adeleken and Abegunde (2011) also reported that its toxicity in the soil is rare, but an excessive amount can cause adverse effects in plants and animals.

Cadmium is also a naturally occurring element in the soil and pastures (Alloway, 2013). The release of Cd waste from human activities mainly ends up in soils (Herselman and Steyn, 2001). The mobility and accumulation of cadmium in the soil are mainly influenced by organic matter and the pH (Kabata-Pendias and Pendias, 2001). Cadmium is strongly absorbed into organic matter in soils. The lower the pH and clay content, the higher the mobility of cadmium (Alloway, 2013). High levels of Cd in soils can influence soil processes of microorganisms and threaten the whole soil ecosystem (Herselman and Steyn, 2001). Subsequently, it may become more accessible to pastures and goats grazing on such pastures. Miranda *et al*. (2005) reported that cadmium is a non-essential and toxic metal to pastures, animals, and human beings.

Mercury, on the other hand, is considered highly toxic and is a true heavy metal with a density of 13.5g/cm^3 (Alloway, 2013). The main source of Hg release is the combustion of fossil fuel and gold mining (Han *et al*., 2006). Han *et al*. (2006) also indicated that once the Hg released into the environment, maybe deposited into soil, pastures and water. This is a potential threat to the animals that are dependent upon the water and pastures for survival. Furthermore, mercury exists in different forms in the environmental compartments (Dheeba and Sampathkumar, 2012). Han *et al*. (2006) reported that the mercury ionic form (Hg^{2+}) is predominant and high levels of Hg^{2+} can result in observable physiological disorders in plants and animals.

Lead is a chemical element that occurs naturally in the rocks and soils (Herselman *et al*., 2006). It is the most abundant and toxic heavy metal (Alloway, 2013). Soil can be contaminated through particulate accumulation from lead metallurgical industry, traffic, filling station, mining, and releases from leaded gasoline (Herselman and Steyn, 2001). Lead accumulates in the topsoil due to the low mobility and bind to soil properties (Kabata-Pendias and Pendias, 2001). Hence, pastures growing along such areas can take up lead from the soil (Herselman *et al*., 2006). Kabata-Pendias and Pendias (2001) indicated that high levels of lead in pastures pose a threat to animal and human health.

Nickel is a transition element in the centre of the periodic table, acts as a catalyst and found in the environment at low concentrations (Cempel and Nikel, 2006). Higher levels of Ni compound that are released into the environment will be absorbed by soil particles and become immobile as a result (Kabata-Pendias and Pendias, 2001). High concentration of nickel in the soil retards plant growth and development of soil microorganisms (Cempel and Nikel, 2006). However, the high levels of Ni in the soil are dependent on the nickel content of parent rocks since it is gathered during the weathering process (Kabata-Pendias and Pendias, 2001). Herselman *et al*. (2006) found that the excessive levels of nickel in the soil cause various physiological alteration and toxicity in pastures and animals.

2.5.5 Heavy metals in pastures

Pastures play a significant role in the food chain (Khan *et al*., 2008). Anthropogenic activities harm the environment and the ecosystem as indicated in Figure 2.1. Sharma *et al*. (2007) found that pastures can accumulate heavy metals because of their ability to adapt to various chemical properties of the environment. The concentration of metals in the top 0.075m of the soil is of relevance because roots of most grasses are in this region, and it is the surface soil that may be ingested along with herbage by grazing ruminants (Alloway, 2013). The grazing animal can ingest the metal either by consuming pastures that are internally or externally contaminated or by consuming contaminated soil (Wilkinson *et al*., 2003). Alloway (1999) and Khan *et al*. (2008) indicated that the main factors affecting toxic metal uptake by pastures are the chemical speciation of the mineral fraction of the soil, the soil organic matter content, and soil permeability and chemical properties. Pastures are intermediate reservoirs which transport heavy metals from soil to grazing animals (Hobbs and Kennedy, 2011). Heavy metals such as Cd, Hg, Pb are non-essential for plant growth and others like Cu, Zn, Ni are essentially required in low levels for normal growth and metabolic processes of plants (Khan *et al*., 2008). Heavy metal levels in plants generally reflect that in the soil, only in the case of Cd, Hg, Zn and Cr (Alloway, 1999).

Pastures which grow in contaminated environments may be stressed and stress limits plant photosynthesis (Bonanno and Lo Giudice, 2010). Bonanno and Lo Giudice (2010) showed that stressed plants change the chlorophyll content before any physical signs of stress are evident. Usually, contaminated pastures may result in animals being contaminated with heavy metals. Humans who eat such contaminated meat may, also, become contaminated (Sharma *et al*., 2007). Zinc is an essential metal that affects numerous metabolic processes of plants (Zhang *et al*., 2009). The level of Zn in plants varies with the level in soil, plants that grow in soils that are Zn deficient are susceptible to diseases (Alloway, 1999). The higher levels of Zn in soil prevent plants metabolism, resulting in reduce growth and causing senescence (Herselman *et al*., 2006). Excessive level of Zn is toxic to plants and animals. The regulatory standard for zinc in plants as recommended by WHO is 50 mg/kg.

Nickel is not a significant metal for plant growth and development; however, it is an essential micronutrient required for normal metabolic functions (Cempel and Nikel, 2005). High levels of Ni on sandy soils can damage plants. Cempel and Nikel (2005) reported that higher levels of nickel in pastures cause various toxicity signs such as chlorosis, etc. (Cempel and Nikel, 2005). Similarly, Khalid and Tinsley (1986) reported that the leaves of ryegrass (*Lotium perenne*) turned yellowish when treated with a high amount of nickel. The permissible limit of Ni in pastures as set by WHO is 10 mg/kg. The permissible limit of cadmium in plants is 0.020 mg/kg as set by WHO (2011).

When the cadmium is present in soils it can be dangerous, as the uptake through food will increase (WHO, 2011). However, soil that is acidified enhances the Cd uptake by plants (Alloway, 1999). Pastures growing in soil with high levels of cadmium show symptoms of chlorosis and growth inhibition (Zhang *et al*., 2009).

Chromium (III) is an essential metal in pastures and pastures contain systems that arrange the Cr uptake to be adequate not to cause any harm (Bonanno and Lo Giudice, 2010). But, when the essential Cr (III) exceeds a certain level, negative effects can occur (Herselman *et al*., 2006). Acidification of soil can also influence Cr uptake by pastures (Alloway, 1999). The higher levels of Cr in plants affect the physiological process of seed germination (Zhang *et al*., 2009). The regulatory standard for chromium in pastures as suggested by WHO is 1.300 mg/kg. Lead occurs naturally in soil and water (Herselman *et al*., 2006). Environmental Pb can compete with other metals found in and on plant surfaces, potentially inhibiting photosynthesis processes (Bonanno and Lo Giudice, 2010). Contamination of soils and plants can allow Pb to go up the food chain affecting animals and humans. The permissible limit of Pb in plants as suggested by WHO is 2 mg/kg. Mercury is considered highly toxic in plants and animals (Alloway, 2013). High levels of Hg are strongly phytotoxic to plant cells (Messer *et al*., 2005). Excessive Hg may result in physiological disorders such as disturbance of metabolic functions (Messer *et al*., 2005). The maximum permissible limit of Hg in plants as recommended by WHO is 0.002 mg/kg. Normally, high levels of heavy metals in pastures above the permissible limits harm grazing animals (WHO, 2011).

Urochloa mosambicensis (witbuffels grass, common name in South Africa) is an abundant grass growing along the riverbanks (Harwood *et al*., 1996). This grass is a perennial, loosely tufted grass sometimes rooting and branching from the lower nodes, occasionally with stolon, hairy leaf blades and rare rhizomes (Burt *et al*., 1980). It is usually found near the riverbanks, wooded grassland and on disturbed sites where the soil is fertile. Burt *et al*. (1980) indicated that witbuffels grass is mostly used as supplements for animals during dry seasons and erosion control. Harwood *et al*. (1996) found that the *urochloa mosambicensis* prefer well-drained soils and can withstand high temperatures. Its nutritive value varies with the age of regrowth and soil fertility (Harwood *et al*., 1996). This grass is selectively grazed by animals when it is still young and is more palatable than other grasses when mature (Mclvor *et al*., 1992). This grass is, therefore, a good indicator of the level of heavy metals as they grow along the riverbanks.

2.5.6 Heavy metals in livestock meat

Meat and milk are the most essential products of goat rearing. Heavy metals can be transferred to these animals through drinking contaminated water and grazing contaminated pastures. Therefore, heavy metals can bio-accumulate in the tissues and organs of these animals (Alonso *et al*., 2004). The concentrations of heavy metals in the South African environment have been studied. The presence of heavy metals at high levels has been reported in fish, water, and soil (Herselman *et al*., 2001, 2006; Okonkwo and Mothiba, 2005; Addo-Bediako *et al*., 2014a, 2014b; Jooste *et al*., 2014, 2015; Lebepe *et al*., 2016). Across the world, some studies have been made on the levels of heavy metals in animal species (Miranda *et al*., 2005; Okoye and uGu, 2010).

The pH is one of the basic factors that can affect meat quality (Simela *et al*., 2004a). The significant pH value in goat carcasses ranges between 5.8 and 6.2 (Simela *et al*., 2004a, b). Simela *et al*. (2004b) indicated that the alterations with low pH (pale, soft and exudative) or high pH (dark, firm, and dry) are not usual in goat carcasses. However, meat with low pH tends to be more tender, better colorimetric and with low shear force than those with high pH values (Simela *et al*., 2004a). Simela *et al*. (2004b) reported that the minimum glycogen concentration of 50 μmol/g in the carcass is vital for enough lactatic acid production to attain an acceptable pH value. Palatability, free of pathogens and toxins determines the quality of meat (Webb *et al*., 2005). Casey *et al*. (2003) indicated that goat meat has a high nutritional value, and it is beneficial for health-conscious consumers.

Metals which have non-nutritional requirements, that is Pb, Cd, Cr and Ni may react with biological systems to cause adverse effects in animals and humans (Akan *et al.,* 2010). Okoto *et al*. (2014) reported above maximum permissible levels of heavy metals in goats. Cadmium accumulates, mainly, in the kidneys and livers of animals because of their lower rates of elimination (Demirezen, and Uruç, 2006). Animal uptake of Cd takes place through contaminated food and water. Pastures and water that are rich in Cd can enhance the Cd level in the animal body. High levels of cadmium can lead to kidney defects, bone and pulmonary damages, renal degradation, intestinal dysfunction, and anaemia (ATSDR, 2005). ATSDR (2005) indicated that the higher levels of cadmium were responsible for the itai-itai disease in humans (painful screams in the Japanese language) because of the severe discomfort in the joints and spine. El-Salam *et al*. (2013) found that the Cd levels in muscle, liver and kidneys of cattle were higher in mining areas than in rural areas. Demirezen and Uruç (2006) indicated that the accumulation of Cd in goat tissues increases with age. Similarly, Akan *et al*. (2014) found that the levels of cadmium in animal blood were mainly used for determining recent exposure to cadmium contamination.

Lead in animal systems has no confirmed biological role and there is no confirmed safe level of lead exposure (WHO, 1991). Lead is a highly lethal metal, affecting almost every organ and system in the animal and human body (Miranda *et al*., 2009). Okoye and Ugwu (2010) reported that the levels of lead in the blood indicate the lead concentrations in other vital organs. Most ingested Pb is absorbed into the bloodstream (Okoye and Ugwu, 2010). Snezena *et al*. (2010) found the higher Pb levels in the kidneys and livers of domestic animals at contaminated localities. Lead toxicity is well known for interfering with the proper functioning of enzymes (FAO/WHO, 2007). High levels of lead are known to cause health problems in red blood cells, kidney, and liver damages in animals (Miranda *et al*., 2005). In humans, it causes poor cognitive development, increases blood pressure and cardiovascular diseases, and ultimately death (WHO, 1991).

Chromium (Cr) is an essential element for animals and humans, helping the body to use sugar, protein, and fat while at the same time it is carcinogenic (Akan *et al*., 2010). According to EI-Salam *et al*. (2013), an excessive amount of Cr may cause adverse health effects such as reducing the liver size and weight and causing liver and kidney damages in animals and human beings. El-Salam *et al*. (2013) and Akan *et al*. (2014) indicated that blood helps in the circulation of substances around the body, thus, unwanted substances such as chromium may be trapped in the blood during this process. The kidney and liver tend to accumulate a higher level of chromium (Demireze and Uruç, 2006). Demireze and Uruç (2006) reported that the concentrations of contaminants in the liver and kidney are due to their inability to filter off contaminants completely.

Mercury is not naturally present in a living organism (IARC, 2014). Mercury is a toxic substance with no known function in the physiology or biochemistry of living organisms (WHO, 1991). Akoto *et al*. (2014) found that mercury levels in meat tissues of free-ranging sheep and goats were above the permissible limit at a gold mining town in Ghana. Chen *et al.* (2012) indicated that the toxicity of mercury depends on its chemical form, thus, the methyl mercury being the most lethal metal in animals and humans. The methyl mercury is more soluble in fats compared to water and the deposition of mercury is rapid, but its elimination is slow (Akoto *et al*., 2014). High levels of mercury preferentially accumulate in the kidneys, while the accumulation in the liver and other organs is lower (Demireze and Uruç, 2006). Furthermore, high levels of methyl mercury in the bloodstreams of animals and humans may affect hearing, vision, immunologic system, and brain damages (WHO, 1991).

Nickel is an essential metal for animals at low levels (WHO, 1991). It can be harmful when the maximum permissible limits are exceeded (Cempel and Nickel, 2006). According to Alonso *et al*. (2004), nickel plays an essential role as an activator for some enzymatic reactions such as the synthesis of red blood cells. Akan *et al*. (2010) reported higher levels of Ni in the liver than in the kidney in local chickens reared in cocoa-producing areas of Cross River State in Nigeria. Similarly, Akan *et al.* (2010) also reported the low levels of Ni in the meat and organs of goats and sheep reared in Maiduguri Metropolitan, Nigeria. WHO (1991) reported that the low levels of Ni in the human body play a significant role in regulating prolactin hormone and stabilization of RNA and DNA structures. Excessive intake of Ni can cause various kinds of cancer within the bodies of animals and humans (WHO, 1991).

Zinc, unlike other heavy metals, is essential for normal functioning of cells including protein synthesis, carbohydrate metabolism, cell growth and cell division in animals and humans (Mohod and Dhote, 2013). Alonso *et al.* (2004) indicated that muscles are important tissues for zinc accumulation, like zinc concentrations in the liver and kidneys. Zinc deficiency or high levels of Zn may cause adverse health effects in animals and humans (Demireze and Uruç, 2005; Miranda *et al*., 2009).

2.6 Conclusion

Pedi goats are common in rural areas of Limpopo province. They are nutritionally, economically, and culturally very important. However, these goats graze along the

Olifants riverbanks. Olifants river water is contaminated with heavy metals (Hg, Cd, Pb, Zn, Ni and Cr). Mining, industrial, and agricultural activities are major sources of heavy metal pollution in Limpopo province. Heavy metals constitute serious environmental problems. Animals that graze on contaminated pastures and drink polluted water accumulate heavy metals in their bodies. These elements tend to bio-accumulative, increasing in meat tissues and organs of animals, especially the liver and kidneys. People eating contaminated meat may have higher levels of heavy metals in their bodies. Thus, consumption of such meat may lead to lung cancer, high blood pressure, gastrointestinal cancer, and kidney and bone problems in humans. However, information on the levels of heavy metals in meat tissues of yearling Pedi goats reared in the Middle Olifants river catchment area is not available. Thus, there is a need to determine heavy metal levels in meat tissues from such goats. There is, also, need to determine heavy metal levels in pastures grown along these rivers.

CHAPTER 3

LEVELS OF SELECTED HEAVY METALS IN WATER, SOIL AND PASTURES GROWING ALONG THE MIDDLE OLIFANTS AND MOGALAKWENA RIVER BANKS

Abstract

The study was carried out to determine the levels of Cr, Ni, Cd, Pb, Hg and Zn in water, soil and witbuffels grass growing along the banks of Middle Olifants and Mogalakwena rivers. The samples were collected from river water, and soils and grass grown along the river banks and analysed for heavy metals with an inductively coupled plasma mass spectroscopy (ICP-MS). Data was analysed as in a complete randomised design. The results of the selected heavy metals in water of both rivers ranged from 0.00 mg/litre of water (Ni and Cr) to 0.04 mg/litre of water (Hg). The concentrations of the selected heavy metals in water were similar *(P>0.05)* for Middle Olifants and Mogalakwena rivers. The concentrations of Zn, Pb and Cd in water from both sites were above the internationally permissible levels, indicating that the water from these rivers was not safe for fish, humans, and animals. The concentrations of selected heavy metals in the soils along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM soil (Hg and Cd) to 63.70 mg/kg DM soil (Cr). There were similar *(P>0.05)* concentrations of the selected heavy metals in the soils along the banks of Middle Olifants and Mogalakwena rivers. The concentrations of Ni and Pb in soils from both sites were above the internationally recommended limits of 50 and 6.60 mg/kg DM of soil, indicating that the soils along the banks of these rivers were not good for crop production. Heavy metal concentrations in the witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM of grass (Hg and Cd) to 5.05 mg/kg DM of grass (Zn). Similar *(P>0.05)* concentrations of the selected heavy metals were observed in witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers. The concentrations of Zn, Ni, Pb, Hg and Cd in pastures grown along the banks of both rivers were within the maximum permissible levels for plant growth. However, chromium concentrations in witbuffels grass from both sites were above the recommended limits for livestock, indicating that the grass was not safe for consumption by livestock. It is concluded that water, soils, and pastures from the study areas contain some heavy metal concentration levels higher than the maximum permissible levels.

Keywords: Heavy metals, water, soil, witbuffels grass, Middle Olifants river, Mogalakwena river.

3.1 Introduction

Heavy metals are serious contaminants because of their toxicity, persistence, and ability to be combined into the food chain (Howard, 2016). Heavy metals are found naturally in the piles of the earth crust. Various anthropogenic activities such as mining, smelting, burning of fossil fuels and industries have led to the introduction of heavy metals into the environment resulting in deleterious effects (Hilson, 2006). The soil and pastures growing along the riverbanks are recognised to have a large capacity to accumulate heavy metals, thus, retaining heavy metals that can have toxic effects on animals and humans (Prokisch *et al*., 2009). Jeffrey (2005a) demonstrated that the Limpopo province is noted for its rich variety of mineral wealth. The heavy metals such as Pb, Zn, Cu, Cr, Cd and Ni are of most concern in South African soils (Herselman *et al*., 2006). Heavy metals are some of the major causes of toxicity in livestock production. Heavy metal contamination has raised public and scientific interest throughout the world due to their toxic effects even at very low levels (Mann *et al*., 2011). The high levels of heavy metals found in water, soil and pasture have a significant impact on livestock production. Livestock and humans get exposed to the levels of heavy metals mainly through ingestion of contaminated food and water (Mann *et al*., 2011; Jabeen *et al.,* 2012).

Heavy metals are normally present in water and soils at low levels. Contamination of water and soil may prove harmful to pasture through its uptake of heavy metals to toxic levels, thus, assisting its entry into the food chain (Pollard *et al*., 2014). Pastures may absorb toxic metals from the soil. Ruminants such as goats may feed on pastures which have absorbed and accumulated elements from the soil over time. Some metals such as Ni, Cr and Zn are essential in low amounts, for animals and human health (FAO/WHO, 2007). However, excessively higher levels of Hg, Cd, Cr, Zn, Ni and Pb in blood and tissues of animals suggest an exposure either from the water, soil, pastures, and air or from all these sources (El-Salam *et al*., 2013). Humans, as the final consumers in the food chain, may accumulate high levels of some heavy metals in their tissues from contaminated food (Correll *et al*., 2004). Accumulation of the studied Hg, Cd, Cr, Zn, Ni and Pb in water, soil and pastures could be useful indicators of potentially toxic effects on livestock and the consumers. High levels of heavy metals in the food of animal and plant origin are directly related to human illnesses (FAO/WHO, 2007). Their potential toxicity to animals and humans is a source of concern. The measurement of heavy metal levels in the water, soil and pasture is helpful not only in determining risks to animal and human health but also in the assessment of environmental quality (Okoye and Ugwu, 2010). Therefore, there was need to determine the levels of heavy metals in water and witbuffels grass growing along the Middle Olifants and Mogalakwena river basins and the two river basins sustain the rural communities with water for household consumption and drinking of animals. Such information is important for designing strategies to reduce heavy metal contamination among Pedi goats grazing in the catchment areas.

3.2 Objective

The objective of the study was to determine the levels of Pb, Hg, Zn, Cd, Ni and Cr in water, soil and witbuffels grass (*Urochloa mosambicensis*) growing along the banks of Middle Olifants and Mogalakwena rivers.

3.3 Hypothesis

There were low levels of Zn, Cd, Hg, Ni, Pb and Cr in water, soil and witbuffels grass (*Urochloa mosambicensis*) growing along the banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papeggai village) rivers.

3.4 Methodology and analytical analysis

3.4.1 Study site

The study was conducted in Mogalatsana village (Middle Olifants river) (latitude 24°46′ S, longitude 29°25′ E) and in Papeggai village (Mogalakwena River) (Latitude 23°11′30″S, longitude 28°41′5″E) in Limpopo province, South Africa (Figures 3.1 and 3.2, respectively). The temperatures in the study sites range between 18 and 36 ºC during summer months and between 10 and 25 ºC during winter months (Peacock, 1996). The topography of the study areas is generally mountainous and flat to rolling. The vegetation is veld type that is dominated by thorny acacia bushes, grassland and shrubs that cover most of the terrain (DWAF, 1996; Peacock, 1996).

Fig 3.1 Location of sampling site at Mogalatsana village (Middle Olifants river)

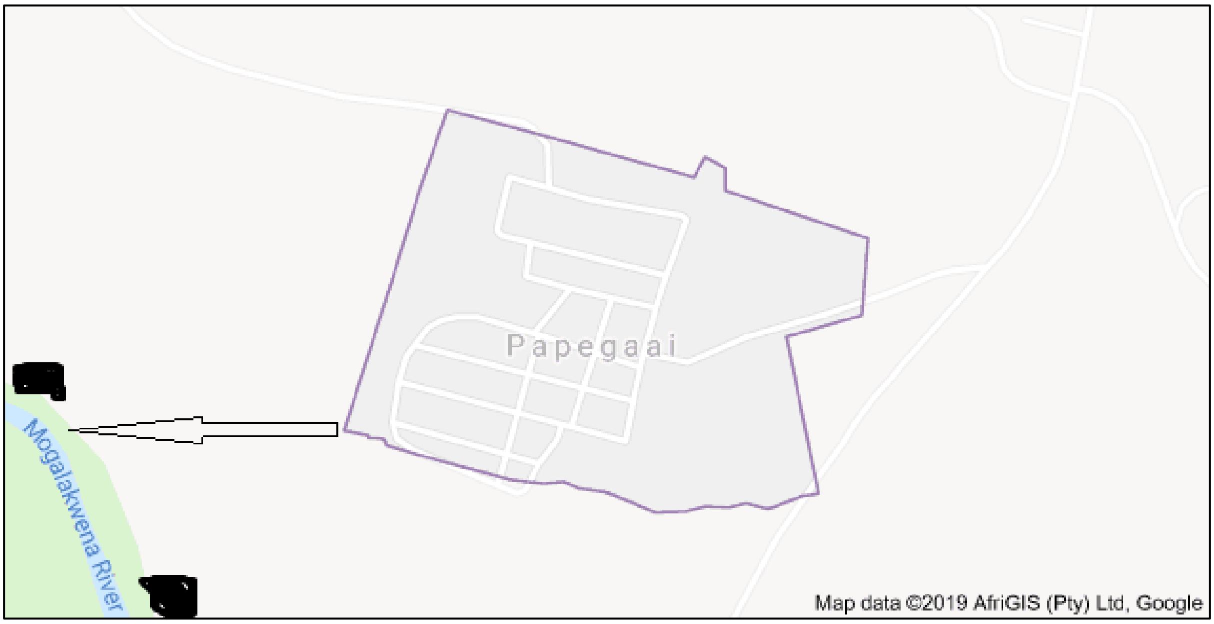

Fig 3.2 Location of sampling site at Papegaai village (Mogalakwena river)

3.4.2 Sample collection and analysis

1. **Water samples**

Water samples were randomly collected from the rivers, about 2 meters. The water was collected in 500 ml plastic bottles. Water was collected from two sites along the

Middle Olifants river and Mogalakwena river basins, on the 14th of December, 2019. The water samples were properly labelled and stored in the refrigerator (−4°C) before being transported to the laboratory for Pb, Hg, Cd, Cr, Zn and Ni analysis. The samples were sent to an accredited laboratory, WaterLab (PTY) Ltd in Pretoria for analysis. At the laboratory water samples were stored at −5 °C before analysis at a SANAS-accredited laboratory (ISO/IEC 17025:2005) in Pretoria. Water was analysed using inductively coupled plasma mass spectroscopy (ICP-MS) methods and reported as mg/ℓ (DWAF, 1996). Heavy metals (Pb, Hg, Cr and Zn) were selected due to their significant high levels recorded over the past decade in the water, sediment, and fish tissues from the Olifants river systems (Coetzee *et al*., 2002; Addo-Bediako *et al*., 2014a, 2014b; Jooste *et al*., 2014, 2015).

Fig 3.3 The river site at the Mogalatsana village (Middle Olifants river) (December, 2019)

Fig 3.4 The river site at the Papegaai village (Mogalakwena river) (December, 2019)

2. **Soil samples**

Composite soil samples were collected from Mogalatsana village along the riverbanks of Middle Olifants and from Papeggai village along the riverbanks of Mogalakwena on the 14^{th} of December, 2019 using a soil auger. Soil samples were randomly collected at a depth of 1-10 cm because the depth of roots of most grasses in the area is within this range. The texture of the soil was mainly clay particles at both riverbanks. The soil samples were kept in zip-locked plastic bags, properly labelled, and stored at room temperature before being transported to an accredited laboratory, WaterLab (PTY) Ltd in Pretoria for heavy metal analysis.

At the SANAS-accredited laboratory in Pretoria, the samples were frozen and stored at −8 °C before analysis for heavy metals. Soil samples were dried at 105 °C to a constant weight at room temperature followed by the sample preparation with the help of pastel and mortar. The dried samples were desiccated and were digested in microwave assisted Kjeldahl digester. Soil samples were mixed with 10ml of concentrated nitric acid, 5ml perchloric acid and 2ml hydrochloride acid. The mixture was digested under a fume hood chamber according to the method of Association of Official Analytical Chemists (2005). The digested soil samples were analysed for the levels of heavy metals using inductively coupled plasma mass spectroscopy (ICP-MS) and reported as mg/kg dry weight soil (Herselman *et al*., 2006).

3. Witbuffels grass samples

Witbuffels grass **(*Urochloa mosambiscensis*)** samples in each village were randomly collected from each of the two locations at Middle Olifants riverbanks and from two locations at Mogalakwena riverbanks on the 14th of December, 2019. In a close proximate from where the soil samples were collected, witbutffels grass was sampled down to the depth where the roots can be found and uprooted (Figure 3.5). The uprooted grasses were washed with distilled water. The grasses were kept in a khaki bag, properly labelled, and stored at room temperature before being transported to an accredited laboratory, WaterLab (PTY) Ltd in Pretoria to be analysed for Cr, Pb, Cd, Ni, Zn and Hg.

At the laboratory, the samples were stored at the room temperature before analysis for heavy metals. The samples were oven-dried at 60 °C temperature to a constant weight and ground to powder. The desiccated samples were weighed for digestion. The dried samples were mixed with 10ml of concentrated nitric acid and 5ml perchloric acid. The mixture was digested in microwave assisted Kjeldahl digester. The digested grass samples were analysed for heavy metal concentration through the flame method by inductively coupled plasma mass spectroscopy (ICP-MS). The heavy metal concentration in samples were calculated in mg per kg of dry pasture (WHO, 2011).

Fig 3.5 Collection of witbuffels grass samples at Papegaai village (Mogalakwena river) (December, 2019)

3.4.3 Statistical analysis

Data on water, soil and pasture were subjected to analysis of variance (ANOVA) (Minitab, 18.1 Version). Tukey's HSD test was used to test the significant difference between treatment means at 5 % level of probability (Minitab, 18.1 Version). General linear model procedure (GML) was used to compare heavy metal levels in water, soil, and pasture samples. The following model was used:

$$Y_{ij} = \mu + T_i + \varepsilon_{ij}$$

Where Y= variables measured (concentration levels of Zn, Hg, Cr, Cd, Ni and Pb in water, soil, and pastures); T_i = fixed effect of the river (Middle Olifants or Mogalakwena); e = experimental error.

3.5 Results

3.5.1 Heavy metal concentration in Middle Olifants and Mogalakwena rivers

The results of the effect of the river on levels of selected heavy metals (Zn, Hg, Cr, Cd, Ni and Pb) in water are presented in Table 3.1. The levels of selected heavy metals in water were similar (P>0.05) for Middle Olifants and Mogalakwena rivers. Heavy metal concentrations in water ranged from 0.00 mg/litre of water (Ni and Cr) to 0.04 mg/litre of water (Zn).

Table 3.1 Effect of the river on levels of selected heavy metals (mg/litre) in water*

Heavy metal	River location		P-value
	Middle Olifants river at Mogalatsana village	Mogalakwena river at Papegaai village	
Zinc	$0.03^{a} \pm 0.000$	$0.03^{a} \pm 0.000$	1.000
Nickel	$0.00^{a} \pm 0.000$	$0.00^{a} \pm 0.000$	0.391
Mercury	$0.04^{a} \pm 0.003$	$0.04^{a} \pm 0.003$	1.000
Lead	$0.01^{a} \pm 0.000$	$0.01^{a} \pm 0.000$	0.241
Chromium	$0.00^{a} \pm 0.000$	$0.00^{a} \pm 0.000$	0.995
Cadmium	$0.03^{a} \pm 0.000$	$0.03^{a} \pm 0.000$	1.000

* : Values presented as mean ± standard error (SE)

3.5.2 Heavy metal concentration in soils along the banks of Middle Olifants and Mogalakwena rivers

The results of the effect of the river on levels of selected heavy metals in the soils along its banks are presented in Table 3.2. The levels of selected heavy metals were similar (P>0.05) in the soils along the banks of Middle Olifants and Mogalakwena rivers. Heavy metal concentrations in the soils along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM soil (Hg and Cd) to 63.70 mg/kg DM soil (Cr).

Table 3.2 Effect of the river on levels of selected heavy metals in the soils (mg/kg DM soil) along its banks*

Heavy metal	River location		P-value
	Middle Olifants river at Mogalatsana village	Mogalakwena river at Papegaai village	
Zinc	2.78[a] ± 1.390	1.39[a] ± 0.000	0.339
Nickel	63.50[a] ± 31.100	31.10[a] ± 4.400	0.391
Mercury	0.00[a] ± 0.000	0.00[a] ± 0.000	1.000
Lead	8.02[a] ± 4.020	5.51[a] ± 4.020	0.241
Chromium	63.70[a] ± 34.900	57.60[a] ± 34.900	0.221
Cadmium	0.00[a] ± 0.000	0.00[a] ± 0.000	1.000

* : Values presented as mean ± standard error (SE)

5.5.3 Heavy metal concentration in witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers

The results of the effect of the river on levels of selected heavy metals in witbuffels grass grown along its banks are presented in Table 3.3. The levels of selected heavy metals were similar (P>0.05) in witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers. Heavy metal concentrations in the witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM of grass (Hg and Cd) to 5.05 mg/kg DM of grass (Zn).

Table 3.3 Effect of the river on levels of selected heavy metals in witbuffels grass (mg/kg DM of grass) grown along its banks*

Heavy metal	River location		P-value
	Middle Olifants river at Mogalatsana village	Mogalakwena river at Papegaai village	
Zinc	3.75[a] ± 2.540	5.05[a] ± 5.050	0.336
Nickel	0.90[a] ± 0.610	1.20[a] ± 0.610	0.391
Mercury	0.00[a] ± 0.000	0.00[a] ± 0.000	1.000
Lead	0.45[a] ± 0.260	0.45[a] ± 0.260	0.241
Chromium	1.70[a] ± 0.950	1.70[a] ± 0.950	0.221
Cadmium	0.00[a] ± 0.000	0.00[a] ± 0.000	1.000

* : Values presented as mean ± standard error (SE)

3.6 Discussion

The results of the present study indicate that the concentrations of the selected heavy metals (zinc, nickel, mercury, lead, chromium, and cadmium) in Middle Olifants and Mogalakwena rivers were statistically similar. Heavy metal concentrations ranged from 0.00 mg/litre of water (Ni and Cr) to 0.04 mg/litre of water (Zn). Water having higher concentration levels than the maximum permissible levels may pose harm to humans and animals that drink it (WHO, 2011; DWAF, 1996). The recommended regional and international guidelines for maximum permissible limits of the selected heavy metals in water, soil and pastures are presented in Table 3.4. The concentrations of nickel and chromium in the water of both rivers were within the maximum permissible levels for human, animal, and fish consumption. Studies of Addo-Bediako *et al*. (2014a) also indicated that Olifants river water concentrations of Ni and Cr were within the maximum permissible levels for consumption. However, the present study indicates that the concentrations of zinc, mercury, lead, and cadmium in both rivers were above the maximum permissible levels for human, animal, and fish consumption. This means that the water from these rivers is not good for human, animal, and fish consumption. Zhengfu *et al.* (2010) showed that the anthropogenic activities discharge metal-containing pollutants into the environment, subsequently increasing heavy metal levels in the surface and ground water. South Africa's surface and groundwater display changes in water quality (WRC, 2017). Toxic metals from mining operations find their way into the rivers, streams, and vegetation (Netshitungulwana and Yibas, 2012). The Olifants river in South Africa is one of the most polluted river systems due to mining, industrial and agricultural activities (Oberholster *et al*., 2010; Ashton and Dabrowski, 2011).

The water from Middle Olifants and Mogalakwena rivers had a zinc concentration level of 0.03 mg per litre of water. This concentration level is above the maximum permissible zinc concentration level of 0.002 mg per litre of water recommended by WHO (2011). Lebepe *et al*. (2016) also reported a higher than maximum permissible zinc concentration level of 0.003 mg per litre of water in both Loskop and Flag Boshielo dams along the Olifants river. The differences in Zn concentrations in river water could be due to seasonal influences and the position where the samples were taken (Heath *et al*., 2010). The main sources of zinc pollution in Limpopo province are anthropogenic sources such as mines, industries, agriculture, and municipal wastes (Ashton and Dabrowski, 2011; Batchelor and Engelbrecht, 1992). Excessive Zn consumption is toxic to humans, animals, and fish. Chronic effects of zinc toxicity in humans, animals and fish include immunity declines and organ damage and failure, leading to death (WHO, 2011).

Table 3.4 Regional and international recommended guidelines for maximum permissible limits of the selected heavy metals in water, soil, and pastures

Heavy metal	**Water (mg/L)[1]**	**Soil (mg/kg DM)[2]**	**Pasture (mg/kg DM)[3]**
Zinc	0.002	46.4	50.0
Nickel	0.020	50.0	10.0
Mercury	0.010	1.20	0.002
Lead	0.0002	6.60	2.00
Chromium	0.050	80.0	0.020
Cadmium	0.003	2.0	1.300

[1] : DWAF (1996) and WHO (2011)

[2] : USEPA (1995) and Herselman *et al*. (2006)

[3] : WHO (2011)

The mercury (Hg) concentration levels in water samples collected from Middle Olifants and Mogalakwena rivers were way above the maximum permissible limit of 0.010 mg per litre of water. Methyl mercury is soluble in fats and its deposition is rapid, but its elimination is slow (Akoto *et al*., 2014). High levels of mercury preferentially accumulate in the kidneys, liver, and other organs (Demireze and Uruç, 2006). Excessive consumption of Hg is usually associated with various diseases leading to damage of the nervous, digestive, and immune systems in humans, animals, and fish (Chen *et al.,* 2012). Thus, the water from Middle Olifants and Mogalakwena rivers is not safe for consumption by humans, animals, and fish. Addo-Bediako *et al*. (2014b) also observed that the water from the Olifants river contained mercury levels above the maximum permissible limits for fish and human consumption. Mining and smelting are the main sources of mercury pollution in Limpopo province of South Africa (Ashton and Dabrowski, 2011; Batchelor and Engelbrecht, 1992).

The present finding of 0.01 mg of lead per litre of water from both Middle Olifants and Mogalakwena rivers exceeds the WHO (2011) maximum permissible limit of 0.0002 mg of lead per litre of water. Lead is one of the most toxic metals in nature (WHO, 1991). The high lead (Pb) concentration levels observed in the present study pose harm to humans, animals, and fish drinking water from these rivers (DWAF, 1996). Excessive consumption of lead adversely affects the central nervous system and may prevent the formation of haemoglobin. It may, also, cause liver damage and hence death (WHO, 2011). High lead concentration levels in these rivers, also, pose harm to the surrounding environment (DWAF, 1996). Lebepe *et al*. (2016) reported similar high Pb concentration levels in Loskop and Flag Boshielo dams along the Olifants river. The authors reported Pb concentration levels ranging from 0.003 to 0.010 and from 0.01 to 0.011 mg/litre of water in Loskop and Flag Boshielo dams, respectively. Mining, smelting, and agricultural activities are the main sources of Pb pollution in Limpopo province of South Africa (Ashton and Dabrowski, 2011; Batchelor and Engelbrecht, 1992).

Middle Olifants and Mogalakwena rivers contained a cadmium (Cd) concentration level of 0.03 mg per litre of water. This concentration level is above the maximum permissible Cd concentration level of 0.003 mg per litre of water recommended by WHO (2011). The main sources of Cd pollution in Limpopo province are mines, industries, agriculture, and municipal wastes (Mohod and Dhote, 2013; Ashton and Dabrowski, 2011; Lopez *et al*., 2006; Batchelor and Engelbrecht, 1992). Thus, the higher than the maximum permissible limits of water Cd concentration levels observed in the present study pose harm to humans, animals, and fish drinking water from these rivers. However, Edokpayi *et al*. (2015) reported values of less than the maximum permissible limit of 0.003 mg of Cd per litre of water from Olifants river. The differences in reported Cd concentrations in Olifants river water could be due to seasonal influences and the position where the samples were taken (Heath *et al*., 2010).

The concentration levels of selected heavy metals in the soils along the banks of Middle Olifants and Mogalakwena rivers were statistically similar. Heavy metal concentrations in the soils along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM soil (Hg and Cd) to 63.70 mg/kg DM soil (Cr). Soils having higher concentration levels than the maximum permissible levels may pose harm to plants growing there (USEPA, 1995; Herselman *et al*., 2006). The recommended regional and international guidelines for maximum permissible limits of the selected heavy metals in soils are presented in Table 3.4. The concentrations of all selected heavy metals in the soils along the banks of Mogalakwena river were within the maximum permissible levels, thus posing no adverse effects on the growth of pastures in the areas. Similarly, zinc, mercury, chromium, and cadmium concentrations in the soils along the banks of Middle Olifants river were within the maximum permissible levels for crop production. Herselman *et al*. (2006) made similar observations. However, nickel and lead concentrations in the soils along the banks of Middle Olifants river were above the maximum permissible levels of 50 and 6.60 mg/kg DM of soil, respectively, for crop production (USEPA, 1995; Herselman *et al*., 2006). Higher than the maximum permissible levels of nickel in the soils along the banks of Middle Olifants river could be due to the presence of many mining industries in the area. The effluents from metal industries are discharged into rivers and land areas, causing accumulation of Ni in the soils (Herselman *et al*., 2006). Higher concentrations of Ni in the soils retard plant growth and development of soil microorganisms (Cempel and Nikel, 2006).

Higher than the maximum permissible concentration levels of lead in the soils along the banks of Middle Olifants river could, also, be due to the presence of many mine industries in the area. The effluents from metal industries, heavy traffic and filling stations may be responsible for accumulation of Pb in the soils along the banks of

Middle Olifants river (Herselman and Steyn, 2001). Herselman *et al*. (2006) stated that lead accumulates in the topsoil due to its low mobility and tends to bind to soil properties. Therefore, pastures growing along such areas can take up lead from the soil. Higher than the maximum permissible Pb concentration levels in the soil affect soil microbial processes, thus minimizing the number and activities of soil microorganisms (Herselman *et al*., 2006). The resultant is poor soils for plant growth.

Pastures play a significant role in the food chain (Khan *et al*., 2008). Sharma *et al*. (2007) found that pastures can accumulate heavy metals because of their ability to adapt to various chemical properties of the soil and environment. The grazing animal can ingest the metal either by consuming pastures that are internally or externally contaminated or by consuming contaminated soils (Wilkinson *et al*., 2003). Thus, pastures are intermediate reservoirs which transport heavy metals from soil to grazing animals (Hobbs and Kennedy, 2011). Heavy metal concentration levels in plants, generally, reflect those in the soil (Alloway, 1999). Pastures which grow in contaminated environments may be stressed, and stress limits plant photosynthesis (Bonanno and Lo Giudice, 2010). Witbuffels grass grows along the river banks, and it is, therefore, a good grass to use for testing accumulation of heavy metals in pastures.

In the present study, there were no statistical differences in heavy metal concentration levels between witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers. Heavy metal concentrations in the witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers ranged from 0.00 mg/kg DM of grass (Hg and Cd) to 5.05 mg/kg DM of grass (Zn). Pastures having higher concentration levels than the maximum permissible levels may pose harm to animals consuming them (WHO, 2011). The recommended maximum permissible limits of the selected heavy metals in pastures are presented in Table 3.4. The concentrations of zinc, nickel, mercury, lead, and cadmium in pastures grown along the banks of both rivers were within the maximum permissible levels for plant growth. However, chromium concentration levels in the pastures grown along the banks of Middle Olifants and Mogalakwena rivers were above the maximum permissible levels of 0.02 mg/kg DM of pastures (WHO, 2011). Higher than the maximum permissible levels of chromium (Cr) in pastures grown along the banks of Middle Olifants and Mogalakwena rivers could be due to the presence of many mining and industries in the area. The effluents from metal industries, agricultural activities, heavy traffic, and filling stations may be responsible for accumulation of Cr in pastures grown along the banks of Middle Olifants and Mogalakwena rivers (Herselman *et al*., 2006; Herselman and Steyn, 2001). Higher concentration levels of Cr in the pastures than permissible levels retard plant growth and may pose harm to animals grazing the pasture (Cempel and Nikel, 2006). Pastures growing in soils with high levels of cadmium show symptoms of chlorosis and growth inhibition (Zhang *et al*., 2009). Thus, results of the present study show that pastures grown along the banks of the two rivers have chromium concentration levels higher than a permissible level of 0.02 mg/kg DM of pasture, and hence they are not suitable for grazing by livestock. Contamination of pastures with chromium can allow the metal to go up the food chain, affecting animals and human beings (WHO, 2011). Information on heavy metal levels in pastures in the study areas is not available.

3.7 Conclusion

The concentration levels of the selected heavy metals (zinc, nickel, mercury, lead, chromium, and cadmium) in water samples from Middle Olifants and Mogalakwena rivers were similar. The concentration levels of nickel and chromium in the water of both rivers were within the maximum permissible levels recommended by WHO (2011) and DWAF (1996) for human, animal, and fish consumption. However, the present study indicates that the concentration levels of zinc, mercury, lead, and cadmium in both rivers were way above the maximum permissible levels for human, animal, and fish consumption. This means that the water from these rivers is not safe for human, animal, and fish consumption. There is, therefore, need to prevent the flow of these metals from the sources into the rivers. This may require determined efforts by all the stakeholders, that is the government of South Africa, the mines, farmers, the people, etc.

The concentration levels of selected heavy metals (zinc, mercury, nickel, chromium, lead, and cadmium) in the soils along the banks of Middle Olifants and Mogalakwena rivers were similar. The concentration levels of all selected heavy metals in the soils along the banks of Mogalakwena river were within the USEPA (1995) and Herselman *et al*. (2006) maximum permissible levels, thus posing no adverse effects on the growth of pastures and crops in the areas. Similarly, zinc, mercury, chromium, and cadmium concentration levels in the soils along the banks of Middle Olifants river were within the maximum permissible levels for crop production and hence posing no harm to crops and pastures grown in the areas. However, nickel and lead concentration levels in the soils along the banks of Middle Olifants river were above the maximum permissible levels of 50 and 6.60 mg/kg DM of soil for crop production (USEPA, 1995; Herselman *et al*., 2006), respectively. There would, also, be accumulation of these metals (nickel and lead) in the crops grown there, posing harm to animals and humans that may consume the crops.

Witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers had zinc, nickel, mercury, lead, and cadmium concentration levels lower than the maximum permissible concentration levels suggested by WHO (2011). However, chromium concentration levels in witbuffels grass grown along the banks of both rivers were higher than the maximum permissible level of 0.02 mg/kg DM of grass. This means that the grass grown in these areas is not suitable for grazing by livestock. Meat from livestock grazing such contaminated grass would pose harm to human beings eating it. It is, therefore, suggested to mitigate this contamination at the sources. There is evidence that mining and agricultural activities in Limpopo are the main sources of heavy metal contamination in water, soils, and pastures. Thus, reducing heavy metal contamination in water, soils and pastures in Limpopo province requires determined efforts by all stakeholders, that is mining companies, the government of South Africa, farmers, etc.

Heavy metal concentrations in water, soil and pastures are seasonal, depending on the amounts discharged from the sources. For example, higher values are observed during the rainy season when there is high discharge of the metals from agricultural activities (Lebepe *et al*., 2016; Addo-Bediako *et al*., 2014b; DWAF, 1996). Since heavy metal concentrations in water, soils and pastures vary every season, it is advisable that the government of South Africa or its appointed body monitors seasonal heavy metal concentration levels.

CHAPTER 4

LEVELS OF SELECTED HEAVY METALS IN BLOOD, LIVER, KIDNEY AND MEAT TISSUES OF YEARLING MALE PEDI GOATS REARED ALONG THE MIDDLE OLIFANTS AND MOGALAKWENA RIVERBANKS

Abstract

This study was carried out to determine concentration levels of zinc (Zn), chromium (Cr), mercury (Hg), cadmium (Cd), lead (Pb) and nickel (Ni) in blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants and Mogalakwena rivers in Limpopo province of South Africa. Data was analysed as in a complete randomised design. The concentration levels of these selected heavy metals were analysed using inductively coupled plasma mass spectroscopy (ICP-MS). Blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) had similar ($P>0.05$) Cr, Cd, Hg, Ni and Pb concentration levels. However, goat liver samples had higher ($P<0.05$) Zn concentrations than meat, kidney, and blood samples. Samples of goat meat contained higher ($P<0.05$) Zn concentrations than those of kidneys and blood. Similarly, goat kidney samples contained more ($P<0.05$) Zn than blood samples. Blood, liver, kidney, and meat samples of Pedi goats grazing along the banks of Mogalakwena river (Papegaai village) contained similar ($P>0.05$) concentration levels of Cr, Cd, Hg, Ni and Pb, respectively. However, goat meat samples contained higher ($P<0.05$) Zn concentrations than liver, kidney, and blood samples. Samples of goat liver contained higher ($P<0.05$) Zn concentrations than kidney and blood samples. Similarly, goat kidney samples contained more ($P<0.05$) Zn than blood samples. It is concluded that within each village (Mogalatsana or Papegaai) blood, liver, kidney, and meat samples of yearling male Pedi goats had similar Cr, Cd, Hg, Ni and Pb concentration levels. However, highest Zn concentrations were found in Mogalatsana and Papegaai goat liver and meat samples, respectively.

Meat, blood, liver, and kidney samples of male Pedi goats raised in Mogalatsana and Papegaai villages had similar ($P>0.05$) chromium, cadmium, mercury, nickel, and lead concentrations, respectively. However, liver and kidney samples of goats from Mogalatsana village had higher ($P<0.05$) zinc levels than those from Papegaai village. Blood and meat samples of goats from Papegaai village had higher ($P<0.05$) zinc levels than those from Mogalatsana village. The concentration levels of Zn, Ni, Pb, Cr and Cd in the blood, liver, kidney, and meat samples of male Pedi goats reared along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels for human consumption. Mercury concentration levels in liver, kidney and meat samples of the goats were within the maximum permissible levels for

human consumption. However, mercury concentration levels in the blood of goats grazing along the banks of Middle Olifants and Mogalakwena rivers were above the maximum permissible limit of 0.2 mg/litre of blood. It was concluded that meat, livers, and kidneys of the goats were fit for human consumption. However, blood from these goats was not fit for human consumption.

Keywords: Pedi goats, Selected heavy metals, Liver, Kidney, Blood and Meat.

4.1 Introduction

Environmental contamination of food is becoming an increasingly important aspect of food safety (El-Salam *et al*., 2013). There is concern with regards to consuming animal and plant products that are potentially contaminated with heavy metals (Snezana and Jordan, 2010). High levels of heavy metals in the food of animal origin are directly related to human illnesses (FAO/WHO, 2007). FAO/WHO (2007) further indicated that some metals otherwise regarded as toxic heavy metals are essential, in small amounts, for animal and human health. An essential heavy metal becomes lethal at high intakes. Grazing animals can be affected by the levels of heavy metals and hence, the carcinogenic, mutagenic, gonadotrophic, and embryonic effects can be detected (Alonso *et al*., 2004). However, these effects can be recognised after a certain period (FAO/WHO, 2007).

The main factors affecting the accumulation of potentially toxic metals by grazing animals are the presence of the metal, its concentration in herbage and at the soil surface, including the duration of exposure to the contaminated water, pasture, and soil (Pollard *et al*., 2014). Contamination of pasture by heavy metals may be due to natural, accidental, and anthropogenic activities (Netshitungulwana and Yibas, 2012). The concentration of the metals in the top 0.075m of the soil is of relevance because the roots of most grasses are in this region, and it is the surface soil that may be ingested along with the herbage by grazing animals (Herselman *et al*., 2006). Wilkinson *et al*. (2003) indicated that the grazing animal can ingest the metals either by consuming herbage that is internally or externally contaminated or by consuming contaminated soil and drinking contaminated water.

Meat, liver, and kidneys of animals are a vital source of a wide range of essential metals for humans but may also carry toxic metals as residues (Alonso *et al*., 2004).

The target edible body tissues for the accumulation of most toxic metals are the liver and kidneys because of their responsibility for storage and detoxification of toxic metals (Teofila *et al*., 2005). The residues measured in animal organs may also indicate the degree of contamination of the grazing area and drinking water (Okoye and Ugwu, 2010). To ensure the safety of goat meat, the metal levels in them should not exceed the permissible limits indicated in Table 4.1 (FAO/WHO, 2007). In South Africa, the liver, kidneys, and meat of goats are widely consumed and a major source of protein for the population. Mining, agricultural, and industrial activities are the main sources of heavy metals in South Africa (Batchelor and Engelbrecht, 1992; Ashton and Dabrowski, 2011). The presence of high levels of Pb, Zn and Cr have been reported in water of Olifants river (Dabrowski *et al*., 2008; Oberholster *et al*., 2010). However, concentration levels of heavy metals in livestock drinking contaminated water have not been determined.

4.2 Objective

The objective of the study was to determine the levels of Pb, Hg, Zn, Cd, Ni and Cr in meat, blood, liver, and kidneys of yearling male Pedi goats reared along the banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers.

4.3 Hypothesis

There are low levels of Pb, Hg, Zn, Cd, Ni and Cr in meat, blood, liver, and kidneys of yearling male Pedi goats reared along the banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers.

Table 4.1 Maximum permissible levels of selected heavy metals in ruminants*

Tissue type	cadmium	chromium	Lead	zinc	nickel	mercury
Blood (mg/litre)	0.5	1.0	0.5	80	0.5	0.2
Liver (mg/kg)	0.5	1.0	0.5	80	2.0	0.2
Kidney (mg/kg)	1.0	1.0	0.5	80	2.0	0.2
Meat (mg/kg)	0.05	1.0	0.1	80	0.5	0.2

* : Source, FAO/WHO (2007)

4.4 Methodology and analytical procedures

4.4.1 Study site

The study was conducted in Mogalatsana village (Middle Olifants river) (latitude 24°46′ S, longitude 29°25′ E) and in Papegaai village (Mogalakwena river) (Latitude 23°11′30″S, longitude 28°41′5″E), in Limpopo province, South Africa (Figures 3.1 and 3.2, respectively). The two villages were selected due to their closeness to the University. The sites selected were Site 1 at Mogalatsana area along the Middle Olifants river and Site 2 at Papegaai area along the Mogalakwena river. These sites were fully described in Chapter 3, Section 3.5.1.

4.4.2 Experimental animals and design

Twelve yearling indigenous male Pedi goats with an average live weight of 17 $\pm$ 3 kg were used in this study. Pedi goats have small to medium frame size with short horns (Snyman, 2014). The goats in the study area were randomly selected and individual goats were used as replicates in a complete randomized block design. The sampled goats were selected with selection and exclusion criteria, which include, whether they had a history of being in the environment since birth or they have been brought into the area for not less than nine months and foraging along the river basins. The Pedi goats with the history of being brought into the area or not foraging along the river basin were excluded in the study. The sampled goats were reared following the ordinary husbandry practice of feeding systems, housing, and health care. Before the commencement of the experiment, the sampled goats were thoroughly inspected for any physical abnormalities, external parasites and the healthy ones were selected.

4.4.3 Sample collection, preparation, and chemical analysis

Eighteen male Pedi goats from each community were gathered and slaughtered under standard conditions that comply with the animal welfare requirements of the University of Limpopo Animal Research Ethics Committee (AREC). Samples of blood, meat, liver, and kidneys were procured from each male Pedi goat on the 14th of December, 2019 and sent for Zn, Hg, Cr, Cd, Ni and Pb analysis

Blood samples were collected from each goat via the jugular vein puncture using hypodermic syringe and needles into heparinized bottles. The goats were properly restrained, and 5 mills of the blood sample were drawn from the jugular vein and immediately transferred into labelled sterile bottles containing ethylene diamine tetra acetic acid (EDTA) as an anticoagulant, thereafter, kept in a cooler box for onward transfer to the laboratory. The EDTA tubes used were coded as MPB (for goat blood). At the laboratory, the blood samples were immediately sent to Limpopo Agro-Food Technology Station (LATS) within the University of Limpopo for Zn, Hg, Cr, Cd, Ni and Pb analysis. At LATS, the blood samples were digested by the microwave digestion method using a standard 75 Ml digestion vessel. Heavy metals were analysed by PerkinElmer Titan MPS (South Africa).

Meat, liver, and kidney samples were kept in a cooler box with ice bags for onward transportation to the accredited laboratory, Water Lab (PTY) Ltd, Pretoria, South Africa for analysis of heavy metals. Lead, Hg, Cd, Cr, Ni and Zn were analysed using inductively coupled plasma mass spectroscopy (ICP-MS).

4.4.4 Statistical analysis

Data on liver, kidney, blood, and thigh muscles of the goats were subjected to analysis of variance (ANOVA) (Minitab, 18.1 Version). Tukey's HSD test was used to test the significant difference between treatment means at $P<0.05$ (Minitab, 18.1 Version). General linear model procedures (GML) were used to compare heavy metal levels in liver, kidney, blood, and meat samples. Correlation among selected heavy metal concentrations, blood, liver, kidney, and meat were further analysed using Pearson correlation coefficient at $P<0.05$.

The responses in liver, kidney, and meat to the levels of metals were modelled using the following equation:

$$Y_{ijk} = \mu + T_i + B_j + b_1(X_1) + b_2(X_2) + \varepsilon_{ijk}$$

Where Y= variables measured (levels of Zn, Cd, Hg, Cr, Ni and Pb in liver, kidney, blood, and meat); Ti= fixed effect of the river (Middle Olifants and Mogalakwena); Bj= fixed effect of animal sex (male); b1: b2= correlation coefficient relating measurements to pasture and water; X1: X2= random effect of the heavy metals in water, pastures, and soil; e= experimental error. The correlation analysis was used to initiate an association between levels of metals in blood, liver, kidney, and meat.

4.5 Results

Heavy metal concentration levels in blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) were compared (Table 4.2). Blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) had similar (P>0.05) concentration levels of Cr, Cd, Hg, Ni and Pb. However, goat liver samples contained higher (P<0.05) Zn concentration levels than meat, kidney, and blood samples. Samples of goat meat contained higher (P<0.05) Zn concentration levels than those of kidneys and blood samples. Similarly, goat kidney samples contained more (P<0.05) Zn concentration levels than blood samples (Table 4.2 and Figure 4.3).

Table 4.2 Selected heavy metal concentration levels in blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) *

Heavy metal	Blood	Liver	Kidney	Meat
Chromium	$0.42^{a} \pm 0.049$	$0.05^{a} \pm 0.010$	$0.05^{a} \pm 0.040$	$0.05^{a} \pm 0.010$
Cadmium	$0.35^{a} \pm 0.032$	$0.04^{a} \pm 0.032$	$0.10^{a} \pm 0.032$	$0.03^{a} \pm 0.023$
Mercury	$1.13^{a} \pm 0.146$	$0.15^{a} \pm 0.010$	$0.15^{a} \pm 0.056$	$0.15^{a} \pm 0.010$
Nickel	$0.21^{a} \pm 0.020$	$0.21^{a} \pm 0.010$	$0.24^{a} \pm 0.205$	$0.21^{a} \pm 0.010$
Lead	$0.47^{a} \pm 0.067$	$0.07^{a} \pm 0.040$	$0.20^{a} \pm 0.067$	$0.07^{a} \pm 0.010$
Zinc	$1.10^{d} \pm 0.120$	$25.00^{a} \pm 1.100$	$15.67^{c} \pm 1.100$	$21.67^{b} \pm 1.100$

* : Values presented as mean ± standard error (SE)

a, b, c, d : Means with different superscripts in the same row indicate significant differences between treatments (P<0.05)

Heavy metal concentration levels in blood, liver, kidneys, and meat samples of yearling male Pedi goats grazing along the banks of Mogalakwena river (Papegaai village) were compared (Table 4.3). Blood, liver, kidney, and meat samples of Pedi goats grazing along the banks of Mogalakwena river contained similar (P>0.05) concentration levels of Cr, Cd, Hg, Ni and Pb, respectively. However, goat meat samples contained higher (P<0.05) Zn concentrations than liver, kidney, and blood samples. Samples of goat liver contained higher (P<0.05) Zn concentrations than kidney and blood samples. Similarly, goat kidney samples contained more (P<0.05) Zn than blood samples (Table 4.3 and Figure 4.4).

Table 4.3 Selected heavy metal concentration levels in blood, liver, kidney, and meat samples of yearling Pedi goats grazing along the banks of Mogalakwena river (Papegaai village) *

Heavy metal	Blood	Liver	Kidney	Meat
Chromium	$0.49^{a} \pm 0.049$	$0.07^{a} \pm 0.049$	$0.05^{a} \pm 0.010$	$0.09^{a} \pm 0.010$
Cadmium	$0.35^{a} \pm 0.032$	$0.03^{a} \pm 0.010$	$0.04^{a} \pm 0.032$	$0.03^{a} \pm 0.010$
Mercury	$1.50^{a} \pm 0.146$	$0.15^{a} \pm 0.010$	$0.15^{a} \pm 0.040$	$0.15^{a} \pm 0.010$
Nickel	$0.21^{a} \pm 0.014$	$0.81^{a} \pm 0.010$	$0.21^{a} \pm 0.167$	$0.21^{a} \pm 0.007$
Lead	$0.17^{a} \pm 0.067$	$0.07^{a} \pm 0.010$	$0.07^{a} \pm 0.040$	$0.07^{a} \pm 0.010$
Zinc	$1.10^{d} \pm 0.190$	$21.67^{b} \pm 1.100$	$14.67^{c} \pm 1.100$	$24.67^{a} \pm 1.100$

* : Values presented as mean ± standard error (SE)

a, b, c, d : Means with different superscripts in the same row indicate significant differences between treatments (P<0.05)

Heavy metal concentrations in meat, blood, liver, and kidneys of male Pedi goats raised in Mogalatsana and Papegaai villages were compared (Table 4.4). Meat, blood, liver, and kidney samples of male Pedi goats raised in Mogalatsana and Papegaai villages had similar (P>0.05) chromium, cadmium, mercury, nickel, and lead concentration levels, respectively. However, liver and kidney samples of goats from Mogalatsana village had higher (P<0.05) zinc levels than those from Papegaai village. Similarly, blood and meat samples of goats from Papegaai village had higher (P<0.05) zinc levels than those from Mogalatsana village.

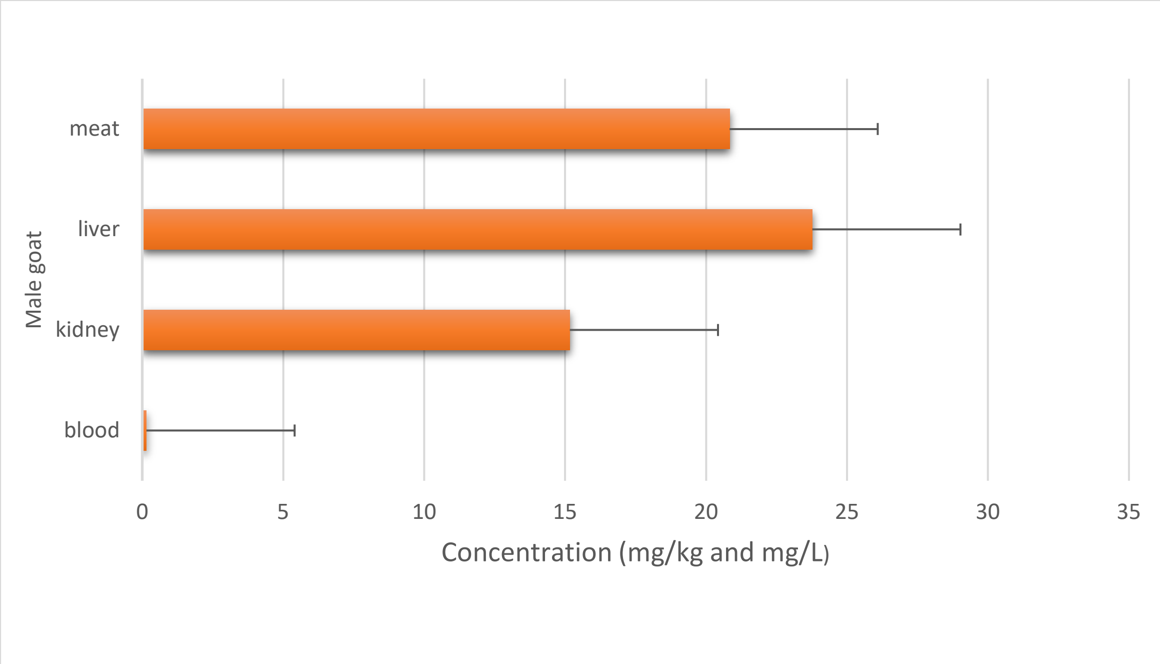

Fig 4.1 Standard error bars for each mean concentration levels of Zn in male yearling Pedi goat organs at Mogalatsana village along the banks of Middle Olifants river

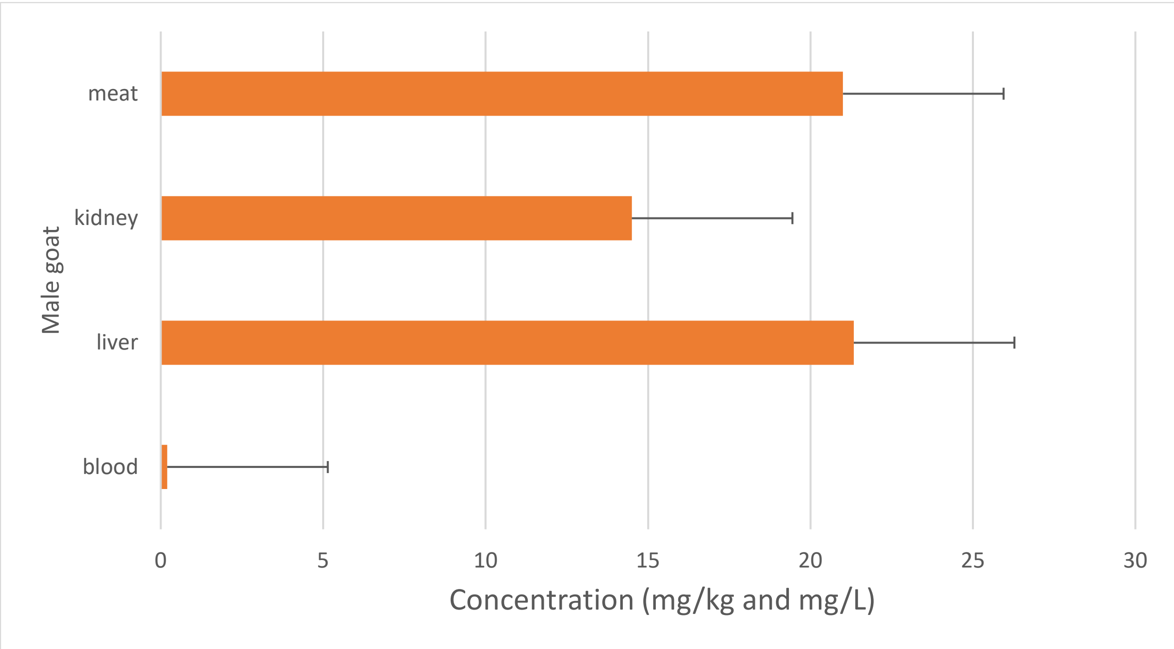

Fig 4.2 Standard error bars for each mean concentration levels of Zn in male Pedi goat organs at Papegaai village along the banks of Mogalakwena river

Table 4.4 Effect of the river on levels of selected heavy metals in the blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers

Tissue type	Middle Olifants river (Mogalatsana village)	Mogalakwena river (Papegaai village)
Blood (mg/litre)		
Chromium	$0.42^{a} \pm 0.049$	$0.49^{a} \pm 0.049$
Cadmium	$0.35^{a} \pm 0.032$	$0.35^{a} \pm 0.032$
Mercury	$1.13^{a} \pm 0.146$	$1.50^{a} \pm 0.146$
Nickel	$0.21^{a} \pm 0.020$	$0.21^{a} \pm 0.014$
Lead	$0.47^{a} \pm 0.067$	$0.17^{a} \pm 0.067$
Zinc	$1.10^{b} \pm 0.120$	$1.10^{a} \pm 0.190$
Liver (mg/kg)		
Chromium	$0.05^{a} \pm 0.010$	$0.07^{a} \pm 0.049$
Cadmium	$0.04^{a} \pm 0.032$	$0.03^{a} \pm 0.010$
Mercury	$0.15^{a} \pm 0.010$	$0.15^{a} \pm 0.010$
Nickel	$0.21^{a} \pm 0.010$	$0.81^{a} \pm 0.010$
Lead	$0.07^{a} \pm 0.040$	$0.07^{a} \pm 0.010$
Zinc	$25.00^{a} \pm 1.100$	$21.67^{b} \pm 0.010$
Kidneys (mg/kg)		
Chromium	$0.05^{a} \pm 0.040$	$0.05^{a} \pm 0.010$
Cadmium	$0.10^{a} \pm 0.032$	$0.04^{a} \pm 0.032$
Mercury	$0.15^{a} \pm 0.056$	$0.15^{a} \pm 0.040$
Nickel	$0.24^{a} \pm 0.205$	$0.21^{a} \pm 0.167$
Lead	$0.20^{a} \pm 0.067$	$0.07^{a} \pm 0.040$
Zinc	$15.67^{a} \pm 1.100$	$14.67^{b} \pm 1.100$
Meat (mg/kg)		
Chromium	$0.05^{a} \pm 0.010$	$0.09^{a} \pm 0.010$
Cadmium	$0.03^{a} \pm 0.023$	$0.03^{a} \pm 0.010$
Mercury	$0.15^{a} \pm 0.010$	$0.15^{a} \pm 0.010$
Nickel	$0.21^{a} \pm 0.010$	$0.21^{a} \pm 0.007$
Lead	$0.07^{a} \pm 0.010$	$0.07^{a} \pm 0.010$
Zinc	$21.67^{b} \pm 1.100$	$24.67^{a} \pm 1.100$

4.6 Discussion

The present study indicates that blood, liver, kidney, and meat samples of yearling male Pedi goats grazing along the banks of Middle Olifants river (Mogalatsana village) had similar concentration levels of Cr, Cd, Hg, Ni and Pb. Other authors indicate that, usually, there are higher concentration levels of these heavy metals in the kidneys, liver, and meat samples of livestock than in the blood (El-Salam *et al*., 2013). The results of the present study indicate that male goat liver samples contained higher Zn concentration levels than meat, kidney, and blood samples. Goat meat samples contained higher Zn concentration levels than those of kidney and blood samples. Livestock liver, usually, contains higher levels of heavy metals because it serves as a site for detoxification and storage of harmful substances (El-Salam *et al*., 2013). Alonso *et al.* (2004) reported that zinc accumulates, mainly, in the livers and meat of animals because of its lower rate of elimination from these organs. Male Pedi goats grazing along the banks of Mogalakwena river (Papegaai village) had similar concentration levels of Cr, Cd, Hg, Ni and Pb. However, male goat liver samples contained higher Zn levels than meat, kidney, and blood samples. Goat meat samples contained higher Zn concentration levels than those of kidney and blood samples. El-Salam *et al*. (2013) observed higher levels of zinc in the livers than in other organs of goats, cows, and buffalos. The authors suggested that this was because the liver serves as a site for detoxification and storage of harmful substances. It, also, accumulates in the livers and meat of animals because of its lower rate of elimination from these organs (Alonso *et al*., 2004).

Meat, blood, liver, and kidney samples of male Pedi goats raised in Mogalatsana (Middle Olifants river) and Papegaai (Mogalakwena river) villages contained similar chromium, cadmium, mercury, nickel, and lead concentration levels, respectively. However, liver and kidney samples of goats from Mogalatsana village had higher zinc concentration levels than those from Papegaai village. On the other hand, blood, and meat samples of goats from Papegaai village had higher zinc concentration levels than those from Mogalatsana village. High levels of zinc in the blood may be an indication of recent exposure of the animals to zinc contamination, either in water or pastures. Zinc is essential for normal functioning of cells, protein synthesis, carbohydrate metabolism, cell growth and cell division in animals and humans (Mohod and Dhote, 2013). Zinc accumulates preferentially in muscles, livers, and kidneys of animals (El-Salam *et al*., 2013).

The concentration levels of zinc, nickel, lead, chromium and cadmium in the blood, liver, kidney, and meat samples of male Pedi goats reared along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels (Table 4.1) for human consumption (FAO/WHO, 2007). Mercury concentration levels in liver, kidney and meat samples of the goats were within the maximum permissible levels for human consumption. However, mercury concentration levels in the blood of goats grazing along the banks of Middle Olifants and Mogalakwena rivers were above the maximum permissible limit of 0.2 mg/litre of blood (FAO/WHO, 2007). Higher levels of mercury in the blood may be an indication of recent exposure of the animals to mercury contamination, either in water or pastures (Akoto *et al*., 2014). Normally, mercury preferentially accumulates in the kidneys (FAO/WHO, 2007). The deposition of mercury in animal organs is rapid but its elimination is slow (Akoto *et al*., 2014). The present findings mean that livers, kidneys, and meat from the goats were fit for human consumption. However, blood from these animals was not fit for human consumption. Consumption of high levels of mercury damages the nervous, digestive, and immune systems of animals and humans (Chen *et al.,* 2012). High levels of methyl mercury in the blood systems of animals and humans may affect hearing, vision, and immunologic systems. Severe cases result in brain damage and death of the affected animals or humans (WHO, 1991). It is likely that mercury contamination in the present study was through animals drinking and eating contaminated water and pastures, respectively. However, the main sources of mercury contamination are the mining and heavy metal industries in the surrounding areas (Herselman *et al*., 2006; Herselman and Steyn, 2001). Akoto *et al*. (2014) found that mercury levels in meat tissues of free-ranging sheep and goats were above the maximum permissible limits at a gold mining town in Ghana. Information on heavy metal levels in livestock raised in the study areas was not available.

4.7 Conclusion

Data from the present study produced useful information about the concentration of Pb, Hg, Ni, Cd, Cr and Zn in blood, kidney, liver, and meat samples of yearling male Pedi goats reared in Mogalatsana (Middle Olifants river) and Papegaai (Mogalakwena river) villages, in Limpopo province of South Africa. The concentration levels of Cr, Cd, Hg, Ni, Pb and Zn in meat, kidney and liver samples of male Pedi goats were below the maximum permissible limits for human consumption. This means that consumption by humans of meat, kidneys and livers from these goats would not cause any harm. However, blood samples of the goats had Hg concentration levels above the maximum permissible limit for human consumption. This means that blood form these goats was not good for human consumption. Consumption by human beings of such contaminated blood can lead to serious health problems. Consumption by human beings of high levels of mercury damages the nervous, digestive, and immune systems (Chen *et al.,* 2012). Severe cases result in brain damage and death of the affected humans (WHO, 1991). It is, therefore, important to stop mercury contamination from the source. The main sources of mercury contamination are the mining and heavy metal industries in the surrounding areas (Herselman *et al*., 2006; Herselman and Steyn, 2001). It is the responsibility of the government of South Africa and other stakeholders to implement strategies aimed at reducing mercury contamination in Limpopo province.

CHAPTER 5

GENERAL DISCUSSION, CONCLUSIONS AND RECOMMENDATIONS

5.1 General discussion

There were no differences in zinc, mercury, lead, nickel, and cadmium concentration levels in water samples collected from Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers. However, the concentrations of zinc, mercury, lead, and cadmium in the water samples from both Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers were above the maximum permissible levels for human, animal, and fish consumption. There are reports indicating that fish in both rivers is contaminated with heavy metals (Addo-Bediako *et al*., 2014a). Information on the health of people in these villages is not available. However, it is known that people drinking water contaminated with heavy metals end up with severe and or fatal health problems (WHO, 2007). It is, therefore, important that a study looking into the effects of consuming such contaminated water on the health of the people be conducted in future. Present literature indicates that the major sources of heavy metal pollution in Limpopo province of South Africa are the mines, heavy metal industries and agricultural activities (Lebepe *et al*., 2016; Addo-Bediako *et al*., 2014b; DWAF, 1996). It is also recommended that strategies for reducing heavy metal contamination in these rivers be developed and implemented by the government of South Africa and other stakeholders. This would be good for humanity.

The soils along the banks of Middle Olifants and Mogalakwena rivers had similar concentration levels of zinc, mercury, nickel, chromium, lead, and cadmium. The concentration levels of zinc, mercury, nickel, chromium, lead, and cadmium in the soils along the banks of Mogalakwena river were within the USEPA (1995) and Herselman et al. (2006) maximum permissible levels, thus posing no harm to the growth of pastures and crops in the areas. Similarly, zinc, mercury, chromium, and cadmium concentration levels in the soils along the banks of Middle Olifants river were within the maximum permissible levels for crop production and hence posing no harm to crops and pastures grown in the areas. However, nickel and lead concentration levels in the soils along the banks of Middle Olifants river were above the maximum permissible levels of 50 and 6.60 mg/kg DM of soil for crop production, respectively (USEPA, 1995; Herselman *et al*., 2006). Accumulation of these metals in the pastures that grow there can cause harm to animals that may consume them. The main sources of nickel and lead in the soils along the banks of Middle Olifants river are the mines and heavy metal industries (Herselman *et al*., 2006; Herselman and Steyn, 2001).

Pastures play a significant role in the food chain (Khan *et al*., 2008). Goats in these areas depend on pastures for their nutrient requirements. Pastures having higher heavy metal concentrations than the maximum permissible levels may pose harm to animals consuming them (WHO, 2011). The concentration levels of zinc, nickel, mercury, lead, and cadmium in pastures grown along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels for pasture growth. However, chromium concentration levels in the pastures grown along the banks of both rivers were above the maximum permissible level of 0.02 mg/kg DM of pasture (WHO, 2011). Thus, such pastures are not good for animal consumption. Contamination of pastures with chromium can allow the metal to go up the food chain, affecting animals and hence human beings (WHO, 2011). The main sources of chromium in these soils are mining and heavy metal industries (Herselman *et al*., 2006; Herselman and Steyn, 2001).

The concentration levels of zinc, nickel, lead, chromium and cadmium in the blood, liver, kidney, and meat samples of male Pedi goats reared along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels for human consumption (FAO/WHO, 2007). Similarly, mercury concentration levels in liver, kidney and meat samples of the goats were within the maximum permissible levels for human consumption. However, mercury concentration levels in the blood of Pedi goats grazing along the banks of Middle Olifants and Mogalakwena rivers were above the maximum permissible level of 0.2 mg/litre of blood. The present findings mean that livers, kidneys, and meat from the goats were fit for human consumption. However, blood from these animals was not fit for human consumption. It is likely that mercury in the male Pedi goat blood in the present study was through animals drinking the water which was high in mercury. The blood and meat of the goats raised in these villages are consumed by the people residing there. However, the impact of consuming such contaminated blood on the health of the people is not known. There is, therefore, need to conduct further studies on the effect of heavy metals on the people residing in the two villages.

5.2 Conclusions

This study determined the concentration levels of zinc, mercury, nickel, cadmium and lead water, soils, pastures, and meat tissues of yearling male Pedi goats reared along the banks of Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers. There were no differences in zinc, mercury, lead, nickel, and cadmium concentration levels in water samples collected from Middle Olifants (Mogalatsana village) and Mogalakwena (Papegaai village) rivers. However, the concentrations of zinc, mercury, lead, and cadmium in the water samples from both rivers were above the maximum permissible levels for human, animal, and fish consumption. This means that the water from these rivers is not good for animal and human consumption. Animals and people drinking water contaminated with heavy metals end up with severe and or fatal health problems (WHO, 2007).

The concentration levels of all selected heavy metals in the soils along the banks of Mogalakwena river were within the maximum permissible levels, thus posing no adverse effects on the growth of pastures in the areas. Similarly, zinc, mercury, chromium, and cadmium concentration levels in the soils along the banks of Middle Olifants river were within the maximum permissible levels for pasture production, and hence, posing no harm to pastures grown in the areas. However, nickel and lead concentration levels in the soils along the banks of Middle Olifants river were above the maximum permissible levels. Accumulation of these metals in the pastures grown there would be harmful to animals that may consume them.

The concentrations of zinc, nickel, mercury, lead, and cadmium in Witbuffels grass grown along the banks of Middle Olifants and Mogalakwena rivers were within the maximum permissible levels for pasture growth. However, chromium concentration levels in the pastures grown along the banks of both rivers were above the maximum permissible level of 0.02 mg/kg DM of pasture (WHO, 2011). This means that the grass grown in these areas is not suitable for grazing by livestock. The grass was, therefore, not fit for animal consumption.

Meat, blood, liver, and kidney samples of male Pedi goats raised in Mogalatsana and Papegaai villages had similar chromium, cadmium, mercury, nickel, and lead concentration levels, respectively. However, liver and kidney samples of goats from Mogalatsana village had P higher zinc levels than those from Papegaai village.

Similarly, blood and meat samples of goats from Papegaai village had higher zinc levels than those from Mogalatsana village. The concentration levels of chromium, cadmium, mercury, nickel, lead and zinc in meat, kidney, and liver samples of male Pedi goats from both villages were below the maximum permissible limits for human consumption. This means that consumption by humans of meat, kidneys and livers from these goats would not cause any harm. However, blood samples of the Pedi goats had mercury concentration levels above the maximum permissible limit for human consumption. This means that blood from these goats was not good for human consumption. Consumption by human beings of high levels of mercury damages the nervous, digestive, and immune systems (Chen *et al.,* 2012).

5.3 Recommendations

Results of this study indicate that water, soils, pastures, and blood of goats from the study areas had one or more heavy metals above the maximum permissible limits. This means water and blood of goats from these areas are not good for human consumption. Thus, it is important to study the effects of these heavy metals on the health of humans who are drinking and eating contaminated water and blood, respectively. Further investigations of the effects of these heavy metals in cattle, sheep and other livestock needs to be addressed.

There is evidence that mining, heavy metal industries and agricultural activities in Limpopo province are the main sources of heavy metal contamination in water, soils, pastures, and goats. There is, therefore, need to formulate and implement strategies aimed at reducing the contamination. Since heavy metal concentrations in water, soils pastures and animals vary every season (Lebepe *et al*., 2016; Addo-Bediako *et al*., 2014b; DWAF, 1996), it is advisable that the government of South Africa or its appointed body monitors seasonal heavy metal concentration levels in the affected areas.

CHAPTER 6

REFERENCES

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