A National Survey of Mercury Levels in South Africa's Water Management Areas

Ms Chavon R. Williams

Student no.: 2773188

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Department of Earth Sciences
Supervisor: Dr Joy Leaner
Co-Supervisor: Mr Jaco Nel

Summary

Mercury (Hg) is a naturally occurring metal found in several matrices. Its presence in the aquatic environment is influenced by temperature, sulphate (SO_4^{2-}), pH, electrical conductivity (EC), dissolved organic carbon (DOC), dissolved oxygen (DO), organic matter (OM), run-off, nutrients and extreme weather conditions. Of the organomercurials (*e.g.* methylmercury, ethylmercury, phenylmercury) present in aquatic ecosystems, methylmercury (MeHg) is the most prevalent. Methylmercury is more toxic to aquatic organisms and humans, than the inorganic (Hg^{2+}) and elemental Hg (Hg^0) forms. Significant physiological and biochemical effects have been reported for aquatic organisms and humans that have been exposed to high Hg concentrations mainly through consumption of contaminated fish. The ingestion of predatory fish species has caused concern with regards to human health risks. These concerns are mostly due to the higher Hg species concentrations (predominantly MeHg) found in fish muscle tissue of predatory fish, relative to fish species occupying lower trophic levels of the aquatic food chain.

This study forms part of a broader project co-funded by the Water Research Commission (WRC), and CSIR Parliamentary Grant (PG) and Strategic Research Panel (SRP) research grants, aimed at surveying selected water resources within the 19 Water Management Areas in South Africa. Furthermore, it aims at determining the concentrations of Hg and MeHg in various environmental compartments collected from priority water resources, to identify the potential Hg hotspots, and to assess the degree of compliance with national and international guidelines.

Mercury concentrations in the environment have increased globally and this has caused much anxiety in terms of the adverse effects it has on aquatic ecosystems, their organisms, and the communities they sustain. Human health risks associated with the consumption of fish elevated containing Hg concentrations have received minimal attention particularly in South Africa. It is imperative that any potential adverse impacts of Hg on aquatic ecosystems, and the subsequent impacts on human health, be investigated.

Attestation of Authorship

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published (except where explicitly defined and acknowledge), nor material which has been submitted for the award of any other degree or diploma at any other institution of higher learning.

Chavon Rene Williams March 2010

Signed: CRWilliams

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Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

CRM	Certified Reference Material
CVAFS	Cold Vapour Atomic Fluorescence Spectrometry
DEAT	Department of Environmental Affairs and Tourism
DME	Department of Minerals and Energy
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DWAF	Department of Water Affairs and Forestry
EC	Electrical Conductivity
GC	Gas Chromatography
Hg	Mercury
ILO	International Labour Organization
MeHg	Methylmercury
PPM	Parts per million
PPT	Parts per trillion
QA	Quality Assurance
QC	Quality Control
SADC	Southern African Development Community
SAMA	South African Mercury Assessment Programme
TDS	Total Dissolved Solids
TotHg	Total mercury
UNEP	United Nations Environmental Programme
USA	United States of America
USEPA	United States Environmental Protection Agency
UNIDO	United Nations Industrial Development Organization
WHO	World Health Organization
WMA	Water Management Area

CHAPTER 1: GENERAL INTRODUCTION

1.1 Introduction

Mercury (Hg) is a heavy metal that is found naturally within the earth's crust (Tchounwou *et al*., 2003), and can occur in the environment due to both anthropogenic activities (coal power stations, artisanal gold mining, waste incinerators) and geochemical processes (volcanic activities) (Gilbertson and Carpenter, 2004; Kontas, 2006; Knobeloch *et al*., 2007). Although Hg concentrations have decreased in the developed world (Pacyna *et al*., 2006), concentrations in the developing world have increased as a result of the development of major industries (*i.e.* Hg is widely used in the chemical and engineering industries, in instrumentation and agriculture) in those countries (Kontas, 2006; Pacyna *et al*., 2006). Most Hg emissions are released as elemental Hg (Hg^0) to the atmosphere and as ionic oxidized mercury (Hg^{2+}), from natural and anthropogenic sources (Boening, 2000). In the latter gaseous inorganic form, Hg^{2+} released to the atmosphere is transported and transformed between atmosphere, land and water interfaces (Pirrone *et al*., 2001; Kontas, 2006). It is this form of Hg that is transformed into other Hg derivatives, e.g. methylmercury (MeHg), under anaerobic conditions in aquatic ecosystems.

Inorganic Hg^{2+} found in the water column or at the water-sediment boundary of aquatic ecosystems undergoes methylation by sulphate-reducing bacteria (Scheuhammer and Graham, 1999; Gilbertson and Carpenter, 2004). The resultant MeHg, which is the most toxic Hg species, diffuses rapidly into the water column (Kelly *et al*., 1995; Silbergeld and Devine, 2000; Kontas, 2006; Kinghorn *et al*., 2007).

This form of Hg is readily absorbed into muscle tissues of aquatic organisms, particularly via digestion (US EPA, 1997a; NRC, 2000; Leaner and Mason, 2002; Gilbertson and Carpenter, 2004; Kontas, 2006; Drott *et al*., 2007) and is transferred more effectively to higher trophic levels than Hg^{2+} (Becker and Bigham, 1995; Morel *et al*., 1998). Consequently, MeHg bioaccumulates and biomagnifies up the aquatic food chain (Boudou and Ribeyre, 1997; Mason *et al*., 2000; UNEP, 2002; Virtanen *et al*., 2004; Hope, 2006) and poses a risk to human health when Hg-contaminated fish is consumed. Empirical studies have shown that > 90 % of Hg in fish is in the MeHg form (Mason *et al*., 2000; Leaner and Mason, 2002). Watras *et al*. (1994) concluded that *ca.* 65 % of the total Hg (TotHg) estimated within the water column is sequestered in aquatic organisms. For MeHg, it is approximately 4.7 times more than that present in the water.

The potential risk to human health, as a consequence of consuming Hg-contaminated fish, has been well documented (Carta *et al*.¸ 2003; Tchounwou *et al*., 2003). Women of child-bearing age, children and developing foetuses are most at risk (Clarkson, 1990), causing the impairment of motor neuron activities, speech, gait, and other central nervous system problems in humans (Clarkson, 1990). The ever-increasing global population, the related increases in industrial and economic development and the concomitant increase in Hg concentrations have raised awareness with regards to human health and environmental concerns (Mason *et al*., 2000; UNEP, 2002).

Mercury and its volatile species have been the key focus in research and global environmental initiatives in an attempt to promote a better understanding of Hg dynamics in ecosystems (Pirrone *et al*., 2001). Fish and seafood products are important sources of proteins, essential nutrients and fatty acids, particularly in communities who depend on fish and seafood for their livelihoods. As such, an understanding of the processes involved in the biogeochemical cycling of Hg in the environment, as well as its impacts on the environment and human health is important.

1.2 Mercury in the Environment

1.2.1 The Mercury Cycle

When present in the environment, Hg occurs predominantly in three forms, *viz.* Hg^0, Hg^{2+} and MeHg. Atmospheric deposition, volcanic activities and volatilization from the ocean are the principal sources of naturally occurring Hg^0 to aquatic ecosystems. Approximately 2 700 – 6 000 tons of Hg^0 are released into the atmosphere from the earth's crust or the oceans (Tchounwou *et al*., 2003). In contrast, the primary anthropogenic inputs to the environment include coal combustion, chlorine-alkali processing, waste incineration and metal processing. The Hg sequence is considerably disrupted by anthropogenic emissions and influences the global Hg cycle (Hudson *et al.*, 1995). In natural ecosystems, Hg^0 vapour is oxidized in the atmosphere to ionic Hg^{2+} and is deposited to aquatic ecosystems during deposition events (Figure 1.1). When entering surface waters, Hg is transformed from one form to another and enters sediments by settling on particles. Subsequently, Hg is released by diffusion and resuspension, and enters the aquatic food chain. Further volatilization takes place when Hg is re-released into the atmosphere.

It is evident that natural processes and anthropogenic activities are important sources of atmospheric Hg to the environment. The atmosphere plays a vital role in the biogeochemistry and deposition of Hg to the earth's surface (Fitzgerald *et al*., 1998; Mason *et al*., 2000), and is the initial compartment of Hg's sequestration to the environment. As such, the overall Hg budget depends largely on these changes in natural and anthropogenic activities (Nriagu and Pacyna, 1988), as well as the amount of Hg recycled (Pirrone *et al*., 2001). Current anthropogenic sources of Hg^0 exceed that of natural inputs (Fitzgerald *et al*., 1998); while at least a third of all atmospheric Hg^0 emissions originate from industrial sources (Boening, 2000).

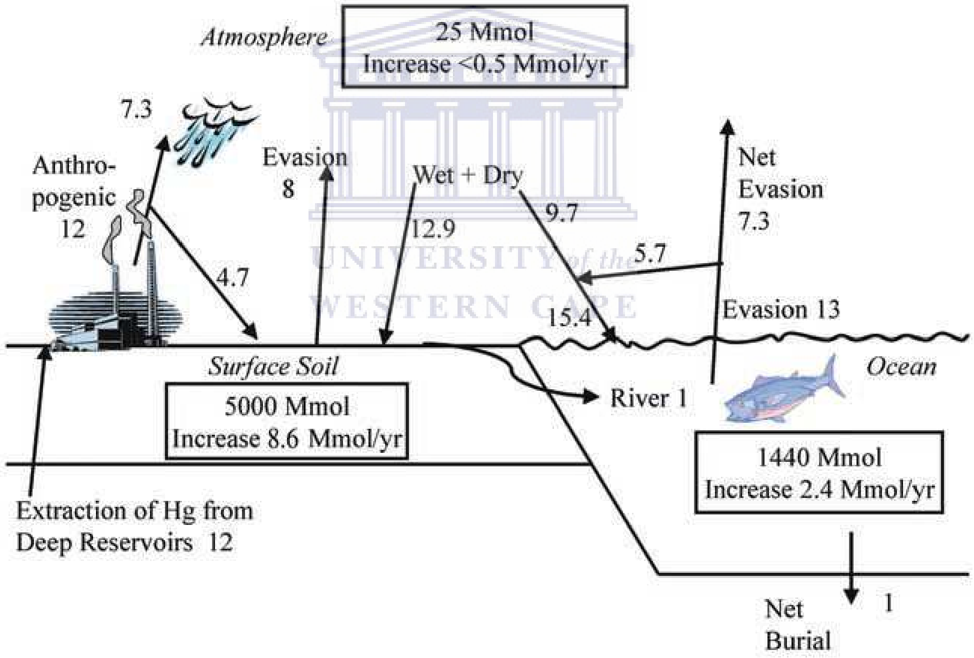

Figure 1.1: Global mercury cycle showing inputs and outputs in ecosystems (fluxes are in Mmol/year) (Mason and Sheu, 2002)

1.2.2 Anthropogenic Sources of Mercury

Anthropogenic sources of Hg to the environment include, amongst others, Hg:gold amalgamation in the artisanal gold mining industry, coal combustion and emissions from coal-fired power plants, waste incineration, cement production units, and chlor-alkali plants (Pacyna *et al.*, 2006). The anthropogenic inputs to the environment have increased on a global scale over the past century (Mason *et al.*, 1994), with its presence in the environment being a consequence of either local anthropogenic emissions or the effect of long-range transportation. Currently, it is estimated that two-thirds of all Hg entering the atmosphere is due to anthropogenic sources (Mason *et al.*, 1994). Mason and Sheu (2002) have suggested that anthropogenic Hg influences are three-fold that of natural inputs. In contrast others (Hylander and Meili, 2003) have suggested that Hg concentrations increased by two-fold since the pre-industrial era, with concentrations in developing countries having increased significantly. A brief synopsis of the Hg sources and likely emissions to the environment is provided in the context of South Africa.

1.2.2.1 Coal Combustion and Emissions from Power Plants

Coal contains small quantities of Hg and is considered to be one of the principal Hg sources to the environment worldwide (Pacyna *et al.*, 2006). When combusted, Hg in coal vaporizes to Hg^0 and Hg^{2+} (Knobeloch *et al.*, 2007), and, coupled with waste incineration, accounts for approximately two-thirds of atmospheric Hg released to the environment via anthropogenic sources (Pacyna *et al.*, 2006). Many countries, including South Africa, require accurate and reliable Hg inventories to minimize any data gaps.

In South Africa, the electricity sector is regarded as a significant source of Hg emissions, as more than 90 % of its requirements are supplied by coal-fired power stations (DME, 2005). Anthropogenic Hg emissions, particularly from coal combustion, are likely to increase as the energy demands increase in South Africa and where renewable energy sources are inadequate. It is also likely that South Africa will rely heavily on electricity and energy sources from coal, as coal constitutes a cost-effective and efficient fuel. Currently, South Africa has ten coal-fired power stations operational within the Olifants and Upper Vaal Water Management Areas (WMAs) of the country. Already, power supply from these stations is inadequate to cater for the increased energy demands of the country, and plans to extend the number of coal-fired power stations are underway (Leaner *et al*., 2009).

An increase in coal-fired power stations would lead to a concomitant increase in the amount of Hg emitted to the environment. Several factors influence the amount of Hg emitted into the atmosphere during coal combustion. These include, amongst others, the Hg content in coal, efficiency of emission control devices employed in the combustion process, and the amount of coal combusted (Dabrowski *et al*., 2008). Moreover, the calcium, chloride and sulphur content in coal, and the operating temperature of the boiler and concentration of ammonia in the flue gas, are all important factors that play a role in the speciation of Hg during coal combustion (Pavlish *et al*., 2003). Pacyna *et al*. (2006) concluded that Hg speciation during coal combustion was largely accounted for by Hg^0 (53 %), followed by Hg^{2+} (37 %) and particle-associated Hg (Hg_p) (10 %).

The amount of airborne Hg during coal combustion, particularly in households that rely on coal for heating and cooking purposes, are unknown. It is known, however, that coal usage and combustion increases during winter when energy demand increases. This is particularly prevalent in developing countries, where coal is used for cooking and heating purposes (Leaner *et al.*, 2009).

Many challenges lie ahead for the South African energy resource industry. The development of new clean coal technologies (directed to increase energy efficiency and to reduce adverse environmental effects) need to be addressed. Pressures from both the environmental and social communities will persist until alternative cleaner coal technologies in southern Africa are implemented.

1.2.2.2 Artisanal Gold Mining

Artisanal gold mining activities employ Hg-amalgamation techniques to extract gold ore (Taylor *et al*., 2005). During this process, Hg vapours released to the atmosphere are subsequently deposited into water resources and sediments, where it can be methylated into the more toxic MeHg form, depending on the prevailing environmental conditions. Artisanal gold miners often follow poor practices, have limited access to advanced or safer techniques for extracting gold, or have limited knowledge about Hg toxicity. In addition, mining practices are accompanied by a variety of environmental impacts including re-routing of river systems, water siltation, landscape dilapidation, deforestation, aquatic ecosystem destruction and Hg pollution (UNIDO, 2003). Mercury wastes originating from poor practices can remain in soil and sediments of mining sites for several years (Ramirez Requelme *et al*., 2003), with long-term deposition of Hg-contaminated sediments posing an environmental risk.

It is estimated that as much as 50 % of Hg used in artisanal gold mining is released into the environment (Veiga, 1997). Pirrone *et al*. (1996) reported that in Africa 85 – 113 tonnes of Hg^0 had been released into the atmosphere per year between 1921 and 2000. Recent estimates also suggest that Asia and Africa ranked amongst the highest in terms of anthropogenic emissions (gold production) to the environment during 2000 (Pacyna *et al*., 2006; Table 1.1).

Although illegal, artisanal gold mining plays an important role in alleviating poverty in Africa, Asia and South America. This industry is a fundamental economic activity in poor communities in developing countries (UNIDO, 2003) and contributes significantly to the livelihoods of the communities. Over 50 % of artisanal gold miners are employed in the Asia/Pacific countries (Table 1.2), with an estimated 2.5 million and 250 000 women and children, respectively, being employed in this trade (ILO, 1999). Artisanal miners are exposed to Hg inhalation when Hg^0 vapours are released to the atmosphere (Lacerda, 2003). As such, the risk of Hg pollution to artisanal gold miners could likely be significant in Asia/Pacific and Africa, while the risk to the environment due to environmental degradation and Hg pollution could also be significant. Improved and safer mining practices are required; and the education of artisanal miners, with regards to Hg pollution is imperative, so as to reduce the occupational hazards associated with this practice.

1.2.2.3 Waste Incineration

Waste incinerators (both medical and municipal) are regarded as a major anthropogenic Hg source to the environment (van Velzen *et al.*, 2002), emitting more than 100 various chemical toxins (including Hg). During the incineration of wastes, inorganic oxidized and gaseous Hg^{2+} forms are released to the atmosphere following the combustion of batteries, thermometers and other Hg-containing equipment. Emission factors of Hg due to waste incineration are in the range of between 0.5 and 9.0 g Hg / tonne (Pacyna and Munch, 1991). However, Pacyna *et al*. (2006) recently reported that the global Hg emissions from waste were 66.4 tonnes with an emission factor of 6.0 g / tonne waste, during 2000. In South Africa, the use of Hg in the health care industry (such as in thermometers, blood pressure cuffs and in dentistry) has already been highlighted as a problem (Groundworks, 2007). Groundworks (2007) have reported that approximately 2.7 tonnes of Hg is emitted from thermometers per year in China.

Extensive research has already been carried out on the combustion process employed at waste incinerators (Reimann, 1989; Giugliano *et al.*¸1991; van Velzen *et al.*, 2002), with the primary focus on the formation, removal and impact minimization of pollution from waste. However, this research has mainly dealt with bulk pollution control and trace organic pollutants, while little is known about the behaviour and distribution of toxic volatile metals such as Hg during the incineration process. In some cases, flue gas clean-up systems have been used to control Hg emissions to the atmosphere (His and Yu, 2007; Poole *et al.*, 2007). A significant proportion of the waste is converted to gaseous end-products during waste incineration, with gaseous Hg^{2+} being one of the more toxic compounds present among the inorganic components released in flue ash. The monitoring of Hg emission from waste incinerators is important in terms of the role it plays towards increased Hg pollution (de la Rosa *et al.*, 2006).

Table 1.1: Estimated global anthropogenic Hg emission for 2000 (Pacyna *et al.*, 2006)

Continent	Stationery Combustion	Cement Production	Non-ferrous Metal	Steel	Caustic Soda	Mercury	Gold	Waste	Other	Total
Africa	205.20	5.30	7.90	0.40	0.30	0.10	177.80	-	1.40	398.40
Asia	878.70	89.90	87.60	11.60	30.70	0.10	472.20	32.60	0.90	1179.30
Australasia	112.60	0.80	4.40	0.30	0.70	-	7.70	0.10	-	126.60
Europe	88.80	26.50	10.00	10.60	12.40	-	-	11.50	15.30	175.10
Russia	26.50	3.70	6.90	2.70	8.00	-	3.10	3.50	18.20	72.60
S. America	31.00	6.50	25.40	1.40	5.00	22.80	-	-	-	92.10
N. America	79.60	7.70	6.40	4.30	8.00	0.10	12.20	18.70	8.80	145.80
Total	**1422.40**	**140.40**	**148.60**	**31.30**	**65.10**	**23.10**	**248**	**66.40**	**44.60**	**2189.90**

Table 1.2: Employment in artisanal mining (in millions) (ILO, 1999)

Continent	Number of Miners
Asia/Pacific	6.7 - 7.2
Africa	3.0 - 3.7
Latin America	1.4 - 1.6
Developed countries	0.4 - 0.7
TOTAL	**11.5 - 13.2**

1.2.2.4 Cement Production Units

Cement production units contribute to the atmospheric Hg burden due to the dust produced at these facilities. Mercury is introduced into cement kiln systems via raw materials (*e.g.* limestone), in fuels used to power the kilns (*e.g.* coal) and it is released via Hg^0 emissions (US EPA, 1997b). The amount of Hg present in fuel, coupled with the efficiency of emission control devices, are the primary factors controlling Hg emissions (Pacyna *et al.*, 2006).

Increasing concentration of metals (*e.g.* Cadmium, Hg) are deposited in agricultural soils via airborne particles released from cement production units. Although they are usually located far from city centres, cement production facilities impact on local towns and areas due to the long-range transport of Hg (Mason *et al.*, 1999). Environmental parameters, such as rain and wind, play a major role in transporting cement dust which accumulate on plants, animals and soils leading to widespread pollution. The long-range transport of Hg therefore carries it across long distances to the surrounding environments. The impact of cement production and its associated Hg releases are unknown in South Africa, and require further investigation.

1.2.2.5 Chlor-alkali Industries

The pulp and paper industry use chlor-alkali facilities to produce chlorine, caustic soda and hydrochloric acid. The Hg-cell process is commonly found at these plants and these operations result in large quantities of Hg discharged to wastewater, solid waste, and to the atmosphere (Wang *et al*.¸ 2006; Raldua *et al*., 2007). Briefly, the chlor-alkali electrolysis process uses an Hg-electrolytic cell which consists of a decomposer unit and electrolyser (*viz*. a NaCl brine solution that flows concurrently with a Hg cathode). The electrolytic cell allows chlorine (Cl_2) gas to form at the anode, while sodium (Na) forms an amalgam with Hg at the cathode. The amalgam is then separated from the brine and enters the decomposer unit, where it reacts with deionised water to produce sodium hydroxide (NaOH) and volatile hydrogen gas. Although the Hg released from the amalgam is returned to the electrolyser, the effluents from these industries contain high Hg^{2+} concentrations, which results in severe Hg pollution when it enters aquatic ecosystems (Hissler and Probst, 2006; Raldua *et al*., 2007). Despite international studies on the impact of this industry on the environment (Johnes *et al.*, 1991; Lodenius, 2004), the impact on South African ecosystems has, as yet, not been determined in terms of any Hg releases to the environment, and are therefore unknown.

1.2.2.6 Forest Fires

Forest fires contribute further to increased Hg concentrations in ecosystems. Several ionic substances, including Hg, are present in particulate matter associated with runoff after forest fires (Leitch *et al*., 2007). When suspended in air, Hg^0

attaches to particles, which increases the Hg concentrations in water resources when deposited to the aquatic environment (Meili, 1991; Cinnirella and Pirrone, 2006). Brunke *et al*. (2001) measured total gaseous Hg downwind of a fire at Cape Point on the Cape Peninsula and suggested that biomass burning could be a substantial source of Hg in the southern hemisphere.

In the above-mentioned, it is evident that coal combustion is the primary source of atmospheric Hg emissions, while gold processing in the artisanal gold mining industry also ranks high on the list of anthropogenic Hg sources to the environment. Overall, the Hg present in aquatic systems can be a consequence of local anthropogenic emissions and / or long-range transportation (Mason *et al*., 1997).

1.2.3 Mercury Fluxes in the Environment

Mercury fluxes between the atmosphere, water resources and sediment of aquatic ecosystems are influenced by natural and anthropogenic contributions from the above-mentioned point and non-point sources, and occur primarily at the water-sediment boundary (Mason *et al*., 2006). Elevated Hg concentrations in fish are widespread in aquatic systems remote from possible point sources (Fitzgerald *et al*., 1998), and has been ascribed to the long-range transport and deposition of Hg to the aquatic environment. Biological (primary production, availability of dissolved organic matter, DOM), and physiochemical (water and sediment interactions) processes significantly influence the behaviour of Hg in the environment. In oxic waters, Hg^{2+} at the surface/water interface is bound to chloride (*e.g*. $HgCl^+$, $HgCl_2$, $HgCl^{3-}$, $HgCl_4^{2-}$), sulphides (*e.g*. S^{2-}, HS), hydroxide (*e.g*. $Hg(OH)^+$, $Hg(OH)_2$, $Hg(OH)^{3-}$) (Morel *et al*., 1998) or to humic substances (*i.e*. a constituent of DOC), depending on the pH and chlorine content. Methylation is, however, most common in anoxic waters and sediments, where Hg^{2+} ions display a high affinity for and is dominated by sulphides (Morel *et al*., 1998).

Methylmercury flux is largely associated with methylation in sediments, further demonstrating the importance of sediments in the overall Hg fluxes in the environment (Holmes and Lean, 2006). Several factors account for methylation in aquatic ecosystems. These include variables such as dissolved organic carbon (DOC), DOM, pH, temperature, photoperiod, sulphates, and the presence of microorganisms. The oxygen content in the adjacent water column is also important, as the MeHg flux increases with a decrease in oxygen content, but is minimal at average oxygen concentrations (Covelli *et al*., 1999). In contrast, the Hg^{2+} flux is unaffected by oxygen fluctuations (Gill *et al*., 1999). In sediments, the MeHg flux is influenced by Hg^{2+} cycling within aquatic ecosystems and an understanding of the processes or factors governing its cycling and its speciation are essential in terms of management and resource conservation strategies.

1.2.4 Mercury Bioavailability and Bioaccumulation in the Environment

As discusses above, aquatic systems remote from point sources have been reported to contain high Hg concentrations, mainly due to the long-range transport of Hg^{2+}, which is subsequently deposited to aquatic systems (Fitzgerald *et al*., 1998). Prominent water bodies, such as rivers and oceans, are excellent avenues for long-range Hg^{2+} transport (UNEP, 2002) and can result in Hg contamination in regions far removed from point sources (*e.g*. Arctic).

Once volatilized, Hg^{2+} enters water resources through both wet and dry deposition, run-off and from direct industrial and domestic waste releases. Sediments play a significant role in the transformation of Hg^{2+} to MeHg (Benoit *et al*., 1999) and can be used to provide an excellent historical account of both the spatial and temporal Hg trends in an ecosystem (Delongchamp *et al.*, 2009). In addition to the anthropogenic Hg inputs to the environment, natural methylation of Hg^{2+} in sediments and the water column contributes to the aquatic Hg burden (Rudd, 1995).

Mercury methylation in aquatic environments occurs via two principal pathways, *viz.* biotic methylation by microbial metabolism and, abiotically by chemical methylation (Celo *et al*., 2006). Both biotic and abiotic methylation enhances the bioavailability capacity of Hg in aquatic systems. Studies have shown that MeHg concentrations in aquatic environments are regulated and influenced by a balance obtained between both methylation and demethylation processes (Hintelmann *et al*., 2000; Canario *et al*., 2007). Sulpate-reducing bacteria in sediments methylate inorganic Hg^{2+} to MeHg and are the primary methylators in anoxic sediments (King *et al*., 2000). Over 95 % of Hg methylation can be attributed to these bacteria (Choi *et al*., 1994). The availability of OM and sulphates, coupled with the associated influence of sulphur-reducing bacteria, are the main factors that control the methylation process within sediment.

The chemistry in the aquatic environment influences the bioaccumulation of Hg in primary producers (Mason *et al*., 2000; Scheuhammer and Graham, 1999), and has also been suggested to influence the relative bioaccumulation of Hg at higher trophic levels. Generally, TotHg and MeHg concentrations increase with trophic levels. Planktonic food webs play a vital role in the ecotoxicological status of the overall aquatic food web, as it transports various toxins to higher trophic levels (Kainz *et al*., 2006). Being at the base of the aquatic food chain, these food webs represent the starting point for MeHg bioaccumulation in aquatic ecosystems. The degree of Hg exposure at the base of the food chain is important due to the transfer effect to higher trophic levels. Similarily, aquatic plants, which accumulate MeHg in their roots (WHO, 1989), and are at the bottom of the aquatic food web, determines the degree to which Hg is passed to higher trophic levels.

The bioaccumulation of MeHg, however, varies between species and thus trophic levels (Lawrence and Mason, 2001). As such, MeHg concentrations in predatory fish (occupying higher trophic levels) are generally higher than in fish feeding at lower trophic positions (Cabana *et al*., 1994). Leaner and Mason (2002) reported that MeHg is transported via an L-cysteine amino acid carrier across intestinal epithelia of fish and is distributed to various organs of the body. For invertebrates, it has been reported that MeHg concentrations are 10 times more lethal than Hg^{2+} (Boening, 2000). Benthic feeders have an additional source of Hg other than from their diet, as they feed near the sediment boundary, and often take in sediment and debris laden with Hg (Lawrence and Mason, 1999).

Apart from the actual trophic position, age (McIntyre and Beauchamp, 2007) and size (Cizdziel *et al*., 2002) further contributes to the TotHg and MeHg sequestered in aquatic organisms. In addition, fish mortalities allow for Hg recycling, thereby re-introducing Hg into the microbial and scavenger food webs (Sarica *et al*., 2005).

1.2.5 Mercury Impacts on Humans

Humans are exposed to Hg and its derivatives primarily through ingestion of MeHg-contaminated fish and seafood products (Tchounwou *et al*., 2003) and via the inhalation of elemental Hg^0 vapours - particularly in artisanal gold mining practices (Clarkson, 1990; UNEP, 2002; Jarup, 2003; Cortes-Maramba *et al*., 2006), as indicated above. The impacts of Hg on populations relying on fish as a subsistence food source has become a major public health concern (Wheatley and Wheatley, 2000). It is estimated that fish and fish products contribute between 20 – 85% of the MeHg present in most humans (Tchounwou *et al*., 2003). In mammals, MeHg is transported via a neutral amino acid carrier (Kerper *et al*., 1992), and is absorbed through the gastrointestinal tract. Because the human body cannot excrete Hg, MeHg is sequestered in the body (Virtanen *et al*., 2004).

When present at toxic concentrations in humans, MeHg can exhibit extensive harmful effects on humans, particularly on the development and performance of the central nervous system (Murata *et al*., 1999), cardiovascular system, (Virtanen *et al*., 2004; Stern, 2005), immune system (NRC, 2000), and is known to cause DNA damage (Sager *et al*., 1984). Pre-natal Hg exposure results in brain and coordination damage (Knobeloch *et al*., 2007), while postnatal effects include slurred speech (NRC, 2000), hearing and visual impairments (Imai *et al*., 1991), as well as other neurological disorders.

Mercury and its associated toxic ramifications were not recognized until the occurrence of locally discharged Hg into Minamata Bay, Japan, during the 1950's. Mercury toxicity in humans following this incident included tremors, numbness and muscle weakness, damage to hearing, vision and speech; the symptoms of which have been termed Minamata disease (Clarkson, 1997). Decades later, the adverse effects of MeHg exposure to local communities through the consumption of MeHg-contaminated fish from Minamata Bay are still evident (Tamashiro *et al*., 1984; 1988; Tomiyasu *et al*., 2000). Another equally disastrous incident as a consequence of an industrial catastrophe occurred in Niigata, Japan during the 1960's. Similar to the Minamata disaster, Hg-containing wastes from an acetaldehyde producing plant using a Hg catalyst was discharged directly in close proximity to a water resource that discharged into the Agano River (60 km from the Showa Denka plant) (D'itri, 1991). Although the degree of Hg contamination impacts is unknown, it is accepted that MeHg concentrations in fish and shellfish in the region were approximately 40 ppm (Myers *et al*., 2004). The effects on the human population in Niigata were much the same as that recorded in Minamata Bay (Myers *et al*., 2004). However, due to the preceding Minamata incident and the subsequent data availability, public health measures could be taken to prevent further exposure and to reduce the concomitant effects (D'itri, 1991).

Mercury guidelines have since been implemented globally to reduce the risks associated with Hg contamination and the consumption of Hg-contaminated fish in humans. Although fish consumption advisories and guidelines are currently lacking in South Africa, the Department of Water Affairs (DWA) has instituted water quality guidelines for total Hg (DWAF, 1996; Table 1.3). The World Health Organization (WHO), limits fish consumption to a tolerable daily intake of 0.48 µg total Hg / kilogram body weight (Oosthuizen and Ehrlich, 2001), while the United States Environmental Protection Agency's (US EPA) has also issued a fish consumption limit for fish meals per month, depending on the Hg concentrations in the fish (Table 1.4).

In addition to this, in response to Hg monitoring in fish caught in the USA's rivers and lakes, the US EPA and US Food and Drug Administration (US FDA) have issued a joint fish consumption advisory which prohibits the consumption of large predatory fish (*i.e*. shark, swordfish and king mackerel) and limits consumption of other fish and shellfish to two meals per week in pregnant / nursing women and children (US EPA, 2004).

Table 1.3: South Africa's Water Quality Guidelines (DWAF, 1996 [a]; CRC Press, 1997 [b])

Resource purpose	**Range (μg/L)**
Aquatic ecosystems [a]	< 0.040
Drinking water [a]	0 – 0.001
Rivers and streams [b]	0.010 – 0.100
Coal mine waters [b]	1.000 – 10.000
Oceans and seas [b]	0.005 – 5.000
Normal groundwaters [b]	0.010 – 0.100
Groundwaters near sulphide deposits [b]	1.000 – 1000.000

Table 1.4: United States Environmental Protection Agency fish consumption limits for methylmercury (US EPA, 2000)

Fish tissue concentrations limits (μg/g ww)	**Consumption limit: fish meals per month**
> 0.029 – 0.059	16
> 0.059 – 0.078	12
> 0.078 – 0.12	8
> 0.120 – 0.230	4
> 0.230 – 0.310	3
> 0.310 – 0.470	2
> 0.470 – 0.940	1
> 0.940 – 1.900	0.5
> 1.900	None

In South Africa, studies on Hg contamination in the environment have focused mainly on the Hg effluent spill into the Umgeni River and its tributaries, associated with the Thor Chemicals plant at Cato Ridge - a Hg waste processing plant in

KwaZulu-Natal (Johnston et al., 1991; Oosthuizen and Ehrlich, 2001). Oosthuizen and Ehrlich (2001) concluded that there was a potential risk to people who consume Hg-contaminated fish in the area, when taking the WHO and US EPA tolerable daily intake and fish consumption limits for Hg into consideration. Two freshwater fish species, *viz.* carp and catfish, were sampled from the Umgeni River and Inanda Dam, which are in close proximity to the Thor Chemicals sites. Mercury concentrations in fish samples in the Umgeni River were higher in both the Inanda Dam and Nagle Dam, averaging at about 0.37 µg/g, 0.16 µg/g and 0.26 µg/g, respectively (Oosthuizen and Ehrlich, 2001). These results were consistent with previous studies by Johnston *et al.* (1991), and demonstrated that this area required further Hg monitoring as the Hg contamination is most likely to persist for several decades.

Both humans and aquatic organisms are susceptible to the adverse effects of Hg and its various forms. The consumption of Hg-contaminated fish and fish products is the major source of Hg toxicity in humans (Clarkson, 1990). Although, the adverse impacts of Hg and MeHg contamination in humans are well known in terms of its toxic actions, its impacts on the South African population and environment are unknown. As such, it is imperative that all Hg sources are recognized and that Hg and MeHg monitoring and / or measurements are made in order to determine its impact on the environment and human health in South Africa.

1.2.6 Importance of study to South Africa

The degree to which anthropogenic sources of Hg are released to or impact on the South African environment is unknown. Very recently, Pacyna *et al.* (2003; 2006) reported that South Africa is the second highest emitter of atmospheric Hg emissions to the environment (> 10 % to the global Hg emissions), based on coal combustion in the country. If this is indeed the case, then high Hg concentrations should be reflected in water resources, fish and in the people living in South Africa. Recent studies (Dabrowski *et al.*, 2008; Leaner *et al.*, 2009) have, however, suggested that Hg emissions in South Africa have likely been significantly overestimated. These recent estimations indicate that Hg emissions to the South African are at least 10-fold lower than reported by Pacyna *et al.* (2003; 2006). Although the recent studies suggest lower Hg emissions to the environment, it is important to verify the Hg emissions estimated by Dabrowski (2008) and Leaner *et al.* (2009).

Major controls on anthropogenic Hg emissions have already been, or are about to be initiated, in the USA, the EU and elsewhere in the world. Additional controls have been proposed at the cost of billions of dollars per year in the USA. The monitoring of Hg emissions from coal combustion (industrial and domestic) and other Hg sources to the environment are required, as well as the potential impact of such sources on the environment and human health. As South Africa and the surrounding SADC region currently lack such Hg controls and / or advisories, a better understanding of the status of Hg in our water resources is needed to understand the fate and transport of Hg under South African conditions. This knowledge, in turn, can help to improve our collective understanding of the Hg cycle in the South African environment.

The urgency of obtaining reliable data on Hg concentrations in South Africa's water resources has grown, particularly since limited information on Hg concentrations are available. A variety of biological factors, *e.g.* trophic position, age and size, impact largely on the amount of Hg and MeHg present in aquatic ecosystems and organisms. Biota are, generally, good environmental indicators and can assist in identifying any Hg hotspots in South Africa. This study focused on identifying Hg hotspots in the 19 Water Management Areas (WMAs) of South Africa. The degree to which potential anthropogenic Hg sources impact on selected water resources in those WMAs, were investigated.

1.3 Aims and Objectives

In order to investigate the extent to which Hg pollution impacts on South Africa's water resources, and the subsequent impacts on aquatic ecosystems and human health, the aims and objectives of this study were to:

i. Quantify Hg concentrations in water, sediments and biota of priority water resources in South Africa's 19 WMAs;
ii. Assess the degree of compliance of the measured Hg concentrations with national and international guidelines; and
iii. Assess the degree to which Hg may be a problematic pollutant in South Africa.

In order to meet the aims and objectives of this study, the selection of water resources for sampling was based on an analysis of the following criteria:

i. Likely Hg sources in the 19 WMAs;
ii. Likelihood of Hg entering local water resources in the 19 WMAs; and
iii. Human use of those water resources or sensitive aquatic ecosystems.

1.4 Outline of present work

Because of the bioaccumulation of MeHg in aquatic ecosystems and its impact on human health, Hg pollution studies are required, both nationally and globally. The present study addressed several pertinent objectives aimed at determining the total Hg (TotHg) and MeHg concentrations in South African water resources and, consequently, mapping of the Hg and MeHg distribution in the country's 19 Water Management Areas.

The study focused on identifying the potential sources of Hg, and to evaluate the extent of conformity of the measured results with both national and international guidelines. In addition to this, the survey formed part of a broader study initiated through the South African Mercury Assessment (SAMA) Programme (www.waternet.co.za/samercury) and Water Research Commission (WRC) funded project.

The research presented is a small step towards the formation of Hg policies and guidelines to control Hg pollution in South Africa and to reduce its associated risks.

In this study, Chapter 1 provides a detailed synopsis of the major natural and anthropogenic Hg sources in the South African environment. It highlights the threats of Hg to aquatic ecosystem and human health. Furthermore, the chapter summarizes the relevance of such a study to South Africa.

Chapter 2 describes the priority water resources and site selection procedures implemented. The potential anthropogenic Hg sources in South Africa are summarized, while the potential adverse effects that these sources have on the selected water resources are highlighted. This chapter also discusses the sampling protocols and analytical techniques employed, and provide an overall view of the

TotHg and MeHg concentrations measured in selected water resources of the 19 WMAs; and the subsequent impacts on the aquatic ecosystem and human health.

Chapter 3 discusses the TotHg and MeHg concentrations in water, sediment and biota (invertebrates and fish) collected at sites located in close proximity to coal-fired power stations and artisanal gold mining. This chapter presents results of samples assessed in the Olifants, Upper Vaal and Inkomati Water Management Areas of the Mpumalanga Province.

Chapter 4 elaborates on the TotHg and MeHg concentrations in water, sediment and biota collected in the vicinity of a historically Hg-contaminated site in KwaZulu-Natal.

The overall impact and severity of Hg as a pollutant in South Africa is summarized in Chapter 5. The chapter also provides recommendations for future studies on Hg impacts in the South African environment.

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CHAPTER 2: DISTRIBUTION OF TOTAL MERCURY AND METHYLMERCURY CONCENTRATIONS IN SELECTED WATER RESOURCES OF SOUTH AFRICA'S 19 WATER MANAGEMENT AREAS

2.1 Introduction

Mercury (Hg) is a global pollutant with its inputs to the environment stemming from both natural and anthropogenic sources (Fitzgerald *et al.*, 1998). Fitzgerald *et al*. (1998) have suggested that current anthropogenic sources of Hg exceeds that of natural inputs; with at least a third of all atmospheric Hg emissions originating from industrial sources (Boening, 2000).

Since Hg inputs and impacts in the environment have escalated since the onset of industrialization (Hylander and Meili, 2003), wide-range worldwide monitoring studies have increased in recent years to assess the extent of Hg contamination in aquatic ecosystems (Pacyna and Munch, 1991). Most studies focused on assessing the importance of water resources on the source, fate, transport and bioavailability of Hg-species, particularly since Hg is a neurotoxin with bioaccumulative properties.

In aquatic ecosystems, inorganic Hg (Hg^{2+}) in the water column or at the water-sediment boundary undergoes microbial methylation by sulphate-reducing bacteria during anaerobic conditions (Scheuhammer and Graham, 1999; Gilbertson and Carpenter, 2004). The resultant methylmercury (MeHg) diffuses into the water column and is taken up by aquatic organisms. Generally, MeHg is more effectively transferred to higher trophic levels than Hg^{2+} (Becker and Bigham, 1995; Morel *et al.*, 1998). Furthermore, predatory fish species at higher trophic levels may contain elevated MeHg concentrations which often exceed consumption limits and advisories (Knobeloch *et al*., 2007).

Methylmercury is a toxic Hg species (Kelly *et al*., 1995; Silbergeld and Devine, 2000; Kontas, 2006; Kinghorn *et al*., 2007) which is readily absorbed into muscle tissue of aquatic organisms (US EPA, 1997; NRC, 2000; Gilbertson and Carpenter, 2004; Kontas, 2006; Drott *et al*., 2007), and bioaccumulates in aquatic organisms and biomagnifies in aquatic food webs (Mason *et al*., 2000; UNEP, 2002; Virtanen *et al*., 2004; Hope, 2006). Planktonic food webs play a vital role in the ecotoxicological status of the overall aquatic food web as it transports toxins to higher trophic levels (Kainz *et al*., 2006).

Digestion is the primary means of MeHg uptake in aquatic organisms (Cope *et al*, 1990). Therefore the bioavailability of MeHg is, to some extent, controlled by digestive processes (Leaner and Mason, 2004). When ingested, MeHg is assimilated, transferred across intestinal epithelial, and is redistributed to different organs in the body, particularly fish muscle tissue (Leaner and Mason, 2002).

In South Africa, anthropogenic Hg sources are likely to be represented by emissions from coal-fired power stations, while gold processing from artisanal gold mining are likely sources (Leaner *et al.,* 2009). Most of South Africa's water resources are in close proximity to such anthropogenic supplies, yet the extent to which Hg impacts on these ecosystems are largely unknown, except for studies associated with Hg contamination in KwaZulu-Natal (Oosthuizen and Erhlich, 2001).

This study assessed the impact of Hg on selected water resources of South Africa's 19 Water Management Areas (WMAs). Total Hg and MeHg concentrations were measured in water, sediment and biota collected in the selected water resources. The main aims of the study was to assess (1) the extent to which Hg pollution impacts on water quality in the selected water resources, and (2) the subsequent impacts on aquatic ecosystems and human health.

2.2 Materials and Methods

2.2.1 Study Area, Site Selection and Site Characterization

Site selection was largely based on the proximity of water resources to likely Hg emission Hg sources (*e.g.* coal-fired power stations, artisanal gold mining and processing, cement production units and wastewater treatment) in South Africa. Figures 2.1 and 2.2 represent the locations of South Africa's coal-fired power stations and cement production units, respectively. Sampling emphasis was concentrated in areas that were likely to have been impacted by these sources.

Details of each WMA and sample site are summarized in appendix 1 - 20, with sampling conducted in several phases during 2007 to 2009. A total of 63 sites (with some sites sampled multiple times) were sampled throughout the 19 WMAs in South Africa, where water, sediment and biota (invertebrates and fish) were collected. Of these selected sites, 17 were potentially impacted by coal-fired power stations; while 12 sites were potentially impacted by artisanal gold mining activities (appendix 20). The remaining sampling sites were selected due to their close proximity to other potential Hg sources, *viz*. cement production works (9 sites); wastewater treatment plants (5 sites); agricultural / urban runoff (12 sites); and at a previously Hg-contaminated site (6 sites) (appendix 20). In addition, 2 sites regarded as being virtually unimpacted by anthropogenic Hg sources were also selected (appendix 20) for comparative purposes.

2.2.2 Sampling Protocol and Collection

Clean handling techniques were employed throughout sample collection since contamination of sampling equipment account largely for erroneous results. Accordingly, all samples were collected using residue-free nitrile gloves, while sampling equipment were acid-cleaned and doubled-bagged, as per the standard protocols for collecting samples for TotHg and MeHg analysis (Mason and Sullivan, 1998).

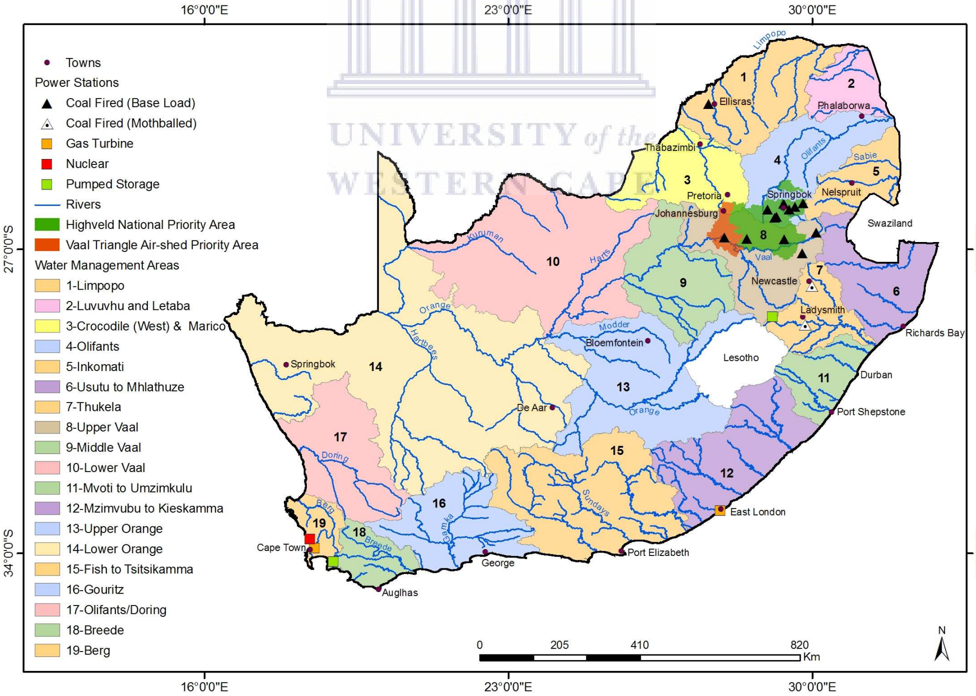

Figure 2.1: Location coal-fired power stations (operational and mothballed) power stations in South Africa.

Surface water samples (~ 500 mL) were collected in acid-cleaned Teflon® bottles, using a peristaltic pump system fitted with acid-clean c-flex tubing, with the inlet immersed *ca.* 10 cm below the water surface. Additional water samples were collected for ancillary measurements of nutrients (SO_4^{2-}, NO_3^-, PO_4^{2-}) and dissolved organic carbon (DOC). Surface sediment cores (up to 4 cm in depth) were extruded using an acid-clean polypropylene cylindrical corer and sectioned at 1 or 2 cm intervals, depending on the size of the core, after which each section was individually transferred into clean 50 mL centrifuge tubes. Biota samples (invertebrates and fish) were collected using a 1 mm-meshed net. All samples were double-bagged and stored on ice until transported to the laboratory at CSIR (Stellenbosch), where they were stored frozen until analyzed.

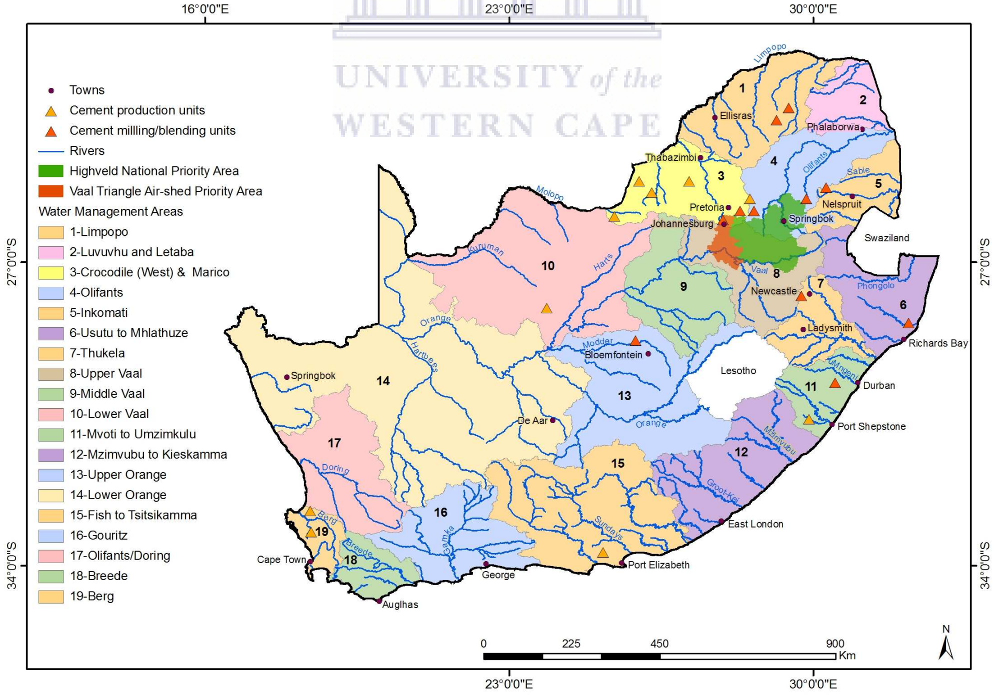

Figure 2.2: Location of current cement production and milling/blending units in South Africa.

2.2.3 Ancillary water quality parameters

Ancillary water quality parameters (*viz.* pH, temperature, DO, EC, TDS and turbidity) were measured on-site, and provided an account of the present ecological state at each site. Temperature (°C), EC (mS/cm), TDS (ppt) and pH were measured using a Hanna Instrument Model 991302; while DO (ppm) was measured using a Hanna Instrument Model 9143.

2.2.4 Sample Preparation and Analytical Techniques

2.2.4.1 Total mercury analyses

Details of the analytical procedures used for the quantification of TotHg in water have been previously described (Horvat *et al.*, 1993). In brief, the determination of TotHg in water followed US EPA Method 1631 (US EPA, 2002), which includes the oxidation of Hg with bromine monochloride (BrCl), pre-reduction with hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) and further reduction with stannous chloride ($SnCl_2$). Quantification of TotHg was performed by cold vapour atomic fluorescence spectrometry (CVAFS) following gold amalgamation trapping (Bloom and Fitzgerald, 1988).

The TotHg in solid samples, *i.e*. sediment and biota, were measured using a DMA-80 Solid Phase Direct Mercury Analyzer (Milestone Inc., Monroe, CT, USA). Details on the procedure have been described by Boylan *et al*. (2001). In brief, *ca.* 0.1 – 1g homogenized wet sample was weighed out into a quartz boat of a DMA-80 Direct Mercury Analyser, and loaded into the combustion chamber of the DMA-80, pre-programmed for automatic TotHg detection.

2.2.4.2 Methylmercury (MeHg) analyses

The analytical methods for the determination of MeHg are well documented (Mason and Lawrence, 1999; Leaner and Mason, 2002; Leaner and Mason, 2004) and followed US EPA Method 1630 (US EPA, 2001a). In brief, water and sediment samples were distilled with 50 % H_2SO_4 and 20 % KCl. The distillate was ethylated with sodium tetraethyl borate, which converts MeHg to volatile methylethylmercury. Following ethylation, all samples were purged through a Tenax^{TM} trap, separated by isothermal gas chromatography, and followed by quantification using CVAFS (Mason *et al*., 2006).

Since MeHg is the most toxic and predominant form (~90 %) of Hg in tissues of invertebrates and fish (Leaner and Mason, 2004), and due to sample mass limitations in the biota collected, the MeHg concentration alone was measured in the invertebrates and fish sampled. Therefore, for MeHg concentrations in biota, all homogenized samples were digested with KOH-methanol and placed in a 65 °C oven for 24h. Sample analysis and quantification was performed via CVAFS.

2.2.4.3 Ancillary Analyses

The percentage organic content of each sediment layer was determined as loss on ignition (LOI) to approximately 550 °C overnight (Kim *et al.*, 2006).

2.2.5 Quality Control Procedures

Analytical QA/QC criteria were maintained for all analytical methods via a standard calibration curve, having an r^2 of at least 0.998, at the beginning and end of each day. Matrix spikes (MS), matrix spike duplicates (MSD), standard reference material (SRM) and matrix blanks were included as part of the daily QA/QC. Where samples size was not limited, duplicates of such samples were analysed to ensure the precision of the analytical techniques used. The following SRM's were employed for the determination of Hg in sediment or biota: (i) MESS-3 Marine Sediment SRM (0.091 ± 0.009 mg/kg) (National Research Council, Canada); (ii) PACS-2 Marine Sediment SRM (3.04 ± 0.20 mg/kg) National Research Council, Canada); (iii) IAEA-405 Trace Elements and Methylmercury in Estuarine Sediment SRM (0.00549 ± 0.00053 mg/kg) (International Atomic Energy Agency, Austria); (iv) TORT-2 Lobster Hepatopancreas Marine SRM (0.27 ± 0.06 mg/kg) (National Research Council, Canada) for biota; and (v) DORM-2 Fish Protein SRM for biota (0.382 ± 0.060 mg/kg) (National Research Council, Canada). Duplicate and triplicate samples analysed yielded marginal error of < 10 %; while all SRM's analysed were within the certified ranges.

2.2.6 Statistical Analyses

The mean standard deviation was obtained for all duplicate and triplicate samples, and was statistically compared. Linear regression equations were determined using Sigmaplot (Sigmaplot 8.0; SPSS Inc., Chicago, IL), and MS Excel (Microsoft Office Excel 2003, Washington, USA). The comparisons of the regression coefficients, using both Simaplot and MS Excel, were not significantly different. A one-way analysis of variance (ANOVA), followed by the Tukey-Kramer HSD means comparison test (JMP 8.0, SAS Institute; SPSS Inc.) was undertaken to determine any significant differences ($p < 0.05$) in the TotHg and MeHg concentrations of the samples analysed.

2.3 Results and Discussion

2.3.1 Mercury in water

The TotHg concentrations in water samples collected varied across the different WMAs and between sampling sites (Figure 2.3). The TotHg concentrations extended over 5 orders of magnitude, and ranged from below the detection limit (0.02 ng/L) to 26.65 ± 3.53 ng/L. Total Hg concentrations were significantly different for WMAs 1, 5, 8, 11, 15, 17 and 19. All TotHg concentrations were below the Target Water Quality Range (TWQR) of < 40 ng/L, as per the South African water quality guidelines for aquatic ecosystems (DWAF, 1996). Approximately 18 % of all analyzed samples had TotHg concentrations exceeding the global average of 5.0 ng/L in water (Mason *et al.*, 1994); while only 8 % of samples analysed were above the US EPA guideline for TotHg concentrations in water, which may result in chronic effects in biota in aquatic ecosystems (12 ng/L; US EPA, 1992).

The highest TotHg concentration was measured at ThU1 (26.65 ng/L ± 3.53) in the Upper Vaal WMA, followed by RtR2 (19.06 ng/L ± 0.99) in the Olifants WMA; while TotHg concentrations in the Inkomati WMA ranged between 0.06 – 16.60 ± 0.28 ng/L for all sampling sites (Figure 2.3). South Africa's coal-fired power stations are mainly located in the Olifants and Upper Vaal WMAs; while artisanal gold mining is the predominant activity in the Inkomati WMA (Dabrowski *et al.*, 2008; Leaner *et al.*, 2009). It is therefore not surprising that the highest TotHg concentrations were measured in water resources of these WMAs. Since Hg exhibit long-range transport properties (Mason *et al*., 1997; Fitzgerald *et al.*, 1998), it is likely that any Hg released to the environment from such sources in the Olifants, Upper Vaal and Inkomati WMAs, would be deposited to water resources, at which point it will enter the corresponding aquatic food chain. The TotHg concentrations in the Inkomati WMA are within the range reported by others for areas impacted by artisanal gold mining, where Hg^0 is used as a gold amalgam (Taylor *et al*, 2005).

Total Hg concentrations measured in water samples collected in close proximity to a historically Hg-contaminated site in the Mvoti-Umzimkulu WMA ranged from 0.13 ± 0.01 to 6.48 ± 0.69 ng/L (Figure 2.3). The highest TotHg concentrations were measured at sites in the Mngceweni River (DM1b) and downstream of the Nagle Dam in the Umgeni River (UR2a) (Figure 2.3; appendix 11), the concentrations of which are above the global average for TotHg in water (Mason *et al.*, 1994).

The sampling sites in the Berg WMAs are at receiving end of wastewater discharges (*i.e.* EK1, EK2, EK3, EK4 and EK5) and had relatively low TotHg concentrations (0.68 ± 0.10 to 1.65 ± 0.24 ng/L) (Figure 2.3). These sampling sites are potentially impacted by five wastewater treatment works, *viz.* Bellville, Macassar, Scottsdene, Stellenbosch and Zandvliet wastewater treatment plants, which discharge into the Kuils, Eerste, Bottelary, Eerste and Kuils Rivers, respectively (Leaner et al., 2008). Any potential Hg would be associated with the solid waste that may enter the water resource from surrounding wastewater treatment works

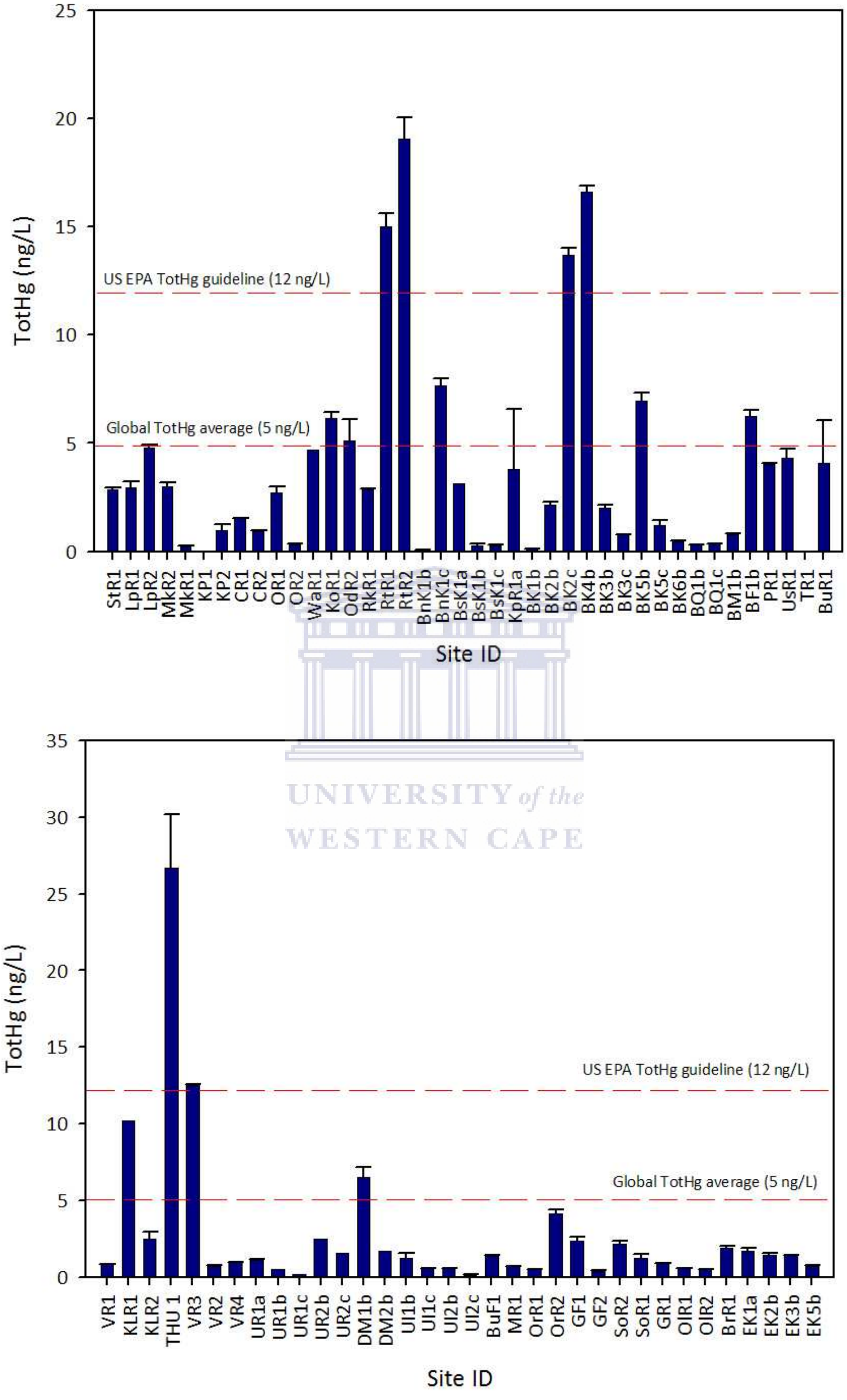

Figure 2.3: Total mercury (TotHg) concentrations in water in the 19 WMAs (top = WMAs 1-7; bottom = WMAs 8-19) (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1).

(Bodaly et al., 1998). However, the low TotHg concentrations in the water column are unexpected.

WMAs impacted by agricultural or urban effluent (*i.e.* Mzimvubu-Keiskamma; Upper Orange; Lower Orange; Fish-Tsitsikamma; Gouritz; Olifants/Doorn; and Breede WMAs) had TotHg concentrations ranging between 0.39 ± 0.01 to 4.13 ± 0.25 ng/L, with the highest TotHg concentration measured at OrR2 in the Lower Orange WMA (Figure 2.3). Total Hg concentrations at sites far removed from point sources (*i.e.* KP1 and KP2 in the Levuvhu-Letaba WMA) were relatively low and measured from below the detection limit (0.02) to 0.95 ± 0.28 ng/L (Figure 2.3).

Overall, the MeHg concentrations were significantly lower ($p < 0.05$) than the TotHg concentrations at most sites (Figure 2.4). The MeHg concentrations extended over four orders of magnitude, and ranged from below the < 0.02 ng/L to 2.73 ± 0.10 ng/L. In contrast to TotHg concentrations, however, MeHg concentrations were generally less than 1 ng/L in the Olifants and Upper Vaal WMAs (< 0.02 – 0.50 ng/L and 0.05 – 0.89 ± 0.02 ng/L, respectively). It is likely that any Hg^{2+} present at sampling sites in these WMAs is not readily converted to MeHg, suggesting low methylation rates and only a minor conversion to MeHg.

Significantly higher MeHg concentrations were measured in the Inkomati WMA (p < 0.05; range: 0.05 to 2.73 ± 0.10 ng/L), relative to other WMAs (Figure 2.4). The MeHg concentrations in the Berg and Crocodile (West) Marico WMAs ranged between 0.07 to 0.29 ± 0.02, and < 0.02 to 0.07, respectively; while MeHg concentrations in the Levuvhu-Letaba WMA ranged between < 0.02 to 0.09 ng/L. Similarly, WMAs affected by agricultural / urban effluent (*i.e.* Mzimvubu-Keiskamma;

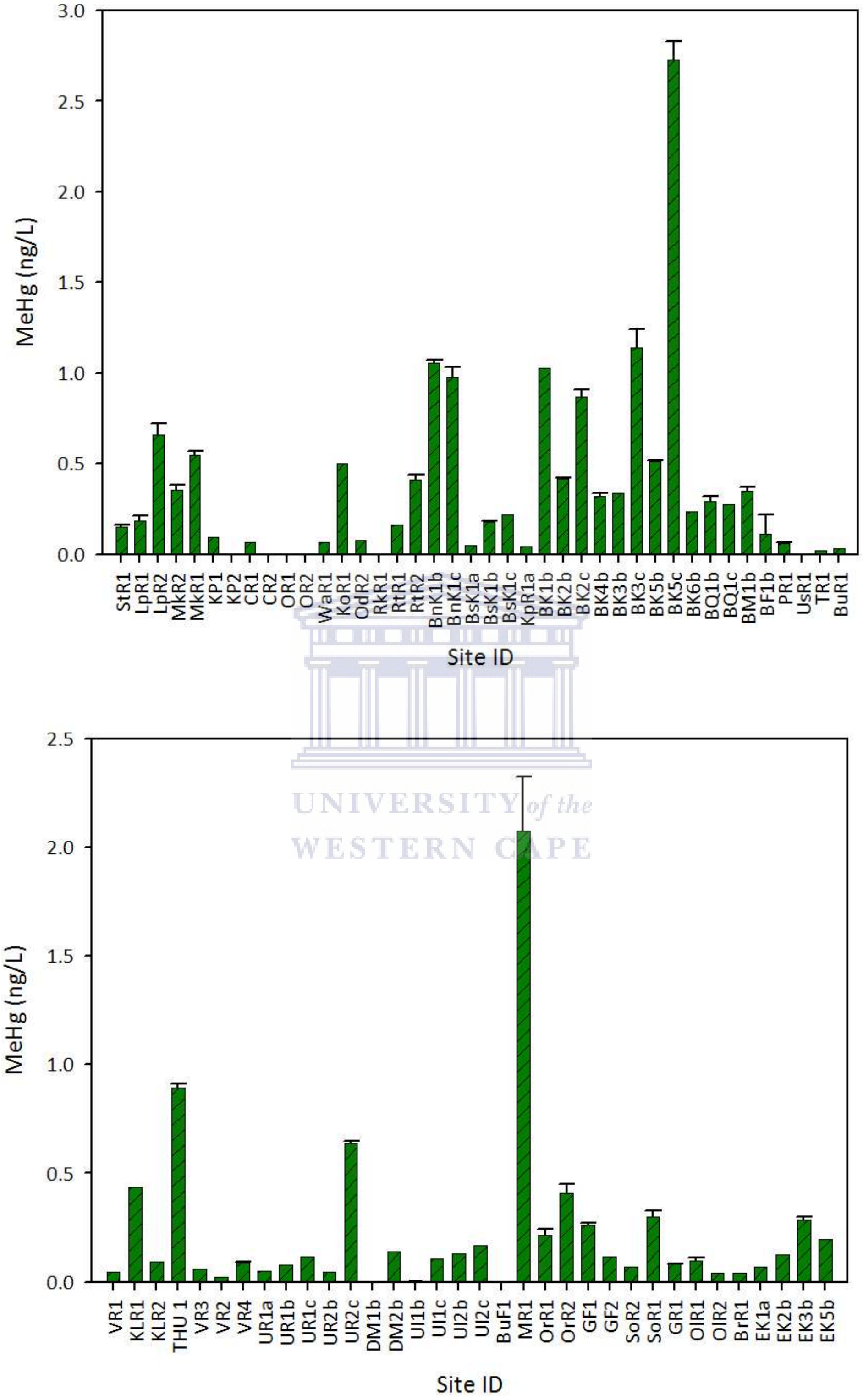

Figure 2.4: Methylmercury (MeHg) concentrations in surface water in the 19 WMAs (top = WMAs 1-6; bottom = WMAs 7-19) (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1).

Upper Orange; Lower Orange; Fish-Tsitsikamma; Gouritz; Olifants/Doorn; and Breede) had low MeHg concentrations, ranging between < 0.02 to 0.41 ± 0.04 ng/L.

Although MeHg concentrations in aqueous samples were overall low, chronic exposure to MeHg can become a concern for biota, if exposed over extended durations. However, MeHg concentrations accounted for approximately 68 % of the TotHg concentrations in water samples. This is above the proportion (1 - 5 %) observed by Mason *et al.* (1993), for water resources in the USA.

2.3.2 Mercury in sediment

Sediments are the main repository for Hg in aquatic environments (Mason and Lawrence, 1999). The TotHg concentrations in sediments for the most significant WMAs are represented in Figures 2.5 – 2.7. The remainder graphical representations are contained in appendix 21. Overall, TotHg concentrations in surface sediments (*i.e.* top 4 cm) ranged from 0.30 to 358.23 ± 76.83 ng/g wet weight (ww), taking all depths and all WMAs into account. All TotHg concentrations were below the US EPA sediment quality guideline of 200 ng/g (US EPA, 2000), except for sites in the Inkomati WMA (*viz.* BK3 and BK4; Figure 2.5). Interestingly, these sites were situated at or immediately downstream of two gold mines in the Inkomati WMA (appendix 20).

Sediment collected in the Inkomati WMA generally had the highest TotHg concentrations, and measured 0.87 ± 0.09 to 358.23 ± 76.83 ng/g ww at < 2 cm depth, and 0.75 ± 0.01 to 115.71 ± 3.09 ng/g ww at > 2 cm layers (Figure 2.5). This was followed by TotHg concentrations measured at depths 1 cm (1.82 ± 0.53 to

74.03 ± 6.71 ng/g ww), 2 cm (1.38 ± 0.23 to 75.00 ± 2.10 ng/g ww) and 3 cm (1.04 ± 0.23 to 80.08 ± 8.97 ng/g ww) in the Mvoti-Umzimkulu WMA (Figure 2.6); while the TotHg concentrations in sediment collected in the Crocodile (West) Marico WMA measured 0.67 ± 0.14 to 45.06 ng/g ww, 0.45 to 45.39 ng/g ww, and 0.51 to 46.46 ng/g ww at depths 1 cm, 2 cm and 3 cm layers, respectively (Figure 2.7). For the Inkomati WMA, it is evident that TotHg concentrations in sediment < 2 cm depth were higher than concentrations measured at the > 2 cm depths. This suggests recent sedimentary Hg deposition (Kading *et al*., 2009) or remobilization (Hudson-Edwards, 2003), as is characteristic of regions impacted by some of the major anthropogenic Hg sources.

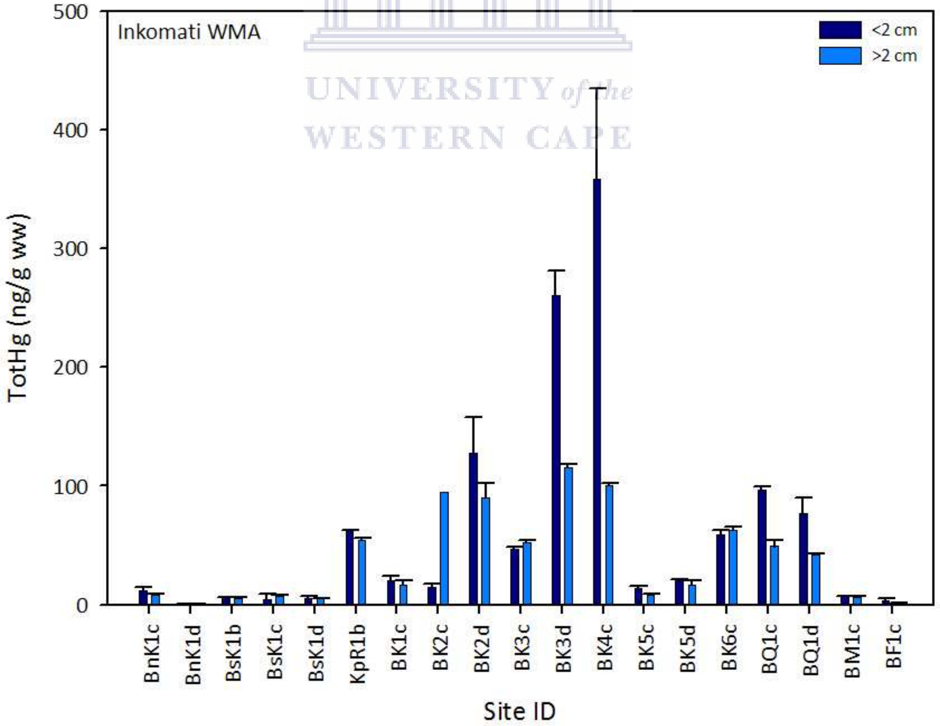

Figure 2.5: Total mercury (TotHg) concentrations in sediments in the Inkomati WMA (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1)

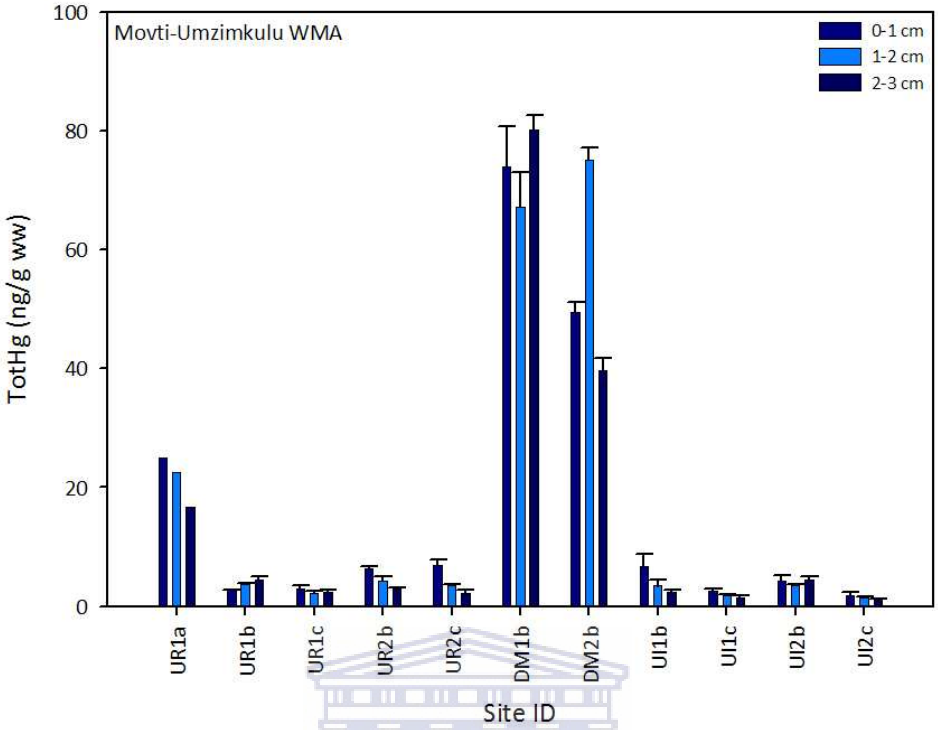

Figure 2.6:Total mercury (TotHg) concentrations in the Mvoti-Umzimkulu WMA
(bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1)

Total Hg concentrations in sediments at sampling sites with little to no human habitation (KP1 and KP2) were relatively low (0.47 to 1.32 ng/g ww; appendix 21). This is comparable with Hg concentrations reported for freshwater systems with no known point sources (0.5 – 7.4 ng/g) (Watras *et al.,* 1998).

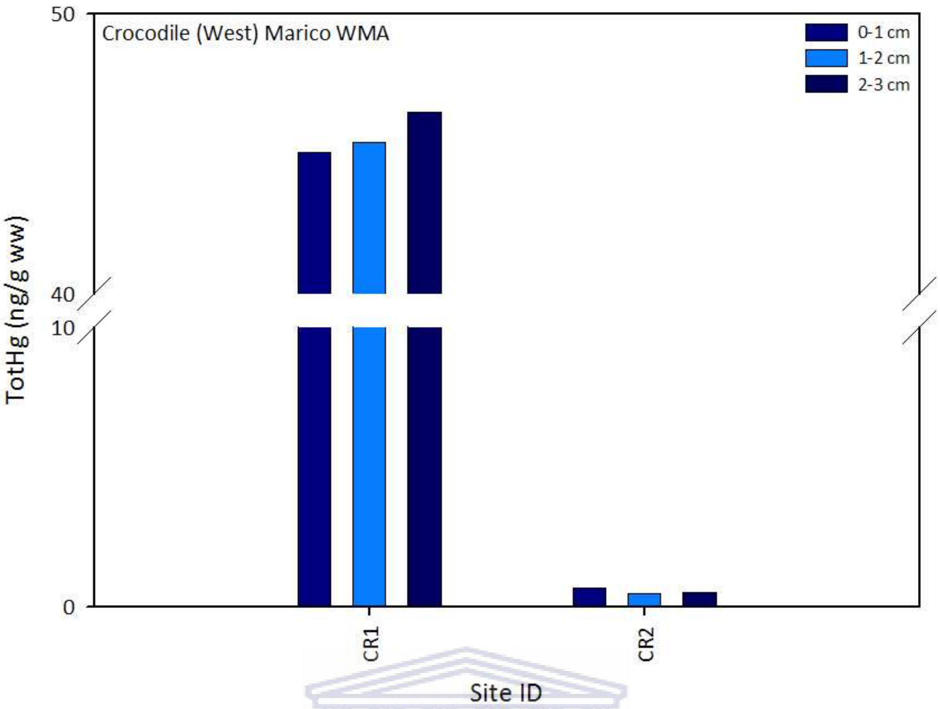

Figure 2.7: Total mercury (TotHg) concentrations in the Crocodile (West) Marico WMA (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1)

The MeHg concentrations in sediments for the most significant WMAs are represented in Figures 2.8 – 2.9, while the remainder graphical representations are contained in appendix 22. As mentioned previously, Hg^{2+} at the water-sediment boundary undergoes microbial methylation by sulphate-reducing bacteria (Scheuhammer and Graham, 1999; Gilbertson and Carpenter, 2004). Overall, MeHg concentrations in surface sediments (*i.e.* top 4 cm) ranged from below the detection limit (0.02 ng/g ww) to 10.99 ng/g ww, taking all depths and all WMAs into account. As with TotHg, the highest MeHg concentrations were measured in the Inkomati WMA at < 2 cm depth (<0.02 to 6.90 ± 2.25 ng/g ww) and at > 2 cm depth (0.02 to 10.99 ng/g ww) (Figure 2.8). This was followed by MeHg concentrations measuring 0.02 to 2.45 ng/g ww at < 2 cm depth, and 0.08 – 1.75 ng/g ww at > 2 cm depth, in the Olifants WMA (Figure 2.9). The MeHg concentrations in the Upper Vaal WMA were also generally low (0.02 – 1.95 ± 0.28 ng/g ww at < 2 cm depth; and 0.13 – 1.74 ± 0.04 ng/g ww at > 2 cm depth).

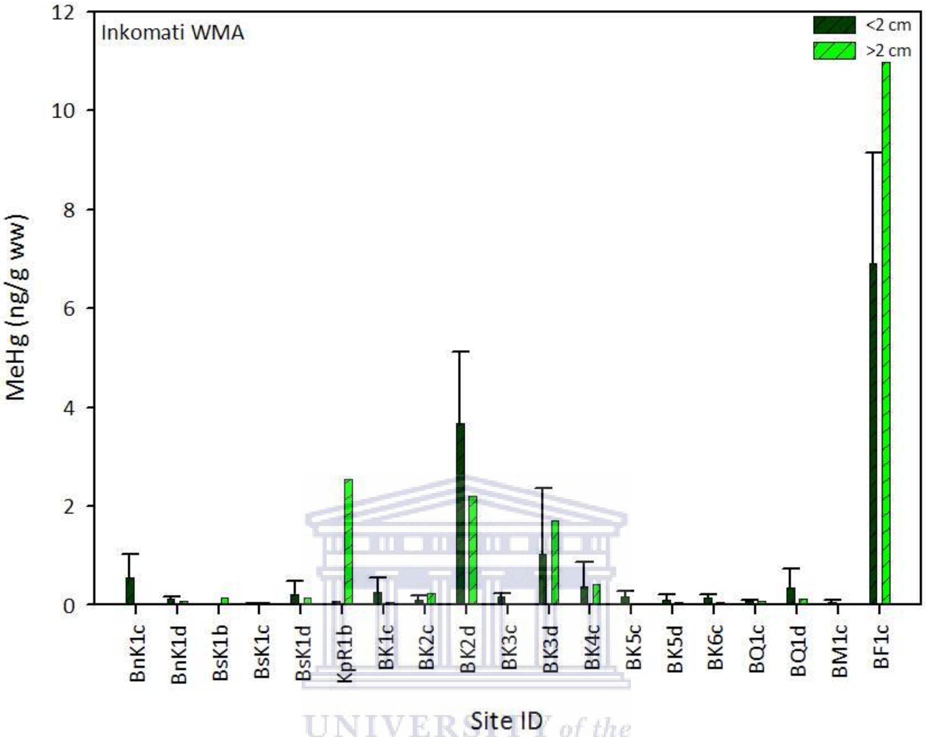

Figure 2.8: Methylmercury (MeHg) concentrations in surface sediments in the Inkomati WMA (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1)

Although both TotHg and MeHg concentrations were highest in sediment collected in the Inkomati WMA, site specific comparisons indicate that the MeHg concentrations did not mimic the same trends as observed for TotHg concentrations. For example, the highest MeHg concentrations were measured in sediment collected at BF1 and BK2 (also situated at or downstream of two different gold mines). This suggests that conditions may not have been favourable for methylation at BK3 and BK4, despite the high TotHg concentrations.

Sediment MeHg concentrations at depths < 2 cm in the Inkomati WMA were weakly correlated with sediment loss on ignition (LOI), which was used as a surrogate for organic carbon content (r^2 = 0.13 and 0.04, in the < 2 cm and > 2 cm layers, respectively). This is unexpected, given that other studies have observed much stronger correlations for similar variables (Lawrence and Mason, 2001). Nevertheless, although weak, it is widely known that organic matter influence the sediment binding capacity of MeHg (Mason and Lawrence, 1999).

The MeHg concentrations in sediment collected in all other WMAs were generally < 1 ng/g ww (refer to appendix 22). Overall, the MeHg concentrations showed a positive relationship with TotHg concentrations in sediment collected in all WMAs (r^2 = 0.68), which suggests that MeHg concentrations were, to some extent, influenced by sediment TotHg concentrations.

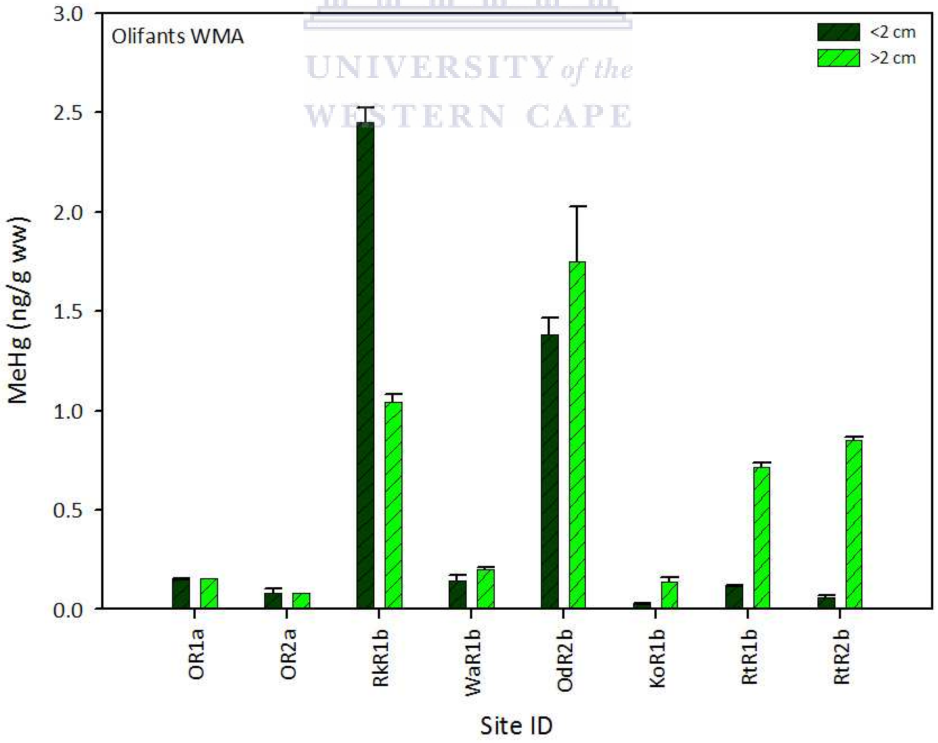

Figure 2.9: Methylmercury (MeHg) concentrations in surface sediments in the Olifants WMA (bars = mean ± SD; n = 3; lower case letters = sample frequency – see Table 2.1)

An assessment of the relative MeHg abundance to TotHg (*i.e.* % MeHg) in surface sediment indicates that, generally, surface cores had a % MeHg ranging from 0.01 to 35.6 %. It is known that MeHg accounts for approximately 1 – 3 % of TotHg in sediment (Revis *et al.*, 1990). The elevated % MeHg values reported, suggest that either these sites have substantial external Hg inputs (direct or indirect) or that enhanced methylation had occurred (Conaway *et al.*, 2003).

Upon inspection of the spatial Hg distributions in sediment, sampling sites were grouped into seven categories depending on its anthropogenic Hg source. These categories were classified as: (1) coal-fired power stations (Limpopo, Olifants, Upper Vaal and Lower Vaal WMAs); (2) artisanal gold mining regions (Inkomati WMA), (3) previously contaminated (Mvoti-Umzimkulu WMA), (4) wastewater treatment works (Berg WMA), (5) cement production (Limpopo, Usutu-Mhlatuze, Thukela and Lower Vaal WMAs, (6) agricultural / urban effluent (Mzimvubu-Keiskamma, Upper Orange, Lower Orange, Fish-Tsitsikamma, Gouritz, Olifants/Doorn and Breede WMAs) and (7) natural / unimpacted (Levuvhu-Letaba WMA). A comparison of the average TotHg concentrations showed that group 2 was significant different from groups 1, 3, 5 and 6 ($p < 0.05$; Figure 2.10); with no significant differences observed for the average MeHg concentrations between these categories.

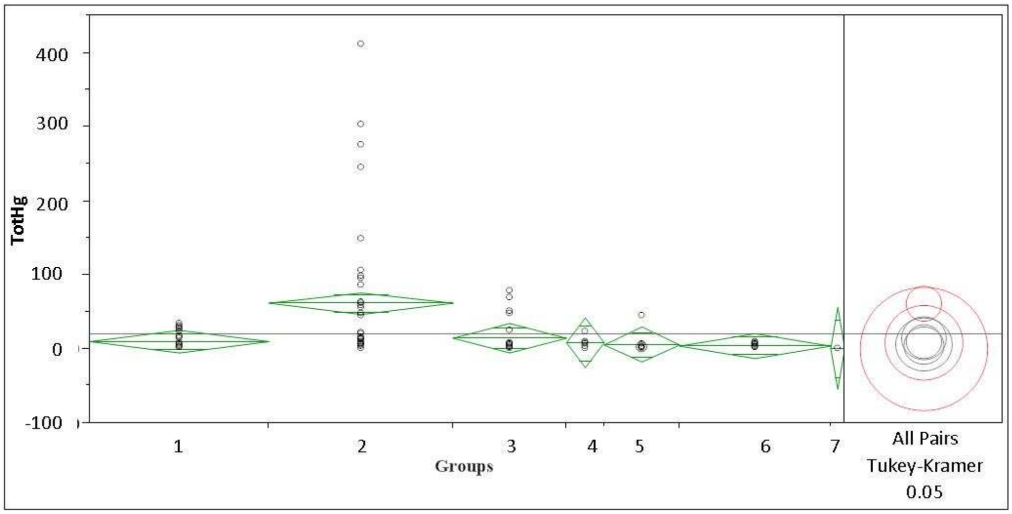

Figure 2. 10: Oneway analysis of variance and Tukey-Kramer test showing significant differences ($p < 0.05$) between group 2 and groups 1, 3, 5, 6.

2.3.3 Mercury in biota

Most of the invertebrates collected in this study are benthic invertebrates (*i.e.* they live at the water-sediment interface or in sediment) (appendix 23). It has been reported that benthic invertebrates often contain elevated concentrations of Hg (Mason and Lawrence, 1999), and therefore provide a mechanism for the transfer of sedimentary Hg to aquatic food chains (Lawrence and Mason, 2001). Hence, the lower trophic levels play a significant role in Hg bioaccumulation in fish.

The MeHg concentrations in invertebrates ranged from 0.16 to 251.19 ng/g ww (refer to appendix 24). In aquatic ecosystems, Hg is readily available for uptake by biota as MeHg, which may result in elevated MeHg concentrations in biota, even at low aqueous MeHg concentrations (Da Silva *et al.*, 2005). Accordingly, the highest MeHg concentrations in invertebrates were measured in the Mvoti-Umzimkulu WMA (0.16 – 251.19 ng/g ww), followed by the Fish-Tsitsikamma WMA (5.98 –

100.09 ± 1.46 ng/g ww) and Levuvhu-Letaba WMA (4.74 ± 0.23 – 85.25 ± 2.99 ng/g ww). The elevated MeHg concentrations measured in invertebrates collected in the Fish-Tsitsikamma and Levuvhu-Letaba WMAs are unexpected since relatively low Hg concentrations were measured, particularly in sediment collected in those WMAs. However, if invertebrates collected at sampling sites LpR2-O and Sor2-S are regarded as outliers, then the Inkomati WMA would have the second highest MeHg concentration range for invertebrates (3.59 ± 1.09 – 76.18 ± 4.97 ng/g ww). This trend would correspond with observed trends in TotHg and MeHg concentrations of sediment in this study, as well as MeHg concentrations in fish collected (see below). Invertebrates are known to acquire Hg through uptake from sediment (Plourde *et al.,* 1997), which reinforces the role of sediment in contributing to the Hg burden in biota.

Overall, MeHg concentrations in fish samples collected extended over four orders of magnitude, and ranged between 0.40 to 268.47 ± 2.82 ng/g ww (Figure 2.11). The highest MeHg concentrations in fish were measured in the Mvoti-Umzimkulu WMA (6.00 ± 2.40 to 268.47 ± 2.82 ng/g ww), followed by MeHg concentrations measured in fish collected in the Inkomati WMA (14.40 ± 2.48 – 217.82 ± 4.14 ng/g ww). Fish Hg concentrations in the former WMA exceeded concentrations previously reported by Barrat and Combrink (2002), *viz.* 50 - 250 ng/g. Most organisms obtain Hg directly from food (Mason *et al.*, 2000) or from sediments (Lawrence and Mason, 2001), or a combination of both. Since most of the fish species collected in this study feed on aquatic invertebrates or organic sediments (appendix 23), their TotHg body burdens would be high due to the high Hg concentrations in both sediment and invertebrates collected in these WMAs.

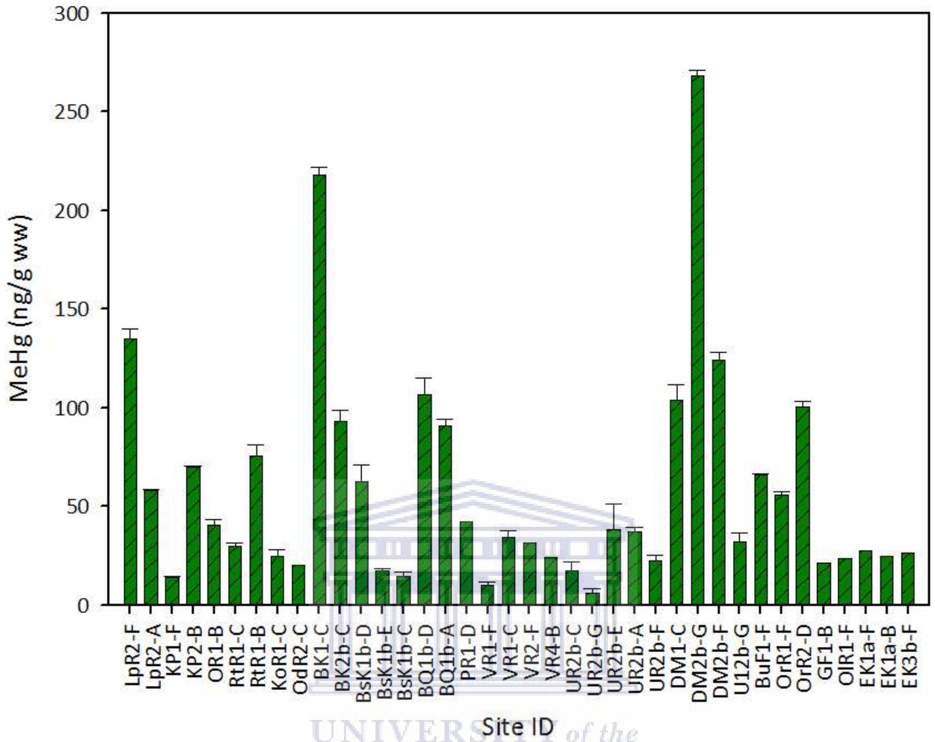

Figure 2.11: Methylmercury (MeHg) concentrations in fish collected from selected WMAs (bars = mean ± SD; n = 3; no error bars = n= 1; lower case letters = sample frequency – see Table 2.1; capital letters denote species name – see Table 2.2).

Several studies have illustrated positive correlations between aqueous DOC and pH (Driscoll *et al.*, 1995) and fish MeHg concentrations. This relationship was, however, not evident in this study, thereby suggesting that fish MeHg burden is largely a product of diet and sediment Hg burden, than physical aqueous characteristics, although this could be due to limited sample size in this study.

When comparing MeHg concentrations between different size classes, it became apparent that higher MeHg concentrations were found in fish of smaller size classes (particularly in the 5-10 cm size class), when compared to fish in a larger size classes

(10-15, 15-20, 20-25, 25-30 and > 30 cm). This is unexpected since MeHg bioaccumulation generally increases with fish size (Boening, 2000). The result observed in this study can likely be attributed to the limited fish sample size as more smaller-sized fish (77 %) were sampled compared to larger-sized fish (23 %).

Chvojka *et al.* (1990) characterized fish TotHg concentration in five categories, *i.e.* 50 – 150 ng/g ww (very low), 150 – 250 ng/g ww (low), 250 – 350 ng/g ww (medium) 350 – 450 ng/g ww (high) and > 450 ng/g ww (very high). Since about 90 % of all Hg present in fish occurs in the MeHg form (Leaner and Mason, 2004), the same categorization can be applied to this study. From the results obtained in this study, no fish analysed can be classified within the "very high" category. However, approximately 3 % of fish analysed can be categorized within "medium" category, while 3 % can be categorized within the "low" and 36 % in the "very low" categories. The remaining 59 % were below 50 ng/g ww. Although MeHg concentrations were below the US EPA guideline for MeHg in fish (300 ng/g ww; US EPA, 2001b), the MeHg concentrations reported in all fish collected in the Inkomati and Mvoti-Umzimkulu WMAs were slightly below the US EPA guideline. Therefore, since MeHg is one of the most toxic forms of Hg in the environment, fish from these two WMAs should be consumed with caution.

2.4 Summary

This study focused on the status of potential Hg impacts on different environmental compartments of selected water resources in the 19 Water

Management Areas (WMAs) of South Africa. Water, sediment and biota samples were collected during 2007 – 2009.

Overall, the results of this study suggests that the Inkomati and Mvoti-Umzimkulu WMAs are likely "hotspots" that are impacted by Hg pollution from artisanal gold mining and the previously historically Hg-contaminated site, respectively. These are the only known Hg sources in the respective WMAs. The highest TotHg concentrations were also observed in the Olifants and Upper Vaal WMAs, where South Africa's coal-fired power stations are mainly located.

The elevated MeHg concentrations in biota, even at low aqueous Hg concentrations suggest that Hg was readily available for uptake by aquatic organisms. Due to the limited fish sample size, MeHg bioaccumulation and biomagnification trends in fish species were not observed. However, there was obvious MeHg bioaccumulation and biomagnification in biota in general, since higher MeHg concentrations were measured in fish, when compared to invertebrates.

Fish consumption is the main exposure pathway of Hg to humans (NRC, 2000). This is especially true in rural areas of the Inkomati and Mvoti-Umzimkulu WMAs, where populations rely on subsistence fishing. Therefore, in light of the MeHg concentrations reported in this study, a human health risk assessment should be undertaken in these communities.

This study has provided a broad overview of the potential Hg "hotspots" in South Africa's water resources, and provides a representation of the TotHg and MeHg concentrations in the selected water resources. Although additional data is required in order to further understand Hg speciation and distribution in water resources, it is clear from this preliminary assessment that Hg contamination is evident in South Africa's water resources, albeit in various degrees. Areas in close proximity to coal-fired power stations, artisanal gold mining activities and a historically Hg-contaminated site, are likely impacted more in the Upper Vaal, Olifants, Inkomati and Mvoti-Umzimkulu WMAs than the other WMAs. An intensive sampling regime, of water, sediment and biota in the water resources of these WMAs, is therefore recommended to inform any human health risk assessments undertaken.

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CHAPTER 3: MERCURY CONCENTRATIONS IN WATER RESOURCES POTENTIALLY IMPACTED BY COAL-FIRED POWER STATIONS AND ARTISANAL GOLD MINING IN SOUTH AFRICA

3.1 Introduction

Mercury (Hg) has been regarded as a major environmental pollutant for several decades. In recent years, numerous studies have focused on improving our understanding of the dynamics of Hg, and its effects on ecosystems and human health. Atmospheric deposition, from both natural and anthropogenic sources, is the primary source of Hg and other heavy metals to aquatic ecosystems (Mason *et al*., 2001; 2004), either directly from wet / dry deposition to the water surface or indirectly via runoff (Mason *et al*., 2000). Atmospheric Hg is reported to contribute approximately 50 % to the global atmospheric anthropogenic Hg emissions (Douglas, 1991). Hylander and Meili (2002) reported that the anthropogenic Hg emissions have doubled the global Hg deposition rates since pre-industrial times, although Mason and Sheu (2002) have reported a three-fold increase. Emissions from coal-fired power stations and artisanal gold mining practices have been identified as major anthropogenic Hg sources (Nriagu and Pacyna, 1988; Pacyna *et al.*, 2006).

Recently, Pacyna *et al*. (2006) ranked South Africa as the second highest anthropogenic Hg emitter, and reported that the country contributed > 10 % to the global Hg emissions. Pacyna *et al.'s* (2006) statement was largely based on coal combustion and artisanal gold mining. Dabrowski *et al.* (2008) and Leaner *et al.* (2009) have since reported such Hg emissions in South Africa to be significantly lower than previously reported. Regardless, South Africa is recognized as the sixth largest coal producer in the world (DME, 2004), and uses relatively low grade quality coal for combustion and energy generation. Although present in trace amounts in coal, it can contribute significantly to the Hg load as coal-fired power stations are the main source of energy production in South Africa. Any increase in the amount of coal combusted will lead to increased Hg emissions to the environment, concomitant with an increase in the demand for electricity (Dabrowski *et al*., 2008; Leaner *et al*., 2009). Nonetheless, the Hg contribution to the global Hg cycle is significant when coal is combusted (Knobeloch *et al*., 2007).

In terms of artisanal gold mining, Veiga, (1997) reported that as much as 50 % of Hg vapours produced during artisanal gold mining practices are emitted and dispersed in the air. These Hg vapours released to the atmosphere are deposited via wet and dry deposition into aquatic ecosystems. Furthermore, Hg wastes from artisanal gold mining can remain in the soil and sediment for several years (Ramirez Requelme *et al*., 2003), with long-term deposition and bioaccumulation of Hg-contaminated soil and sediment posing an environmental threat.

Although often confined to urban areas, the contamination of aquatic ecosystems far removed from point sources is still possible due to the long-range transport of Hg (Mason *et al*., 2000).

From Chapter 2 of this study, it is evident that areas where coal-fired power plants and artisanal gold mining activities occur can be classified as potential Hg "hotspots" in South Africa. The work presented here extends on the latter assertions, and is aimed at assessing TotHg and MeHg concentrations in water resources located in close proximity to the potential Hg "hotspots" as identified in this study. As such, intensive TotHg and MeHg assessment studies were undertaken during 2007 – 2008, in the Olifants, Upper Vaal and Inkomati WMAs, where coal-fired power plants and artisanal gold mining are potentially the major sources of Hg in the Mpumalanga Province.

3.2 Materials and Methods

3.2.1 Study Area, Site Selection and Site Characterization

The Mpumalanga Province, which borders Gauteng on the west and Swaziland and Mozambique on the east, is the centre of South Africa's electricity sector. Witbank, a major town in the area, is the largest coal producer in Africa, and therefore most of South Africa's coal-fired power stations are located in this province. Intense coal mining and emissions from power stations have contributed to the deterioration of both air and water quality, which subsequently, have raised environmental concerns. In response, the Department of Environmental Affairs has declared the Vaal Triangle and Highveld National Priority Areas for air quality (DEAT, 2006; DEAT, 2007).

In South Africa, *ca.* 13 power stations (ten operational and three mothballed) exists, of which 8 of the operational coal-fired power stations are located in the Mpumalanga Province. These are Arnot, Hendrina, Kendal, Kriel, Majuba, Matla, Tutuka, and Duvha power stations (Figure 3.1).

Gold amalgamation practices are also still being used by artisanal gold miners (an illegal practice in South Africa) in the Inkomati WMA in Mpumalanga Province.

These practices occur mostly along the Noordkaap, Suidkaap, and Queens Rivers near the town of Barberton, in the Inkomati WMA (Figure 3.1).

Sampling for water, sediment and biota was undertaken in selected water resources of the Olifants, Inkomati and Upper Vaal WMAs of the Mpumalanga Province. As sampling was undertaken during several phases, the letters "a, b, c, d", at the end of each site ID on Figures 3.2, and 3.4 – 3.7 denotes the sampling period, *i.e.* June 2007 (dry season), November 2007 (wet season), July 2008 (dry season) and October 2008 (wet season), respectively. In this study, sampling sites selected within these WMAs were selected on the basis of their proximity to potential Hg sources (*i.e.* coal-fired power stations and artisanal gold mining activities) (Figure 3.1; Table 3.1).

3.2.2 Sampling Protocol and Collection

This section has previously been described in Chapter 2. Refer to section 2.2.2 for sampling protocol and collection.

3.2.3 Ancillary water quality parameters

This section has previously been described in Chapter 2. Refer to section 2.2.3 for ancillary water quality parameters.

3.2.4 Sample Preparation and Analytical Techniques

This section has previously been described in Chapter 2. Refer to section 2.2.4 for sample preparation and analytical techniques.

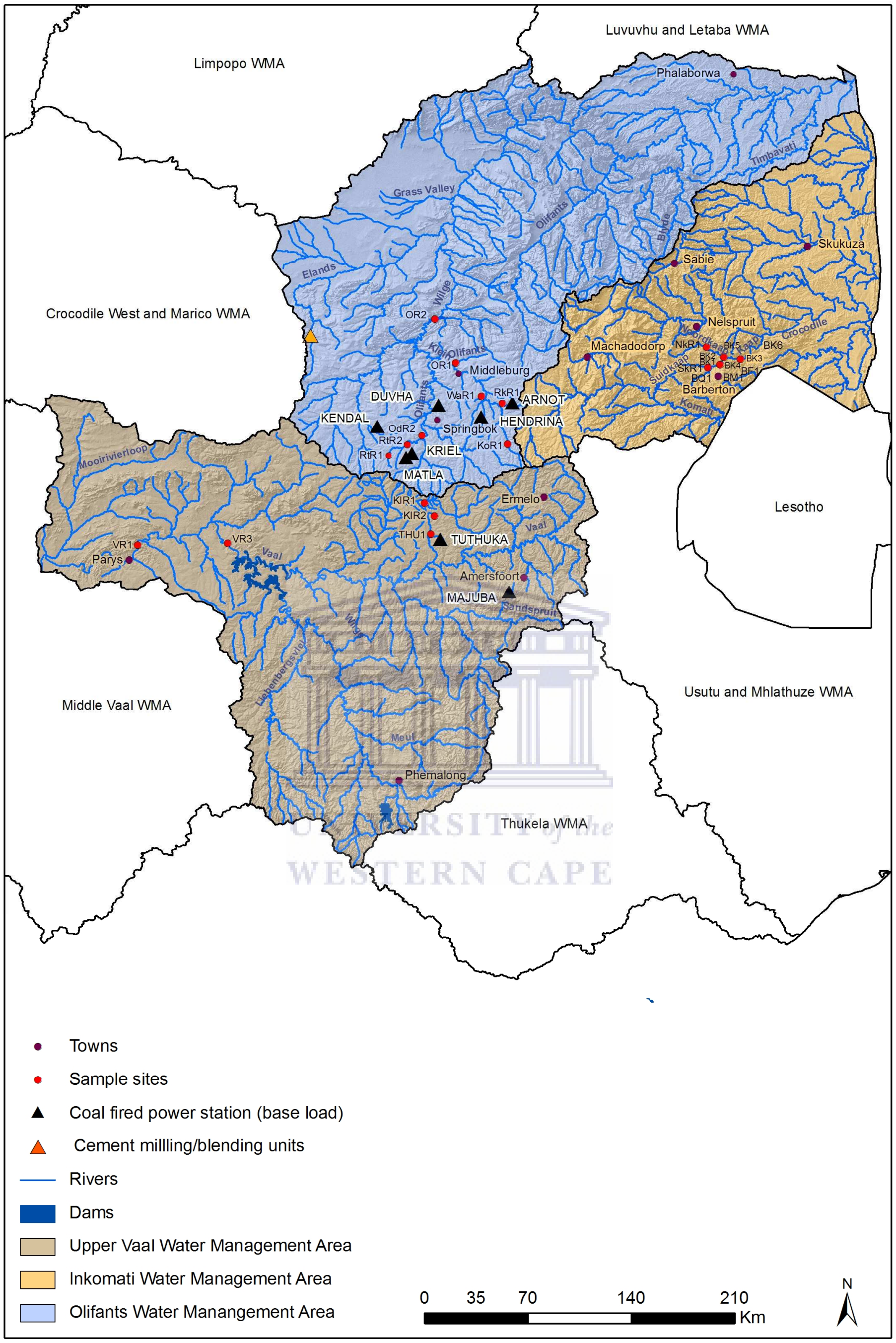

Figure 3.1: Sampling sites in the Olifants, Upper Vaal and Inkomati WMAs as well as location of coal-fired power stations.

Table 3.1: Sampling sites for assessing Hg concentrations in water resources of Mpumalanga Province, including location and major impacts

Site ID	Site Description	WMA	Major Impact	Date(s) sampled
OR1	Olifants River – Middelburg	Olifants	Coal-fired power stations	June 07(a)
OR2	Olifants River – Loskop Dam	Olifants	Coal-fired power stations	June 07(a)
RkR1	Rietkuil River – Downstream of Arnot Power Station	Olifants	Coal-fired power stations	Nov 07(b)
WaR1	Woes-Alleen River – Upstream of Hendrina Power Station	Olifants	Coal-fired power stations	Nov 07(b)
OdR1	Olifants River – Downstream of Duvha Power Station	Olifants	Coal-fired power stations	Nov 07(b)
KoR1	Klein Olifants River – Downstream of Hendrina Power	Olifants	Coal-fired power stations	Nov 07(b)
RtR1	Riet River – Upstream of Kriel Colliery	Olifants	Coal-fired power stations	Nov 07(b)
RtR2	Riet River – Downstream of Kriel Colliery	Olifants	Coal-fired power stations	Nov 07(b)
VR1	Vaal River – Parys	Upper Vaal	Coal-fired power stations	June 07(a)
KlR1	Klip River	Upper Vaal	Coal-fired power stations	Nov 07(b)
KlR2	Klip River – Upstream of Sasol	Upper Vaal	Coal-fired power stations	Nov 07(b)
ThU1	Vaal River – at Thutuka Power Station	Upper Vaal	Coal-fired power stations	Nov 07(b)
VR3	Vaal River – Downstream of Lethabo Power Station	Upper Vaal	Coal-fired power stations	Nov 07(b)
BnK1	Noordkaap River – in nature reserve	Inkomati	Artisanal gold mining	July 08(c)
BsK1	Suidkaap River	Inkomati	Artisanal gold mining	Nov 07(b); July 08(c); Oct 08(d)
KpR1	Kaap River	Inkomati	Artisanal gold mining	Nov 07(b)
BK1	Kaap River – Downstream of Barberton	Inkomati	Artisanal gold mining	July 08(c)
BK2	Kaap River – at New Consort Mine	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK3	Kaap River – at Eureka	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK4	Kaap River – Downstream of New Consort Mine	Inkomati	Artisanal gold mining	July 08(c)
BK5	Kaap River – at Scotia Talc Mine	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK6	Kaap River – Boulders turnoff at R38 and N4 crossing	Inkomati	Artisanal gold mining	July 08(c)
BQ1	Queens River – Barberton at R38	Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BM1	Kaap River – at Barberton Mine Creek	Inkomati	Artisanal gold mining	July 08(c)
BF1	Kaap River – Figtree Creek	Inkomati	Artisanal gold mining	July 08(c)

3.2.5 Quality Control Procedures

This section has previously been described in Chapter 2. Refer to section 2.2.5 for quality control procedures employed in this study.

3.2.6 Statistical Analyses

This section has previously been described in Chapter 2. Refer to section 2.2.6 for statistical analysis protocol.

3.3 Results and Discussion

3.3.1 Mercury in water

Aqueous TotHg concentrations ranged between 0.32 ± 0.02 to 19.06 ± 0.99 ng/, 0.84 ± 0.01 to 26.65 ± 3.53 ng/L, and 0.06 to 16.60 ± 0.28 ng/L in the Olifants, Upper Vaal and Inkomati WMAs, respectively (Figure 3.2). The aqueous TotHg concentrations, on average, exhibited the following order for the WMAs, [TotHg in Upper Vaal] > [TotHg in Olifants] > [TotHg in Inkomati]. A comparison of the mean ± SD of water analysed for each WMA demonstrated significant differences ($p < 0.05$) between the Upper Vaal and Inkomati WMAs. All TotHg concentrations were within the water quality range of 40 ng/L set for TotHg levels in aquatic ecosystems (DWAF, 1996). However, approximately 38 % were above the global average of 5.0 ng/L, while and 19 % were above the concentration that would result in chronic effects to aquatic life (*i.e.* 12 ng/L; US EPA, 1992).

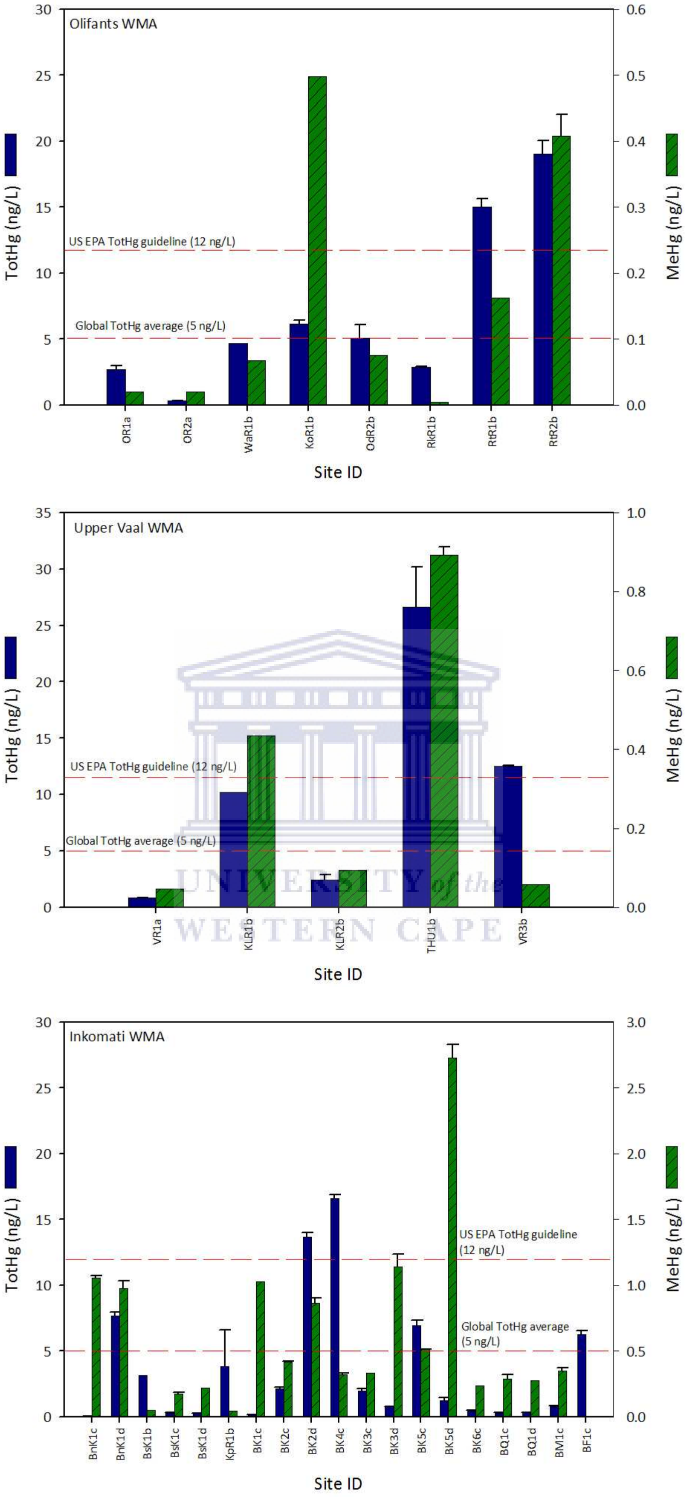

Figure 3.2: Aqueous total mercury (TotHg) and methylmercury (MeHg) concentrations collected in the Olifants, Vaal and Inkomati WMA.
(small letters denote sample period; bars = mean ± SD; n = 3).

The highest TotHg concentration was measured at ThU1 (26.65 ng/L ± 3.53) in the Upper Vaal WMA. The TotHg concentrations measured in the Inkomati WMA were well within the ranges reported in filtered water analysed for TotHg concentrations in an artisanal gold mining centre (10 to 70 ng/L; Taylor *et al.*, 2005).

Seasonal trends in TotHg concentrations were also observed in the Inkomati WMA, where sites were sampled during both the wet and dry season (*i.e.* BnK1, BsK1 BK2, BK3, BK5, BQ1 – see Table 3.1 for sampling frequency). Higher TotHg concentrations were measured in all samples collected in the wet season, when compared to the dry season, except at BsK1, BK3 and BK5. Periods of high rainfall and river discharge most likely cause physical remobilization of fine-grained sediments and resuspension of Hg in the water column, similar to what has been reported by others (Churchill *et al.*, 2004). The TotHg concentrations were also higher in the downstream sites when compared to the upstream sites (*i.e.* Olifants: WAR1b *vs.* OdR2b; Olifants: RtR1b *vs.* RtR2b; Inkomati: BK2d *vs.* BK4d; Upper Vaal: VR1 *vs.* VR3). This can likely be attributed to the downward flow and hence transportation of TotHg in the water column, to the lower reaches of the sampled water resources.

Aqueous MeHg concentrations ranged from below the detection limit (0.02 ng/L) to 0.50 ng/L, 0.05 to 0.89 ± 0.02 ng/L and 0.05 to 2.73 ± 0.10 ng/L in the Olifants, Upper Vaal and Inkomati WMAs, respectively (Figure 3.2). The aqueous MeHg concentrations, on average, exhibited the following order for the WMAs, [MeHg in Inkomati] > [MeHg in Upper Vaal] > [MeHg in Olifants]. In contrast to TotHg, the highest MeHg concentration was measured at BK5 (*viz.* BK5d in the Inkomati WMA).

Evidence of seasonal variation was observed in the MeHg concentrations of water samples collected in the Inkomati WMA, but not in the Olifants and Upper Vaal WMAs (Figure 3.2), since samples in the Inkomati WMA were collected during both the wet and dry seasons for most of the sites sampled. Up to a 5-fold increase in MeHg concentrations were observed in water samples collected at most sites in the Inkomati WMA during the dry *vs.* wet season, except for BnK1 and BQ1 (Figure 3.2). Since water is transient, any MeHg present upstream will be transported downstream (or deposited in sediment), similar to what has been observed for TotHg concentrations in this study. As such, MeHg concentrations were generally higher downstream than at the upstream sampling sites, except at sampling sites BK2 and BK4.

The TotHg and MeHg concentrations in the Olifants and Upper Vaal WMAs were weakly correlated (r^2 = 0.36 and r^2 = 0.76, respectively), and suggest that MeHg concentrations were relatively independent on TotHg concentrations. This is in contrast to what it typically expected (Watras *et al.*, 1998).

Metal speciation is also affected by organic ligands present in the water column (Ravichandran, 2004). Dissolved organic carbon (DOC) concentrations were inconsistent across WMAs, and ranged from 3.62 to 11.53 mg/L, 3.62 to 14.59 mg/L and 1.00 to 10.97 mg/L, in the Olifants, Upper Vaal and Inkomati WMAs, respectively. When TotHg and MeHg concentrations were correlated to DOC, weak positive correlations were observed in the Upper Vaal (TotHg r^2 = 0.51 and MeHg r^2 = 0.78), Olifants (TotHg r^2 = 0.15 and MeHg r^2 = 0.10) and the Inkomati WMAs (TotHg r^2

= 0.04 and MeHg $r^2 = 0.07$). These results suggest that Hg complexation with DOC was more ineffective in all three WMAs.

3.3.2 Mercury in sediment

The TotHg distribution in sediments in the three WMAs is represented in Figure 3.3. A large variability in TotHg concentrations were observed between the different WMAs. Overall, the TotHg concentrations in the Olifants WMA ranged between 1.79 ± 0.38 to 31.43 ± 2.71 ng/g ww and 1.50 to 34.25 ± 2.74 ng/g ww, in the < 2 cm and > 2 cm depths, respectively; while in the Upper Vaal, TotHg concentrations ranged between 1.90 ± 0.54 to 16.10 ± 2.52 ng/g ww and 1.00 to 7.33 ± 0.24 ng/g ww, in the < 2 cm and > 2 cm depths, respectively; and in the Inkomati WMA, TotHg concentrations ranged between 0.87 ± 0.09 to 358.23 ± 76.83 ng/g ww and 0.75 ± 0.01 to 115.71 ± 3.09 ng/g ww, in the < 2 cm and > 2 cm depths, respectively (Figure 3.3).

Significant differences ($p < 0.05$) were observed in TotHg concentrations between the Olifants, Upper Vaal and Inkomati WMA in the < 2 cm depth, and between the Olifants and Upper Vaal WMAs, and the Inkomati WMA in the > 2 cm depth. When compared to other WMAs, the highest TotHg concentrations were observed in sediment collected in the Inkomati WMA (Figure 3.3). This can most likely be attributed to the Hg:Gold amalgam processes employed in the illegal artisanal gold mining industry taking place in the Inkomati WMA. Any Hg released from artisanal gold mining is likely deposited, either directly through runoff or from atmospheric deposition into water resources and sediments, and can be retained for several years. Sediment TotHg concentrations in the Inkomati WMA also exceeded the US EPA's quality guideline of 200 ng/g (US EPA, 2000). However, this result is below the range reported for TotHg in sediments impacted by artisanal gold mining activities (Ikingura *et al.*, 2006; Loredo *et al.*, 2006).

Since this is an illegal trade in South Africa, the scale of artisanal gold mining in the Inkomati WMA could be much lower than in areas where artisanal gold mining is practiced legally in other countries. If this is indeed the situation, then the lower TotHg concentrations observed in sediment collected in water resources in the Inkomati WMA, when compared to the published studies (e.g. Ikingura *et al.*, 2006; Loredo *et al.*, 2006), is not unexpected.

Sediment methylation occurs either biologically (bacterially mediated) (Scheuhammer and Graham, 1999; Gilbertson and Carpenter, 2004) or chemically (Celo *et al*., 2006). The formation of MeHg is affected by several parameters such as sediment TotHg concentration, and microbial activity (Benoit *et al.*, 2002), as well as sediment organic carbon (OC). The MeHg concentrations in the surface sediments showed a high degree of variability when comparing the concentrations in the three WMAs sampled (Figure 3.4). The MeHg concentrations in the Olifants WMA ranged between 0.02 ± 0.01 to 2.45 ± 0.08 ng/g ww and 0.08 to 1.75 ± 0.28 ng/g ww, in the < 2 cm and > 2 cm depths, respectively; while in the Upper Vaal WMA, the MeHg concentrations ranged between 0.02 to 1.95 ± 0.28 ng/g ww and 0.13 to 1.74 ± 0.04 ng/g ww, in the < 2 cm and > 2 cm depths, respectively; and in the Inkomati WMA, the MeHg concentrations ranged between < 0.02 to 6.90 ± 2.25 ng/g ww and 0.02 to 10.99 ng/g ww, in the < 2 cm and > 2 cm depths, respectively.

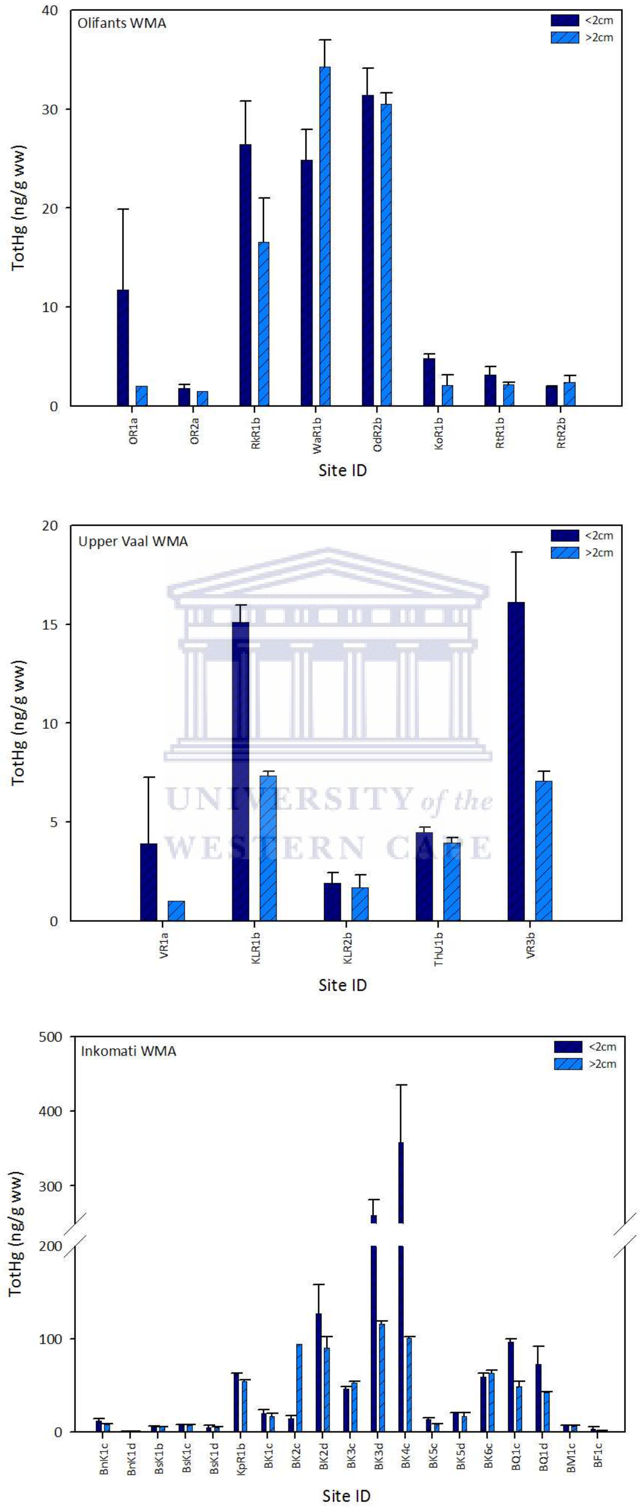

Figure 3.3: Total mercury (TotHg) concentrations in surface sediment (up to 4 cm depth) collected in the (1) Olifants WMA; (2) Upper Vaal WMA and (3) Inkomati WMAs. (small letters denote sample period; bars = mean ± SD; n = 3).

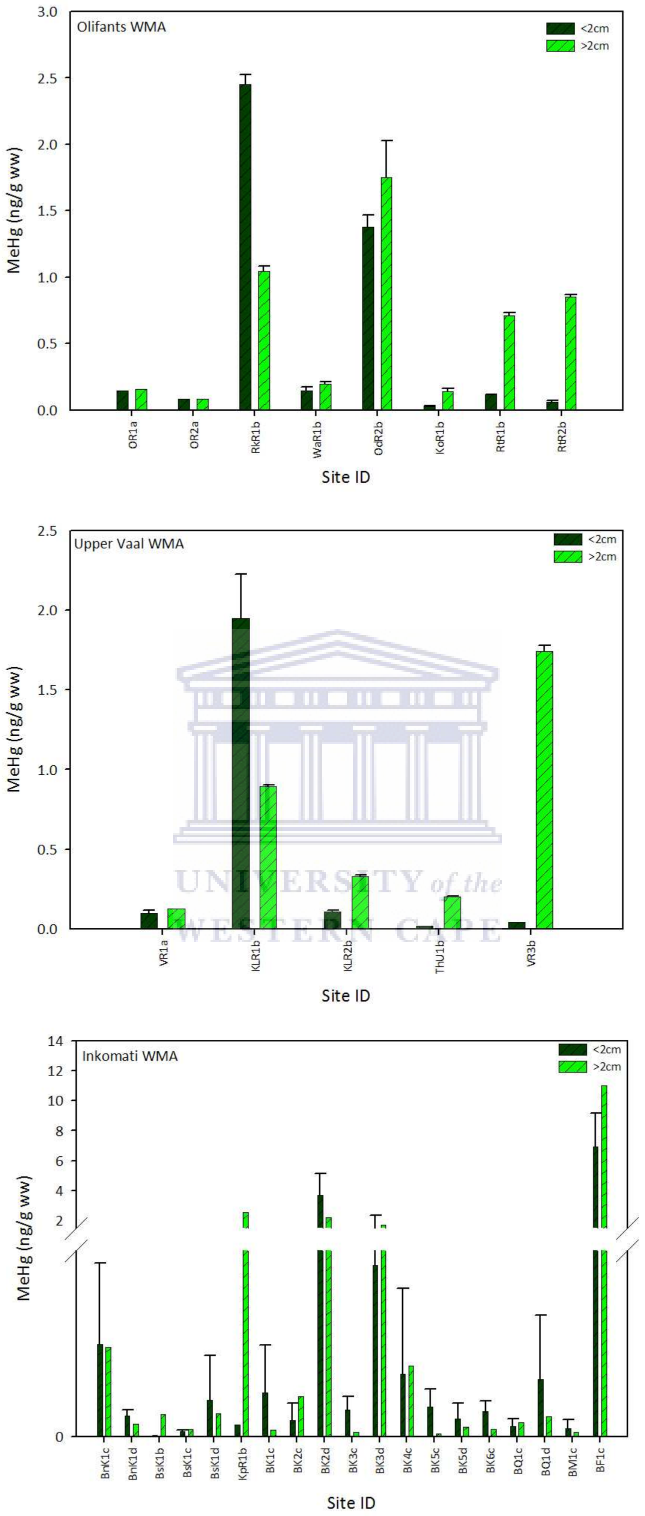

Figure 3.4: Methylmercury (MeHg) concentrations in surface sediment (up to 4 cm depth) collected in the Olifants, Upper Vaal and Inkomati WMAs.
(small letters denote sample period; bars = mean ± SD; n = 3).

The MeHg concentrations measured were highest in the Inkomati WMA at sites BK2 and BF1, when compared to all sites. This is not surprising, and can likely be attributed to the artisanal gold mining activities that take place in the Inkomati WMA.

Conway *et al.* (2003) and Warner *et al.* (2005) showed covariance between TotHg and MeHg concentrations in surface sediment. However, this relationship was not true for sediments layers in the Olifants, Upper Vaal and Inkomati WMAs, as a weak relationship was observed. This suggests that sediment MeHg concentrations in the three WMAs were not controlled by sediment TotHg concentrations. Thus, there are likely several co-depending controlling factors that influence the MeHg concentrations (other than TotHg concentration) in the Olifants, Upper Vaal and Inkomati WMA.

3.3.3 Mercury in biota

Lower trophic levels are significant in the bioaccumulation of Hg in fish. Therefore, predatory and benthic species often contain elevated Hg concentrations. A list of invertebrate and fish species collected is contained in Table 3.2.

The MeHg concentrations for all invertebrates are illustrated in Figure 3.5, and ranged between 5.29 ± 0.23 to 32.25 ± 1.40 ng/g ww, 2.80 ± 0.73 to 20.12 ± 2.34 ng/g ww and 3.59 ± 1.09 to 76.18 ± 4.97 ng/g ww, in the Olifants, Upper Vaal and Inkomati WMAs, respectively. The highest MeHg concentrations were measured in invertebrates collected in the Inkomati WMA (Figure 3.5). All biota (invertebrates

Table 3.2: List of biota collected, species code and diet.

ID	Species Name	Common Name	Diet
Invertebrates			
A	*Aeshnidae*	Dragonfly	Insects; small fish
B	*Atyidae*	Freshwater shrimp	aquatic plants; invertebrates (benthic)
C	*Baetidae*	Small minnow mayfly	aquatic plants
D	*Balastomatidae*	Giant water bug	crustaceans, fish, amphibians
E	*Coenagrionidae*	Damselfly	daphnia, mosquito larvae
F	*Corixidae*	Water boatmen	insects, small fish, tadpoles
G	*Dytiscidae*	Predacious diving	tadpoles; glassworms; small
H	*Gomphidae*	Dragonfly	daphnia, mosquito larvae, small aquatic
I	*Gyrinidae*	Whirligig beetle	benthic invertebrates
J	*Heptageniidae*	Flat-headed mayfly	small invertebrates
K	*Hydropsyches*	Caseless caddishfly	small invertebrates
L	*Libellulidae*	Dragonfly	daphnia, mosquito larvae, small aquatic
M	*Naucoridae*	Creeping water bug	insects; snails
N	*Oligochaeta*	Aquatic earthworm	detritus
O	*Perlidae*	Stonefly	aquatic invertebrates
P	*Simuldae*	Blackfly	organic matter
Fish			
A	*Amphilius spp.*	Catfish	benthic invertebrates
B	*Gambusia affinis*	Mosquitofish	Small aquatic organisms
C	*Labeobarbus spp.*	Yellowfish	detritus; invertebrates
D	*Micropterus*	Small-mouthed bass	fish, crabs
E	*Tilapia sparrmanii*	Banded tilapia	aquatic plants, small invertebrates
F	*Labeo ruddi*	Silver mudfish	organic sediments

and fish) analysed in this study are typically benthic organisms, living and feeding at the water-sediment interface or in sediment (Table 3.2). Benthic organisms generally contain higher Hg concentrations than other (pelagic-dwelling) organisms (Mason and Lawrence, 1999), and therefore provide for the transfer of sedimentary Hg to the aquatic food chain (Lawrence and Mason, 2001). Benthic invertebrates also provide an estimate of the bioavailability of sediments to biota (Mason and Lawrence, 1999). However, weak correlations were observed between sediment MeHg and invertebrate MeHg in the Olifants, Upper Vaal and Inkomati WMAs (r^2 =

0.22; $r^2 = 0.34$; $r^2 = 0.1$, respectively), which suggests that sediment-associated MeHg is not readily available for uptake by biota. The MeHg concentrations in invertebrates collected in the Upper Vaal and Inkomati WMAs, were significantly different ($p < 0.05$) to invertebrates collected in the Olifants WMAs.

The MeHg concentrations in fish samples collected in the three WMAs are represented in Figure 3.6. Fish feeding on organisms at the lower trophic levels bioaccumulate less MeHg, when compared to fish that feed on organisms at higher trophic levels (Sveinsdottir and Mason, 2005). The MeHg concentrations in all fish collected (Table 3.2) ranged between 20.03 to 75.40 ± 5.82 ng/g ww, 10.06 ± 1.44 to 33.92 ± 3.44 ng/g ww, and 14.40 ± 2.48 to 217.82 ± 4.13 ng/g ww in the Olifants, Upper Vaal and Inkomati WMA, respectively (Figure 3.6). The highest MeHg concentration in fish was measured in the Inkomati WMA, which can be attributed to the artisanal gold mining industry in the area and other factors (see below).

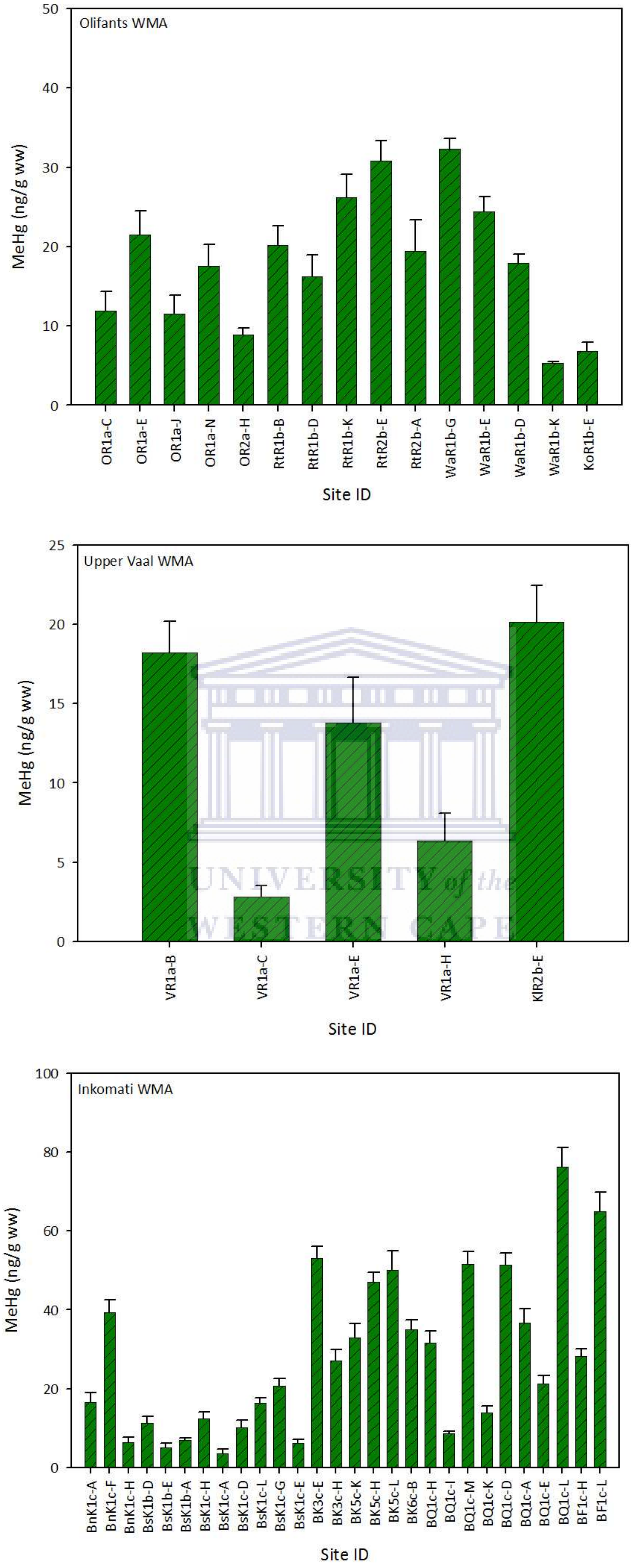

Figure 3.5: Methylmercury (MeHg) concentrations in invertebrates collected in the Olifants, Upper Vaal and Inkomati WMAs
(lower case = sample frequency; capital letters = species in Table 3.2; bars = mean ± SD; n = 3).

Fish species caught in this study feed primarily on invertebrates and organic sediments (Table 3.2). A comparison of MeHg concentration in invertebrates and fish collected in the Inkomati WMA supports the fact that benthic invertebrates facilitate the transport of sedimentary Hg to fish. A positive correlation in fish MeHg concentrations and fish length was observed in the Olifants and Upper Vaal WMAs (r^2 = 0.88; r^2 = 0.90), similar to what has been reported by others (Sveindsottir and Mason, 2005). However, such a correlation was not observed for fish collected in the Inkomati WMA, as higher concentrations were measured in fish of smaller size class. These differences can likely be attributed to the Hg point sources in the Inkomati WMA, *vs.* that of Hg in the Olifants and Upper Vaal WMAs.

Mercury in sediment is also a source of Hg to fish (Gilmour *et al.*, 1992). Brumbaugh *et al.* (2001) supports this reasoning, and reported positive correlations for aqueous and sedimentary MeHg concentrations. In accordance, fish MeHg concentrations were positively correlated to aqueous MeHg and sediment MeHg concentrations in the Inkomati WMA. Although all fish MeHg concentrations were below the US EPA guideline for MeHg (300 ng/g ww; US EPA, 2001b), some MeHg concentrations, particularly in the Inkomati WMA, were approaching this maximum limit. These findings can be attributed to direct Hg inputs into the water resources of the Inkomati WMAs where artisanal gold mining activities take place.

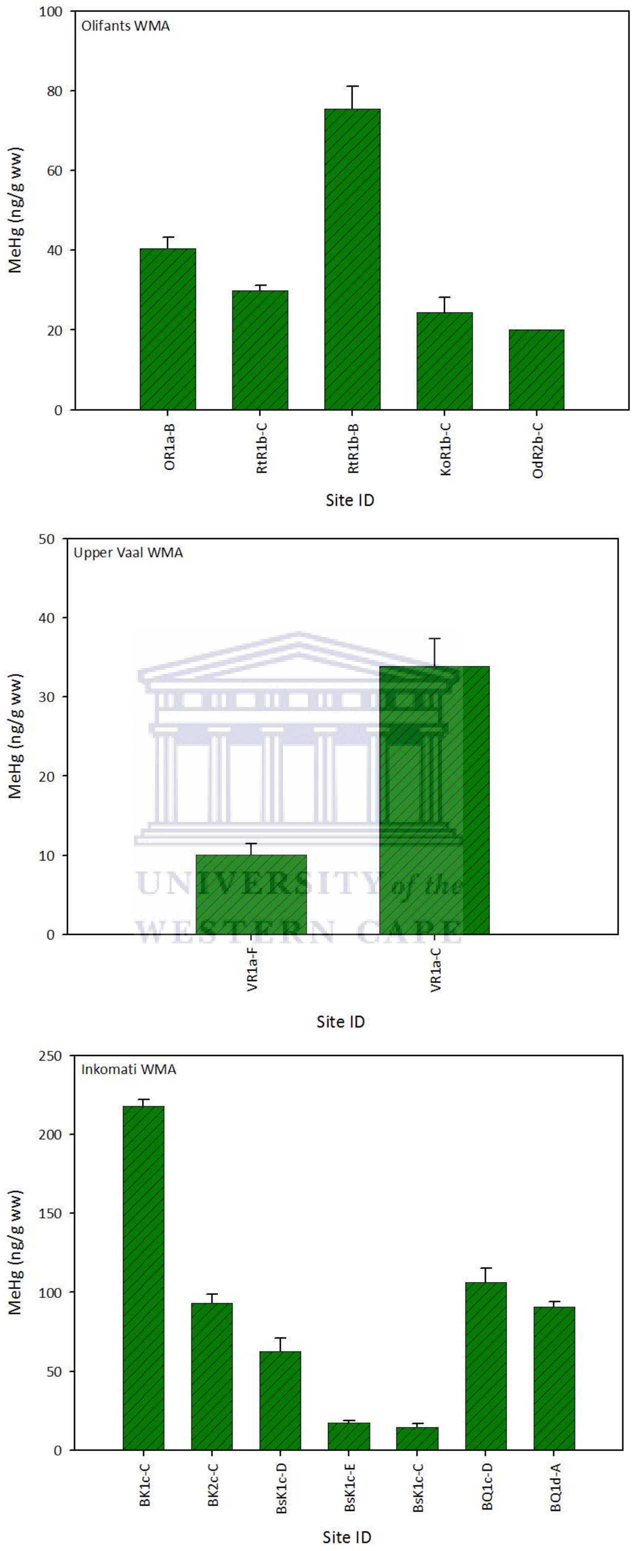

Figure 3.6: Methylmercury (MeHg) concentrations in fish collected in the (1) Olifants; (2) Upper Vaal and (3) Inkomati WMAs
(lower case = sampling frequency; capital letters = species in Table 3.2; bars = mean ± SD; n = 3).

3.4 Summary

This assessment provides an indication of the TotHg and MeHg concentrations in water, sediment, and biota of three WMAs, *viz.* Olifants, Upper Vaal and Inkomati. The TotHg and MeHg concentrations in water samples collected were higher at downstream sites when compared to the upstream sites, and were higher during the wet *vs.* dry season.

Although the sedimentary Hg concentrations varied, the highest Hg concentrations were measured in sediment collected in the Inkomati WMA. This trend was also reflected in both invertebrates (primarily benthic invertebrates) and fish (species feeding on benthic invertebrates and organic matter). The positive correlations between fish MeHg concentrations and sedimentary MeHg concentrations lends support to the significance of sediment, and benthic invertebrates in particular, as the primary mechanism for the transport of sedimentary Hg to aquatic food chains.

The results of this study suggest that coal-fired power plants and artisanal gold mining activities may have some environmental impact in the Mpumalanga Province. In general, the Inkomati WMA appears to be more impacted by anthropogenic sources of Hg, when compared to the Olifants and Upper Vaal WMAs. The impacts of artisanal gold mining activities in the Inkomati WMA are, likely sustained in the cycling and mobilization of Hg-contaminated sediments, in the water column. Furthermore, the elevated MeHg concentrations in fish collected in the Inkomati WMA indicate that MeHg is more readily available in the latter WMA, than in the Olifants and Upper Vaal WMAs.

This study demonstrates that future, more long-term monitoring is needed to fully assess the Hg concentrations in the Inkomati WMA, particularly since subsistence fishing forms part of the daily livelihoods of the communities living near the water resources sampled in this study. Such studies are particularly needed in this WMA, since MeHg concentrations in fish were approaching the US EPA regulatory limits for fish (*i.e*. 300 ng/g ww; US EPA, 2001b).

Overall, the results demonstrate that the impacts of coal-fired power plants and artisanal gold mining activities on water resources and its ecosystems need to be assessed over a much longer timeframe and at a more regular frequency. Such a monitoring programme (with increased samples, sampling sites and sampling frequency) will prove more conclusive in determining the potential impacts of these anthropogenic Hg sources on water resources in these WMAs.

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CHAPTER 4: MERCURY CONCENTRATIONS AT A HISTORICALLY MERCURY-CONTAMINATED SITE IN KWAZULU-NATAL

4.1 Introduction

Mercury (Hg), when present in the aquatic environment, has a high affinity for suspended particles, which promotes its removal from water and settlement in sediment (Lee *et al.*, 1998). As indicated in previous chapters of this study, inorganic Hg (Hg^{2+}) is methylated to more toxic methylmercury (MeHg) under favourable (anoxic) environmental conditions, where it is primarily controlled by pH, temperature and presence of organic matter (OM) (Scheuhammer and Graham, 1999; Gilbertson and Carpenter, 2004). Sediments are the primary reservoir where such methylation occur (Benoit *et al.*¸1999), and any Hg that is sequestered in sediments can be remobilized and re-introduced to the surrounding water column (Covelli *et al,*. 1999).

It is well documented that aquatic organisms are generally at the receiving end of Hg in aquatic ecosystems (Beldowski and Pempkowiak, 2007), and that MeHg bioaccumulates and biomagnifies up the aquatic food chain (Boudou and Ribeyre, 1997; Mason *et al.*, 2000; UNEP, 2002). As discussed in Chapter 2 of this study, fish collected in the Mvoti-Umzimkulu WMA, in the KwaZulu-Natal Province, had MeHg concentrations that ranged between 6.00 – 268.47 ng/g ww. The MeHg concentrations measured can largely be attributed to residual Hg present at a historically Hg-contaminated site at Cato Ridge, in KwaZulu-Natal. Other studies (Johnston *et al.*, 1991; Barrat and Combrink, 2002) undertaken in this area, have also reported high Hg concentrations, particularly in sediment and fish. The water resources in the Cato Ridge area have been subjected to Hg effluent discharges during 1986 to 1990, mainly from a chemicals-manufacturing plant that had released Hg effluent directly into the Mngceweni River (Oosthuizen and Erhlich, 2001).

Since high MeHg concentrations were reported in fish sampled in the water resources of the Mvoti-Umzimkulu WMA in this study, the Mngceweni and Umgeni Rivers became the focus of intensive total Hg (TotHg) and MeHg measurements during 2007 and 2008. The intensive sampling was also undertaken to verify if these water resources were indeed potential Hg "hotspots", as suggested in Chapter 2 of this study. As such, TotHg and MeHg concentrations were measured in water, sediment and biota (invertebrates and fish), of the Mngceweni and Umgeni Rivers, and upstream and downstream of two major dams in the vicinity, *viz.*, Nagle and Inanda (appendix 11).

4.2 Materials and Methods

4.2.1 Site Selection and Characterization

The Umgeni River and its tributary, the Mngceweni River, is located *ca.* 23 km from Pietermaritzburg, and *ca.* 56 km from Durban in the KwaZulu-Natal Province. The Inanda Dam, located *ca.* 35 km downstream of the chemicals-manufacturing plant at Cato Ridge, is the primary source of drinking water to the city of Durban (Oosthuizen and Ehrlich, 2001), and is a source of subsistence fishing to residents in the Valley of a Thousand Hills in the area. The Nagle Dam, on the other hand, is located *ca.* 20 km upstream of the plant.

Sampling sites were located on the Mngceweni River (immediately below the chemicals-manufacturing that had released Hg effluent into the river during the 1990's), on the Umgeni River, and upstream and downstream of the Nagle and Inanda dams (Table 4.1; appendix 11).

Table 4.1: Sampling sites, water resource, site description and sample frequency between 2007 and 2008

Site ID	Water Resource	Site Description	Date sampled
UR1	Umgeni River	Upstream of Nagle Dam	June 2007(a); July 2008(b); Dec 2008 (c)
UR2	Umgeni River	Downstream of Nagle Dam	June 2007(a); July 2008(b); Dec 2008 (c)
DM1	Mngceweni River	Mngceweni River – at bridge	July 2008 (b)
DM2	Mngceweni River	Mngceweni River	July 2008 (b)
UI1	Inanda Dam	Upstream of Inanda Dam	July 2008(b); Dec 2008 (c)
UI2	Inanda Dam	Downstream of Inanda Dam	2008(b); Dec 2008 (c)

4.2.2 Sampling Protocol and Sampling Collection

This section has previously been described in Chapter 2. Refer to section 2.2.2 for sampling protocol and sampling collection.

4.2.3 Ancillary water quality parameters

This section has previously been described in Chapter 2. Refer to section 2.2.3 for ancillary water quality parameters.

4.2.4 Sample Preparation and Analytical Techniques

This section has previously been described in Chapter 2. Refer to section 2.2.4 for sample preparation and analytical techniques.

4.2.5 Quality Control Procedures

This section has previously been described in Chapter 2. Refer to section 2.2.5 for quality control procedures employed in this study.

4.2.6 Statistical Analyses

This section has previously been described in Chapter 2. Refer to section 2.2.6 for statistical analysis protocol.

4.3 Results and Discussion

4.3.1 Mercury in water

Aqueous TotHg concentrations are presented in Figure 4.1. Overall, TotHg concentrations ranged between 0.13 ± 0.01 to 6.48 ± 0.69 ng/L. All TotHg concentrations measured except for concentrations measured at sampling site DM1b, were below the global average of 5.0 ng/L (Mason *et al.*, 1994). All TotHg measurements were also below the South African water quality guidelines for aquatic ecosystems (40 ng/L; DWAF, 1996), as well as the US EPA suggested value of 12 ng/L that could result in chronic effects in aquatic organisms (US EPA, 1992). The TotHg concentrations measured were also within the concentrations reported for river waters near Hg deposits, where the concentrations generally range between 500 and 100 000 ng/L (CRC Press, 1997).

Background TotHg concentrations at sampling site UR1 during all three sampling phases (*i.e.* UR1a, UR1b and UR1c), located upstream of the Nagle Dam (refer to appendix 11) were generally in the range of 0.16 to 1.09 ± 0.05 ng/L, whereas TotHg concentrations at sites (DM1b and DM2b), immediately below the chemicals-manufacturing plant, measured 6.48 ± 0.69 and 1.67 ng/L, respectively. Interestingly, TotHg concentrations generally decreased with distance from the plant; an 11-fold decrease from 6.48 ± 0.69 to 0.55 ± 0.01 ng/L was observed. This decrease in TotHg concentrations further away from the plant can be attributed to pollution dilution effects, as observed by Turner and Lindberg (1978). Seasonal trends were also observed at sampling sites UR1, UR2, UI1 and UI2, where TotHg concentrations generally showed a 50 % reduction in the wet *vs.* dry season, further indicating the pollution dilution effects (Turner and Lindberg, 1978).

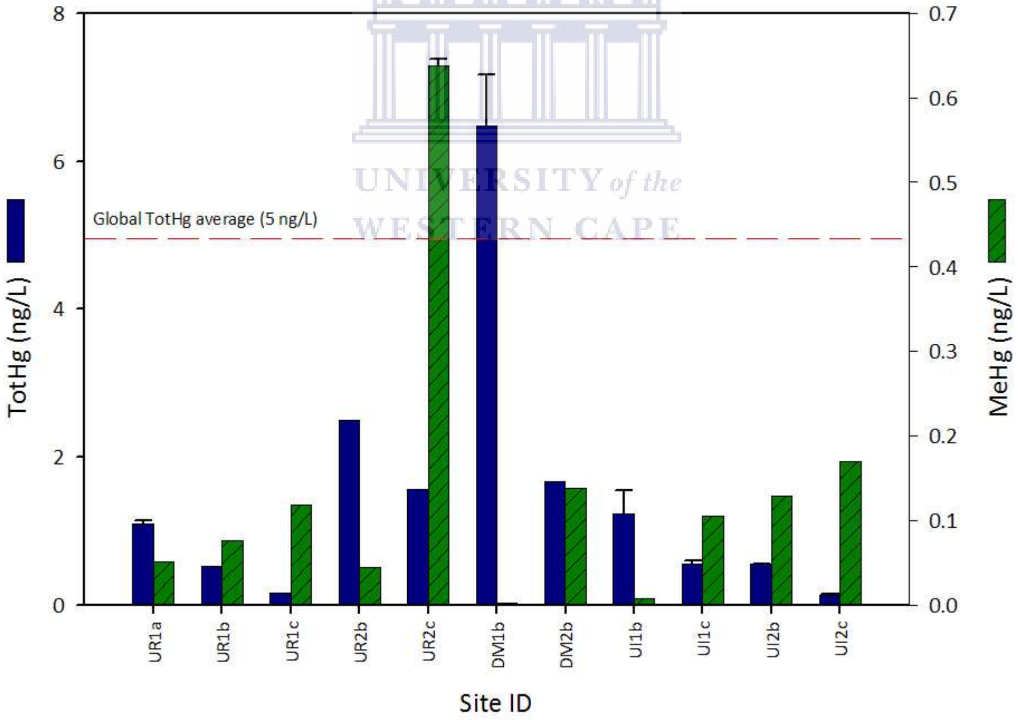

Figure 4.1: Aqueous total mercury (TotHg) and methylmercury (MeHg) concentrations.
(bars = mean ± SD; n = 3).

Aqueous MeHg concentrations ranged from below the detection limit (< 0.02 ng/L) to 0.64 ± 0.01 ng/L, with a gradual increase in MeHg concentrations being observed in all sites sampled during 2007 and 2008 (Figure 4.1). Interestingly, the MeHg concentrations increased more than 20-fold in the wet season (December 2008), and can most likely be attributed to increased inputs via wet deposition during storm events or the resuspension of MeHg (from sediments) into the water column. The highest MeHg concentration was measured at sampling site UR2 (below the Nagle Dam) during the dry season in December 2008 (*i.e.* UR2c). Overall, the increase in MeHg concentrations but decrease in TotHg concentrations, at the same sites from 2007 to 2008, and taking seasonal variation into consideration, suggests that methylation and resuspension of any residual Hg from historical Hg effluent spill may still be released into the system.

Since OM forms strong complexes with Hg, the extent to which Hg binds with dissolved organic carbon (DOC) determines the efficiency of downstream transportation of Hg. DOC affects Hg speciation, solubility, mobility and toxicity (Ravichandran, 2004), and controls the temporal TotHg distribution in systems. The extent of influence is site specific and also depends on the season (Babiarz *et al.*, 1998). The concentrations of DOC ranged from 3.10 to 14.81 mg/L. A positive relationship was observed for TotHg and MeHg concentrations, correlated to DOC at each site during the wet season only. This suggests that during the wet season, Hg was organically complexed, similar to what has been reported in other studies (Watras *et al.*, 1998). This can likely be attributed to increased freshwater flow and associated runoff processes, and flocculation of DOC, as observed by others (Conaway *et al.*, 2003); although a lower pH also promotes DOC complexation to Hg (Miskimmin *et al.*, 1992).

4.3.2 Mercury in sediment

Total Hg concentrations in surface sediment ranged between 1.82 ± 0.53 to 74.03 ± 6.71 ng/g wet weight (ww), at 0 – 1 cm depths; 1.38 ± 0.23 to 75.00 ± 2.10 ng/g ww, at 1 – 2 cm depths; and 1.04 ± 0.23 to 80.08 ± 8.97 ng/g ww, at 2 – 3 cm depths (Figure 4.2). All TotHg concentrations were below the US EPA guideline of 200 ng/g for sediment (US EPA, 2000a). The TotHg concentrations were generally highest at DM1 and DM2 - both sites are located immediately downstream of the chemicals-manufacturing plant at Cato Ridge. However, the TotHg concentrations generally decreased over time (Figure 4.2). For example, TotHg concentrations decreased by up to 90 % from June 2007 to July 2008, in all sediment layers, at sampling site UR1. Similar trends were observed at other sampling sites (Figure 4.2). Seasonally, higher TotHg concentrations were generally measured during the dry season (June 2007; July 2008), when compared to the wet season (December 2008). While most sites showed a decrease in TotHg concentrations in depths (*i.e.* [TotHg] 1 cm depth > [TotHg] 2 cm depth > [TotHg] 3 cm depth), no trend (increasing or decreasing) was observed in sediment organic content.

The overall low TotHg concentrations measured at sampling sites UR1, UI1 and UI2, are expected. The Nagle Dam site (UR2) is located above the area where the Mngceweni River confluences with the Umgeni River, while the other two sites (UI1 and UI2) are located some distance from the Mngceweni River. Any residual Hg from the historical Hg contamination into the Mngceweni River would be trapped in sediment closest to the chemicals-manufacturing plant, as evidenced by the higher TotHg concentrations measured at sampling sites DM1 and DM2 (Figure 4.2).

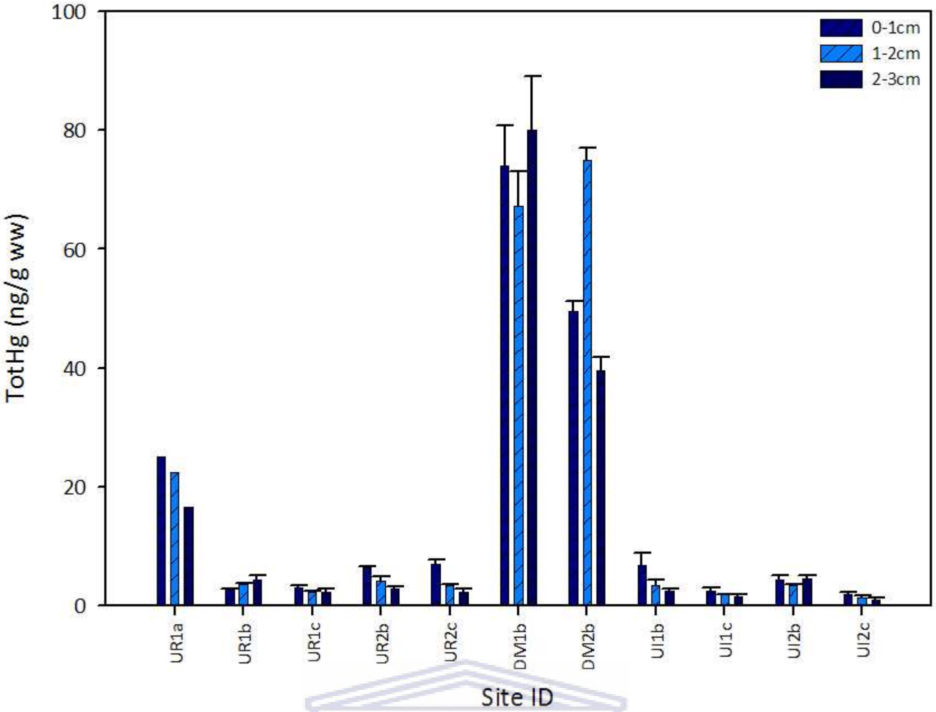

Figure 4.2: Total mercury (TotHg) and methylmercury (MeHg) concentrations in sediment (bars = mean ± SD; n = 3).

The MeHg concentrations in surface sediments were relatively low, and ranged between < 0.02 to 0.23 ± 0.05 ng/g ww, at 0 – 1cm depth; 0.03 to 0.47 ± 0.04 ng/g ww, at 1 – 2 cm depth; and 0.02 to 1.49 ± 0.02 ng/g ww, at 2 – 3 cm depth (Figure 4.3). An increase in MeHg concentrations were generally observed with depth (*i.e.* [MeHg] 1 cm depth > [MeHg] 2 cm depth > [MeHg] 3 cm depth). For most sites, MeHg concentrations increased from the dry (June 2007; July 2008) to wet (December 2008) seasons. The highest MeHg concentration was measured at sampling site DM2 (1.49 ± 0.02 ng/g ww), which is located on the Mngceweni River, below the chemicals-manufacturing plant. The MeHg concentration trends are similar to that of the TotHg concentration trends observed, although the MeHg concentrations are much lower. On average, the fraction of TotHg that occurs as

MeHg was *ca.* 1.86 %, 6.00 % and 3.57%, for the respective sediment depths, *i.e.* 0 – 1, 1 – 2, and 2 – 3 cm.

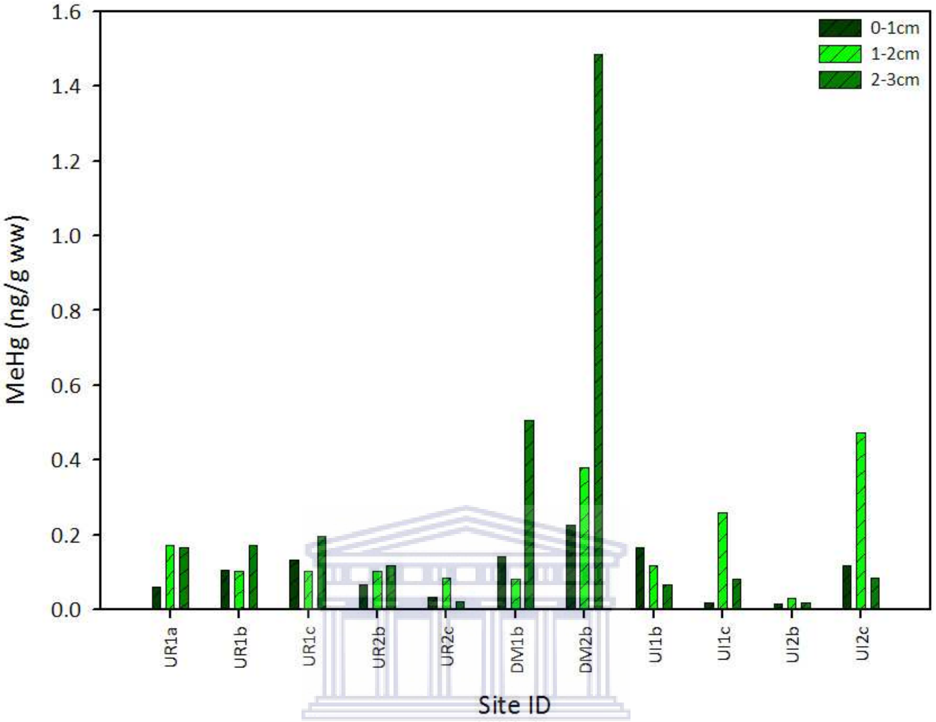

Figure 4.3: Total mercury (TotHg) and methylmercury (MeHg) concentrations in sediment (bars = mean ± SD; n = 3).

Several studies have demonstrated the importance of TotHg concentration (Benoit *et al*., 2002; Conway *et al*., 2003) and sediment organic content (loss on ignition; LOI) (Warner *et al.*, 2005) in controlling methylation rate. Methylmercury showed weak positive correlations with sediment OM (r^2 = 0.71, at 0 – 1 cm depth; r^2 = 0.53, at 1 – 2 cm depth; r^2 = 0.59, at 2 – 3 cm depth). This suggests that MeHg concentrations were not primarily controlled by sediment OM. Overall, however, sediments in this region may be continuously eroded and remobilized, and consequently serve as a Hg source to sites downstream.

4.3.3 Mercury in biota

Invertebrate species, collected during 2007 and 2008, are represented in Table 4.2. In this study, MeHg concentrations in invertebrates extended over four orders of magnitude, and generally ranged between 0.16 to 251.19 ng/g ww (Figure 4.4). The highest MeHg concentration (251.19 ng/g ww) was recorded in water scorpions at sampling site DM2 (DM2b), followed by MeHg concentrations (187.73 ng/g ww) measured in dragonflies collected at UR2 (UR2b). Since sampling site DM2 is located in the Mngceweni River immediately downstream of the chemicals-manufacturing plant at Cato Ridge, the MeHg concentrations observed at this site can be attributed to the uptake of residual Hg present in the system.

Table 4.2: List of biota collected, species code and diet.

ID	Species	Common name	Diet
Invertebrates			
A	*Aeshnidae*	Dragonfly	Insects; small fish
B	*Atyidae*	Freshwater shrimp	Aquatic plants; invertebrates (benthic)
C	*Belastomatidae*	Giant water bug	Crustaceans, fish, amphibians
D	*Coeangrionidae*	Damselfly	Daphnia; mosquito larvae
E	*Corixidae*	Water boatmen	Insects; small fish; tadpoles
F	*Gomphidae*	Dragonfly	Daphnia; mosquito larvae; small aquatic organisms
G	*Libellulidae*	Dragonfly	Daphnia; mosquito larvae; small aquatic organisms
H	*Nepidae*	Water scorpion	Invertebrates
I	*Naucoridae*	Creeping water bug	Insects; snails
J	*Notonectidae*	Backswimmer	Insects; small fish; tadpoles
K	*Thiaridae*	Cony snail	Aquatic plants
L	*Tabanidae*	Horsefly	Males: nectar/pollen; females: blood
Fish			
A	*Amphilius spp*	Catfish	Benthic invertebrates
B	*Labeobarbus natalensis*	Yellowfish	Detritus; invertebrates
C	*Micropterus dolomieu*	Small-mouthed bass	Fish; crabs
E	*Tilapia sparrmanii*	Banded tilapia	Aquatic plants; small invertebrates
D	*Tilapia rendalli*	Red-breasted tilapia	Aquatic plants; small invertebrates

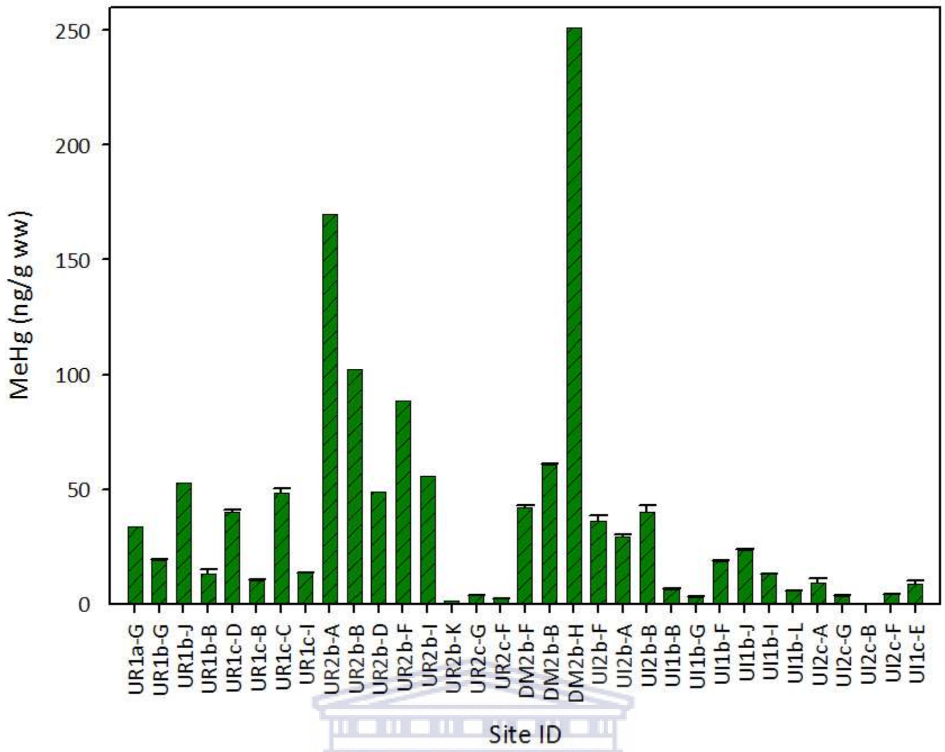

Figure 4.4: Methylmercury (MeHg) concentrations in invertebrates
(bars = mean ± SD; n = 3; capital letters denote species in Table 4.2).

The MeHg concentrations in fish species collected ranged from 6.00 ± 2.40 to 268.47 ± 2.82 ng/g ww, and are represented in Figure 4.5. All MeHg concentrations were well below the US EPA's guideline for Hg in fish muscle tissue (300 ng/g ww; US EPA, 2001b). However, MeHg concentrations measured in banded tilapia collected at sampling site DM2 (DM2b) were just below this guideline (268.47 ± 2.82 ng/g ww; fork tail length = 13.46 cm). Based on the US EPA's fish consumption limits for Hg concentrations in the edible portion of fish, the consumption of fish should be limited to 3 fish meals per month (Table 1.4; US EPA, 2000b). Since MeHg concentrations comprise *ca.* 90 % of the TotHg concentration in fish muscle tissue (Leaner and Mason, 2004), fish caught in the Mngceweni River should be consumed with caution. Generally, MeHg concentrations increase with size and age of fish.

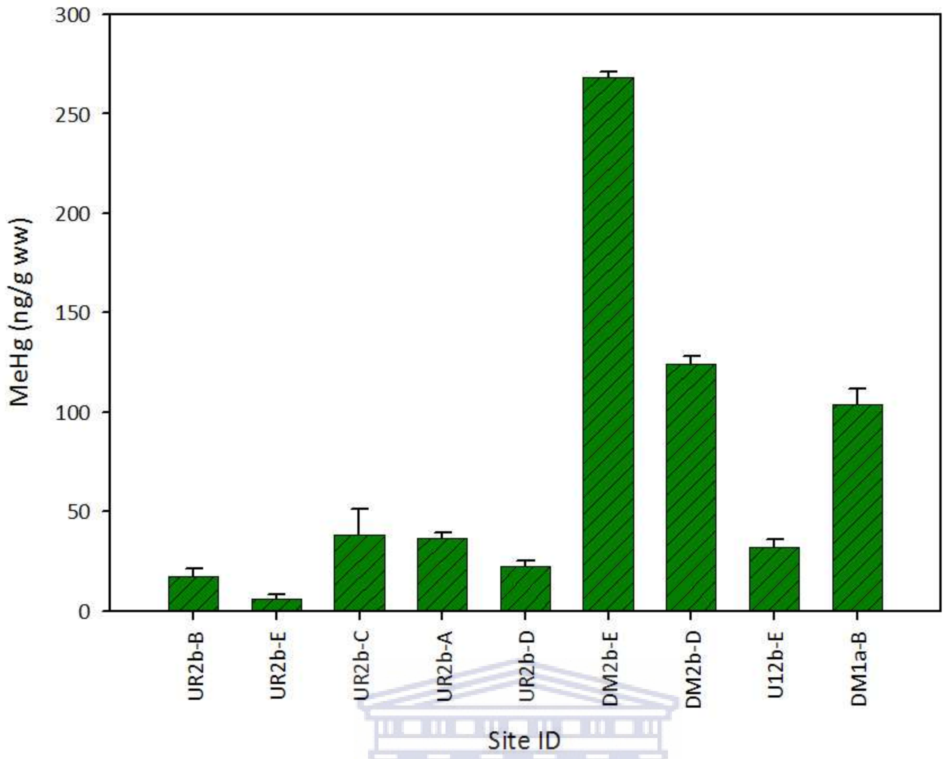

Figure 4.5: Methylmercury (MeHg) concentrations in fish collected (bars = mean ± SD; n = 3; capital letters denote species in Table 4.2)

Nonetheless, the MeHg concentrations measured in fish at sampling site DM2 compares well with Hg concentrations reported by Barrat and Combrink (2002) (50 – 250 ng/g), for freshwater fish caught immediately downstream of the chemicals-manufacturing plant, from which Hg effluent was discharged during the 1990's.

4.4 Summary

This study provided a "snapshot" of the TotHg and MeHg concentrations in water, sediment and biota collected in the Umgeni and Mngceweni Rivers in KwaZulu-Natal. The results suggest that the historically, Hg-contaminated Mngceweni River still represents a Hg source in the Mvoti-Umzimkulu WMA. The Hg concentrations measured in sediment and biota, particularly banded tilapia, supports the classification of the water resources in the Mvoti-Umzimkulu WMA, as a Hg "hotspot". It is evident that residual Hg is likely remobilized from sediment, particularly during the wet season, thereby making it bioavailable for uptake in the aquatic food chain. Although no risk assessment has been undertaken in this study, it is evident that communities living near the Mngceweni River should take caution when consuming fish from the river on a regular basis. Ideally, fish caught in the vicinity should be consumed with caution.

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CHAPTER 5: SUMMARY - MERCURY AS A POLLUTANT IN SOUTH AFRICA

Environmental contamination by mercury (Hg) is a global concern due to its impacts on ecosystems and human health. Most anthropogenic Hg emissions are released into the atmosphere as by-products of industrial process, particularly from sources such as coal-fired power stations (Nriagu and Pacyna, 1988) and artisanal gold mining activities. Other possible sources of Hg into water resources include run-off from wastewater treatment plants and cement production facilities (Isikli *et al.*, 2006).

This research is an assessment of TotHg and MeHg concentrations in water, sediment and biota (invertebrates and fish) of selected water resources in South Africa's 19 Water Management Areas (WMAs; Table 5.1). During 2007 – 2009, surface water, sediment and biota (where possible) were collected at 63 sample sites. Seasonal trends were also investigated during intensive sampling periods, where samples were collected during the wet and dry season of the respective WMAs.

Overall, the results of this study demonstrates that the Olifants, Upper Vaal, Inkomati and Mvoti-Umzimkulu WMAs can potentially be classified as Hg "hotspots", based on the TotHg or MeHg concentrations obtained in different environmental compartments.

Findings in this study are summarized for both TotHg and MeHg concentrations in various environmental compartments, and highlights those WMAs, which are most impacted by anthropogenic Hg sources. Spatial distribution maps of Hg as a pollutant in South Africa are presented, and provide a “snapshot” of the Hg distribution at the sites sampled in the 19 WMAs in South Africa.

Table 5.1: List of Water Management Areas and anthropogenic mercury source

WMA No.	WMA	Anthropogenic Hg source
1	Limpopo	Cement; Coal-fired power stations
2	Levuvhu-Letaba	Unimpacted
3	Crocodile (West) Marico	Cement
4	Olifants	Coal-fired power stations
5	Inkomati	Artisanal gold mining
6	Usutu-Mhlatuze	Cement
7	Thukela	Cement
8	Upper Vaal	Coal-fired power stations
9	Middle Vaal	Coal-fired power stations
10	Lower Vaal	Cement
11	Mvoti-Umzimkulu	Previously contaminated
12	Mzimvubu-Keiskamma	Agricultural / urban effluent
13	Upper Orange	Agricultural / urban effluent
14	Lower Orange	Agricultural / urban effluent
15	Fish-Tsitsikamma	Agricultural / urban effluent
16	Gourtiz	Agricultural / urban effluent
17	Olifants/Doorn	Agricultural / urban effluent
18	Breede	Agricultural / urban effluent
19	Berg	Wastewater treatment plants

5.1 Overview of mercury as a pollutant in South Africa’s water resources

5.1.1 Mercury in Water

Background TotHg concentrations, typically at < 1 ng/L, were measured in the Levuvhu-Letaba (2), Middle Vaal (9), Lower Vaal (10), Upper Orange (13), Gouritz (16) and Olifants/Doorn (17) WMAs. Aqueous TotHg concentrations were generally higher in the Upper Vaal WMA (8) (impacted by coal-fired power stations), followed by the Inkomati (5), Olifants (4) and Mvoti-Umzimkulu (11) WMAs, which are impacted by artisanal gold mining activities, coal-fired power stations, and historical Hg contamination, respectively (appendix 25). These WMAs are located in close proximity to, and are potentially impacted on by the major anthropogenic Hg sources in the areas. Total Hg concentrations in the Olifants (4), Inkomati (5), Upper Vaal (8) and Mvoti-Umzimkulu (11) WMAs were above the 5 ng/L global average for TotHg in aquatic environments (Mason *et al.*, 1994), while only the Olifants (4), Inkomati (5) and Upper Vaal (8) WMAs were above the 12 ng/L maximum limit that will result in chronic effects to ecosystems (US EPA, 1992).

The MeHg concentrations in all 19 WMAs were generally low and typically averaged < 1 ng/L (appendix 26). Average MeHg concentrations were higher in the Inkomati (5), Upper Vaal (8) and Mvoti-Umzimkulu (11) WMAs, when compared with all other WMAs.

5.1.2 Mercury in Sediment

The TotHg concentrations in surface sediments (< 4 cm) were fairly consistent in the central region of South Africa (< 10 ng/g ww), while it was high in the north, east and southern most areas of the country (appendix 27).

The Inkomati WMA (5) is known for illegal artisanal gold mining practices, where Hg is used as a gold amalgam. Thus, the highest TotHg concentrations were observed in the Inkomati WMA (5) and were in excess of the US EPA quality guideline for TotHg in sediments (200 ng/g; US EPA, 2001). Sediment TotHg concentrations in the Mvoti-Umzimkulu WMA (11) were also high, and indicates the resuspension of residual Hg in sediment in the system. The sediment TotHg concentrations demonstrates that emissions from coal-fired power plants in the Olifants (4) and Upper Vaal (8) WMAs, and artisanal gold mining practices in the Inkomati (5) WMA impacted on the water resources sampled.

The MeHg concentrations in surface sediment were generally < 1 ng/g ww, except for the Inkomati (5), Olifants (4) and Upper Vaal WMAs (8) (appendix 28). Overall, the trends in MeHg concentrations reflect those of TotHg concentrations, *viz.* the highest concentrations were generally measured in the Gauteng and Mpumalanga provinces of the country, with fairly lower concentrations measured in the other provinces.

5.1.3 Mercury in Biota

Methylation of Hg is the main pathway for Hg introduction in aquatic food chains. Methylation is a complex process which can occur in both the water column and surface sediment (top 4 cm). The highest MeHg concentrations in invertebrates were measured in the Mvoti-Umzimkulu WMA (11) (appendix 29); while in fish, the highest MeHg concentrations were measured in the Mvoti-Umzimkulu (11) and Inkomati (5) WMAs (appendix 30). These trends compare well with Hg concentrations measured in sediment, particularly since most of the invertebrates collected in this study were benthic and feed at the water-sediment interface. As such, the invertebrates provide a mechanism for the transfer of sedimentary Hg to aquatic food chains (Lawrence and Mason, 2001). The MeHg concentrations measured in fish collected in the Inkomati (5) and Mvoti-Umzimkulu (11) WMAs (appendix 30) were also close to the US EPA fish consumption guideline for Hg (300 ng/g ww; US EPA, 2001).

5.2 Summary

Our current knowledge on the extent of Hg pollution in South Africa's rivers has increased since the onset of this study, which was critical for assessing the potential risks of Hg to both ecosystems and human health. The TotHg and MeHg concentrations measured in water, sediment and biota informed the classification of the Olifants, Upper Vaal, Inkomati and Mvoti-Umzimkulu WMAs as Hg "hotspots" in South Africa. Site specific characterizations found that Hg concentrations in the different environmental compartments are possibly a direct consequence of widespread anthropogenic activities prevalent within the WMAs.

The results of this study indicate that the Inkomati WMA is more impacted by anthropogenic Hg sources, when compared to the Olifants and Upper Vaal WMAs. The illegal artisanal gold mining in the Inkomati WMA has resulted in MeHg concentrations in fish that are approaching the US EPA consumption limits for fish (*i.e.* 300 ng/g ww; US EPA, 2001). Future, long-term monitoring is needed to fully assess the Hg concentrations in the Inkomati WMA.

The Upper Vaal and Olifants WMAs are characterized by coal-fired power stations, and water resources are likely impacted by Hg emissions from coal combustion at these sources via wet and dry deposition. In-stack Hg emissions and ambient Hg monitoring are recommended for these WMAs, particularly with increased sampling frequency, over a longer-term period. Such a Hg monitoring programme will prove more conclusive in determining the potential impacts of coal-fired power stations.

The results further suggest that the Mngceweni River, in the Mvoti-Umzimkulu WMA, still contains residual Hg (likely bound in sediment), and that this river could is still a likely Hg source in the area. Any Hg in sediment can be remobilized, and become bioavailable and bioaccumulate in the ecosystem for decades. In addition, a risk assessment should be undertaken in the vicinity of the Umgeni / Mngceweni river system.

This is the first study that attempted to obtain a representative picture of Hg concentrations in all 19 WMAs of South Africa, where both TotHg and MeHg concentrations were measured in water, sediment and biota (fish and invertebrates).

5.3 Suggestions for future work

Future work, incorporating the data collected in this study, are suggested below:

- Transect sampling should be conducted around specific sampling sites to collect data for both water, sediment and biota samples. Such sampling will prove more representative.
- The wind directions (using wind roses) around Hg sources, such as coal-fired power stations, should be taken into account.
- Water Management Areas with a strong reliance on groundwater should be a primary part of future monitoring studies, particularly where the groundwater recharge areas may be subject to Hg contamination, and there is a strong reliance to groundwater for drinking.
- The results obtained have shown that certain WMAs show signs of contamination and should remain a potential source of bioaccumulation and remobilisation of Hg into the ecosystem, which should be monitored in future.

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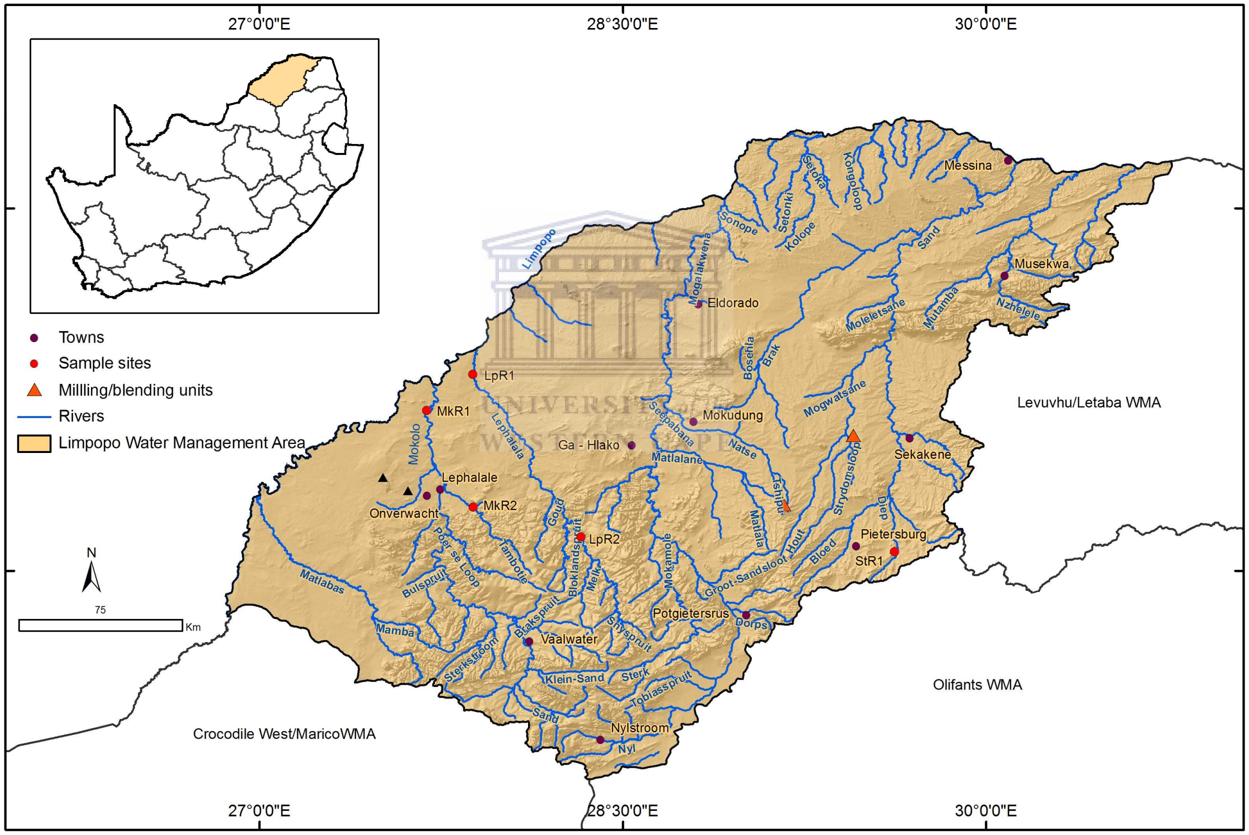
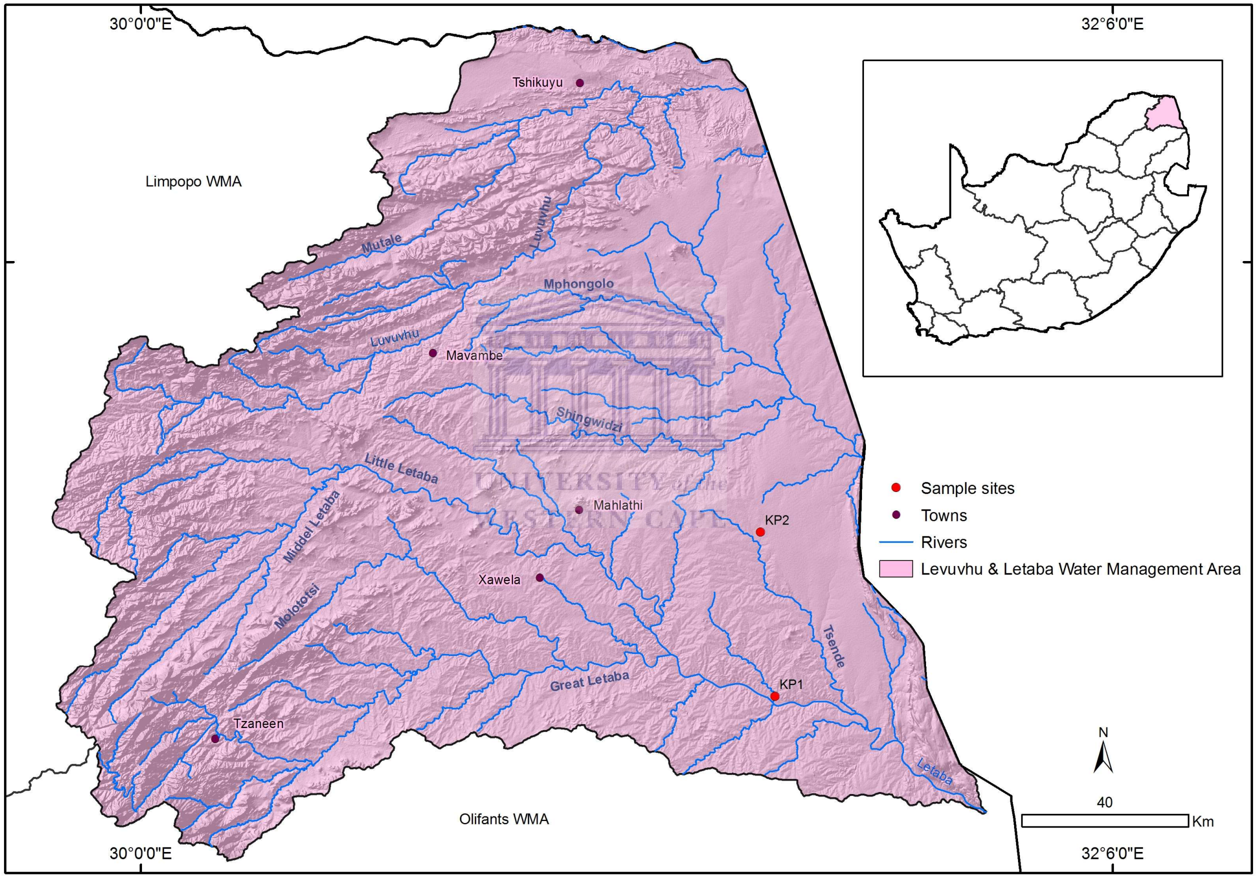
LIST OF APPENDICES

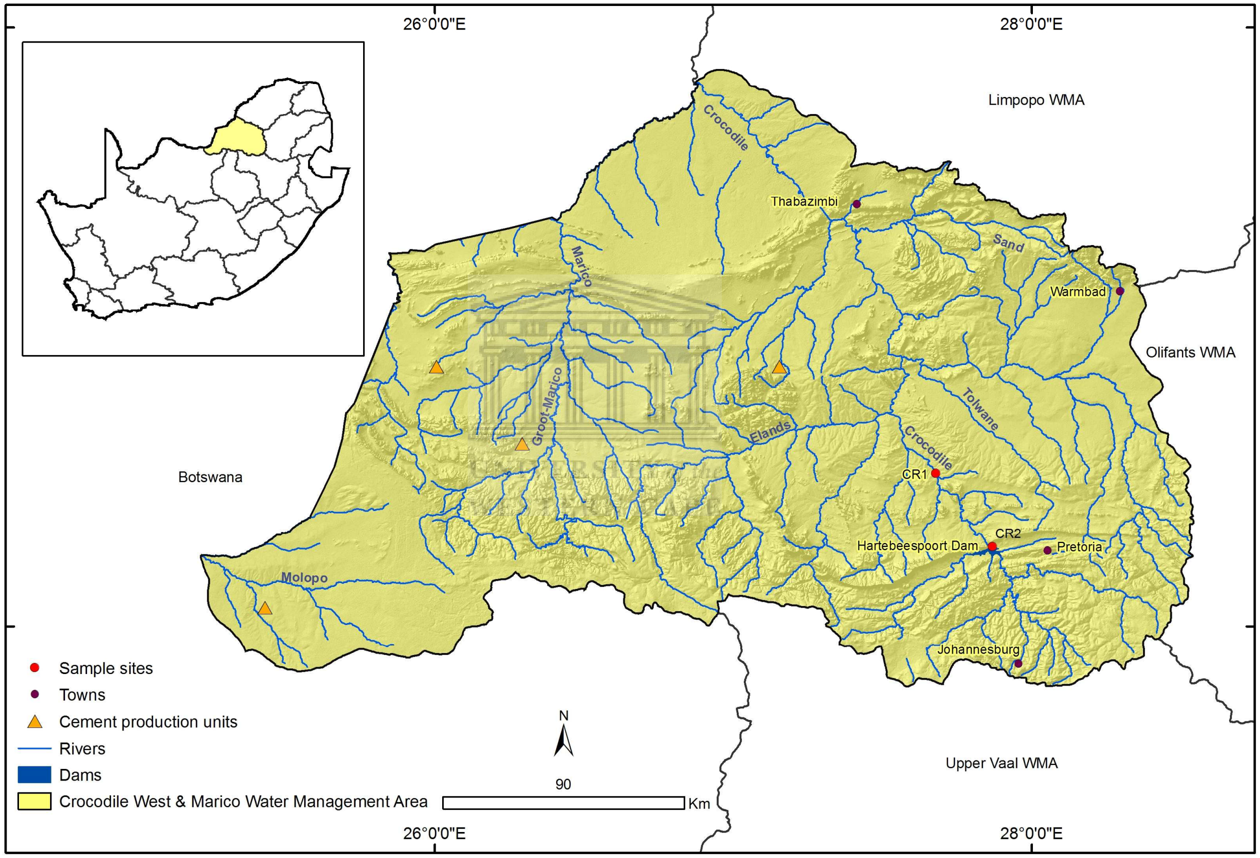
Appendix 1: Sampling sites located in the Limpopo WMA (1)



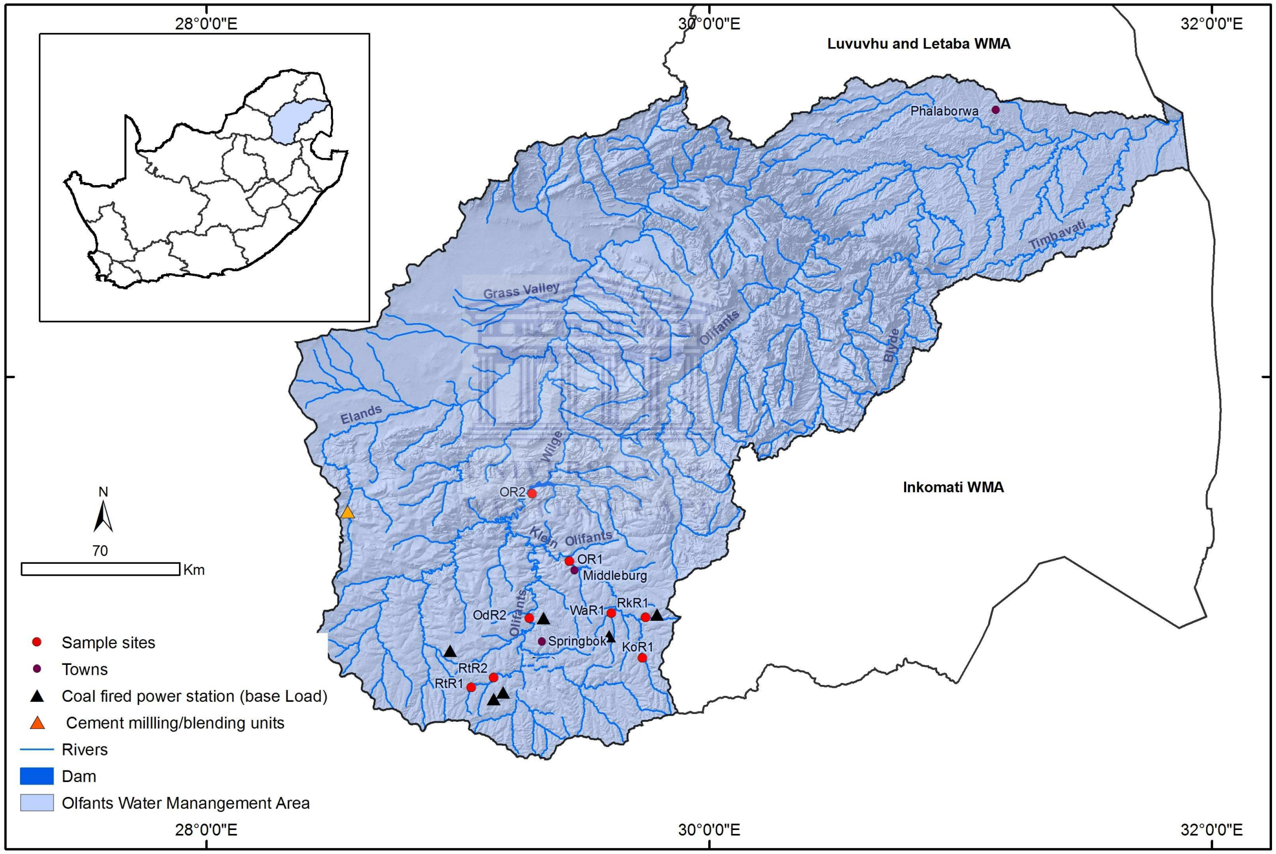
Appendix 2: Sampling sites located in the Levuvhu-Letaba WMA (2)



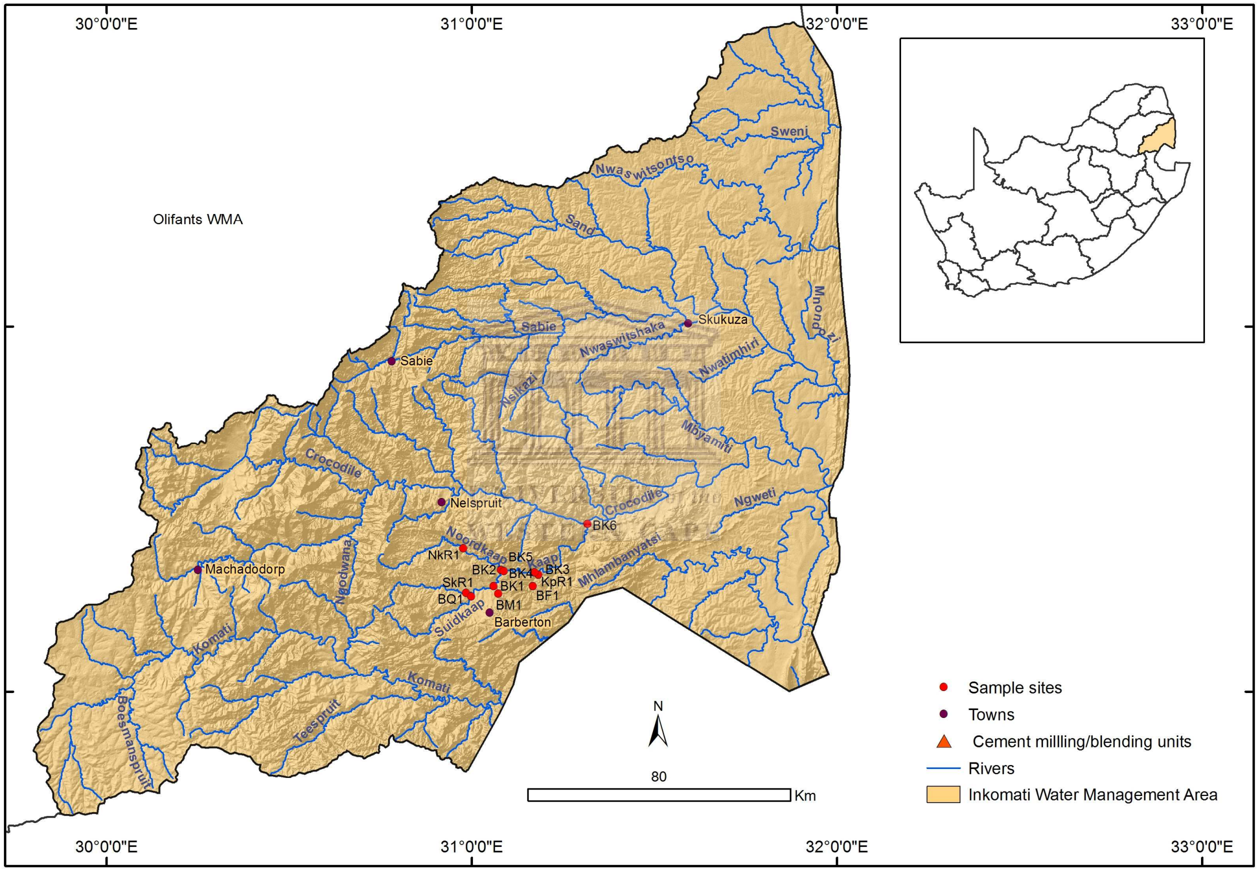
Appendix 3: Sampling sites located in the Crocodile (West) Marico WMA (3)



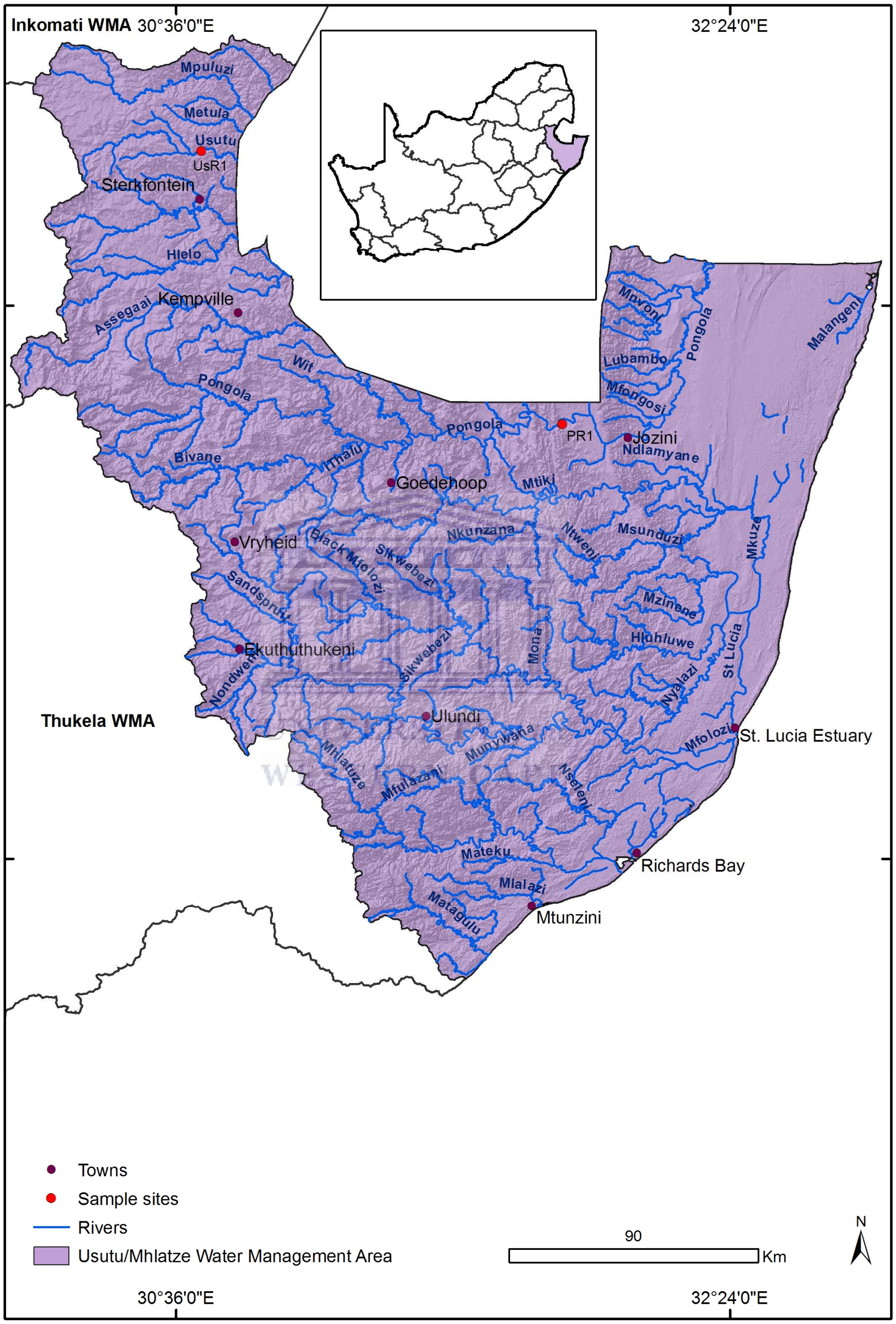
Appendix 4: Sampling sites located in the Olifants WMA (4)



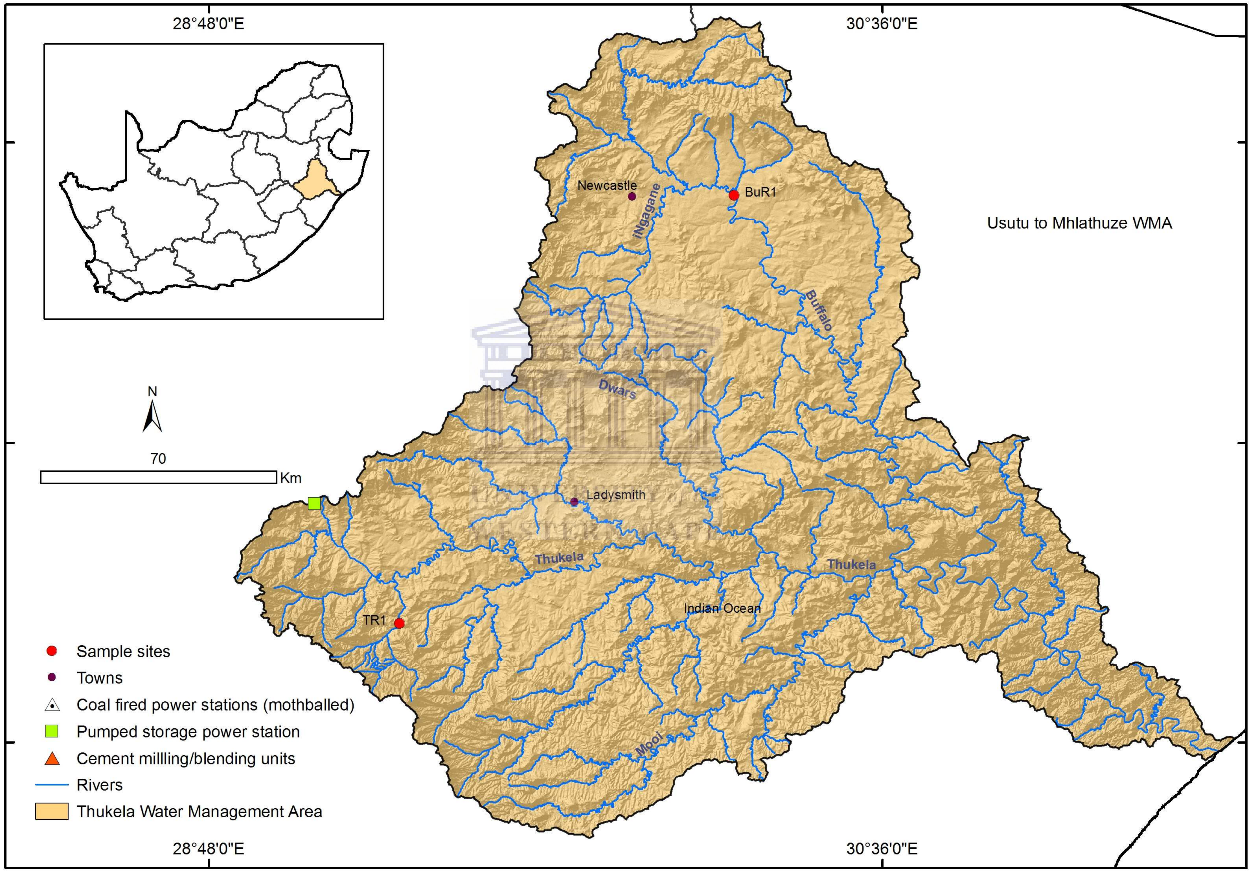
Appendix 5: Sampling sites located in the Inkomati WMA (5)



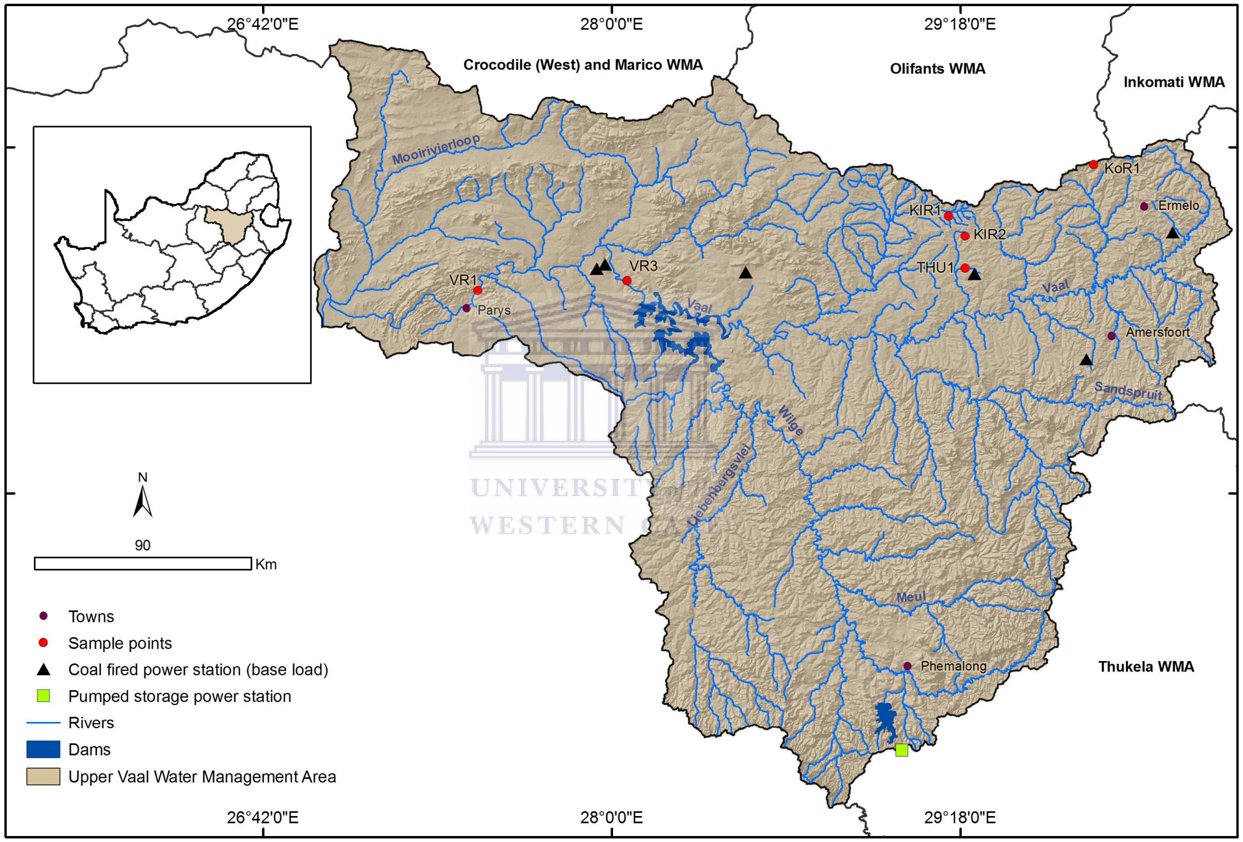
Appendix 6: Sampling sites located in the Usutu-Mhlatuze WMA (6)



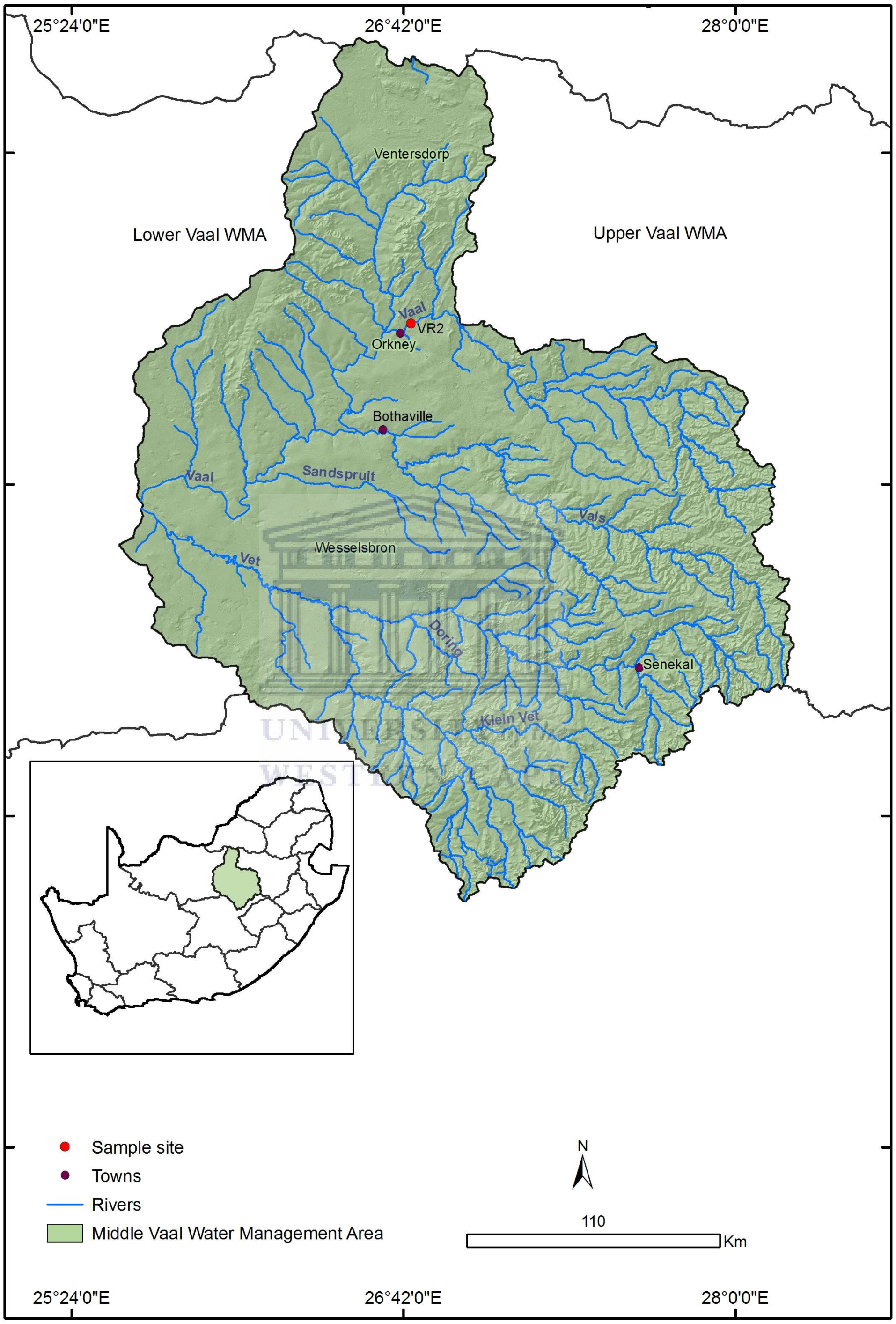
Appendix 7: Sampling sites located in the Thukela WMA (7)



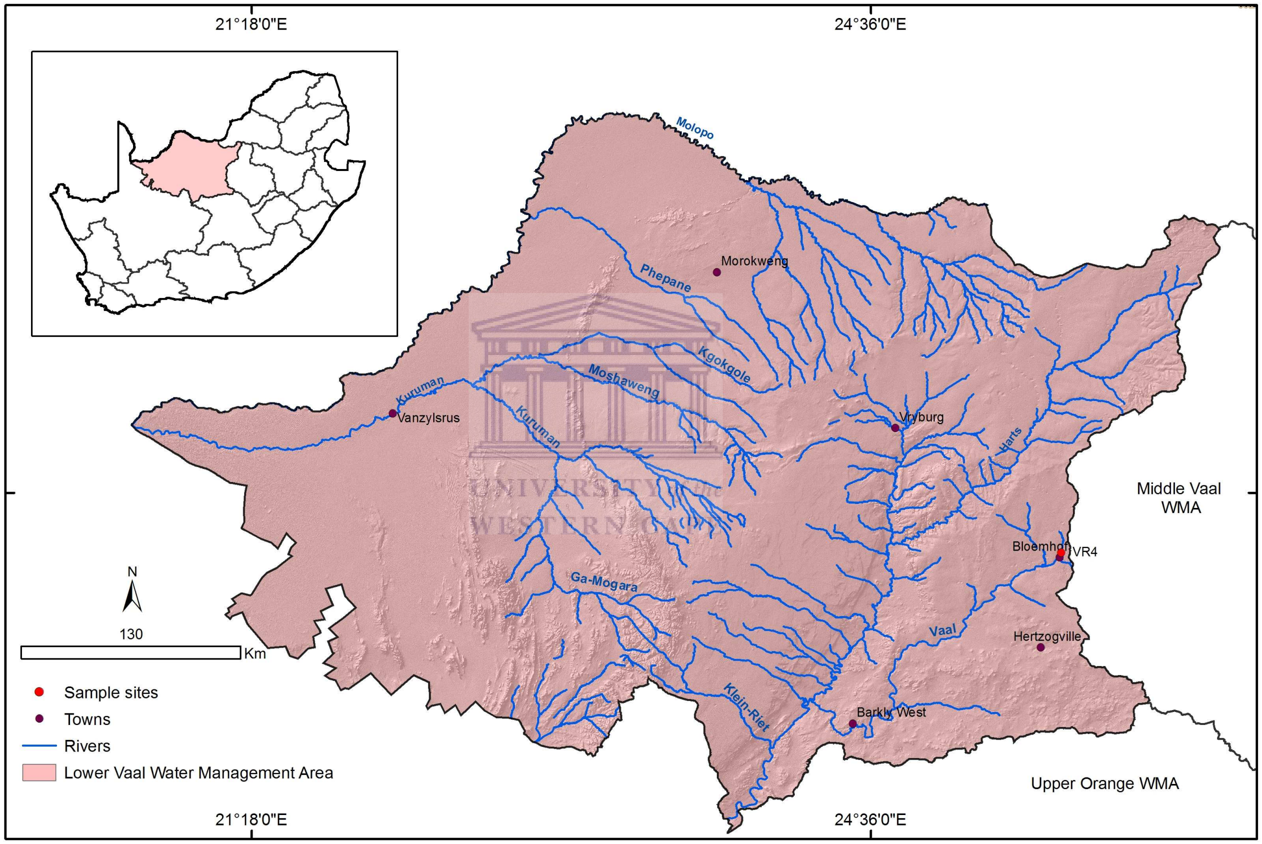
Appendix 8: Sampling sites located in the Upper Vaal WMA (8)



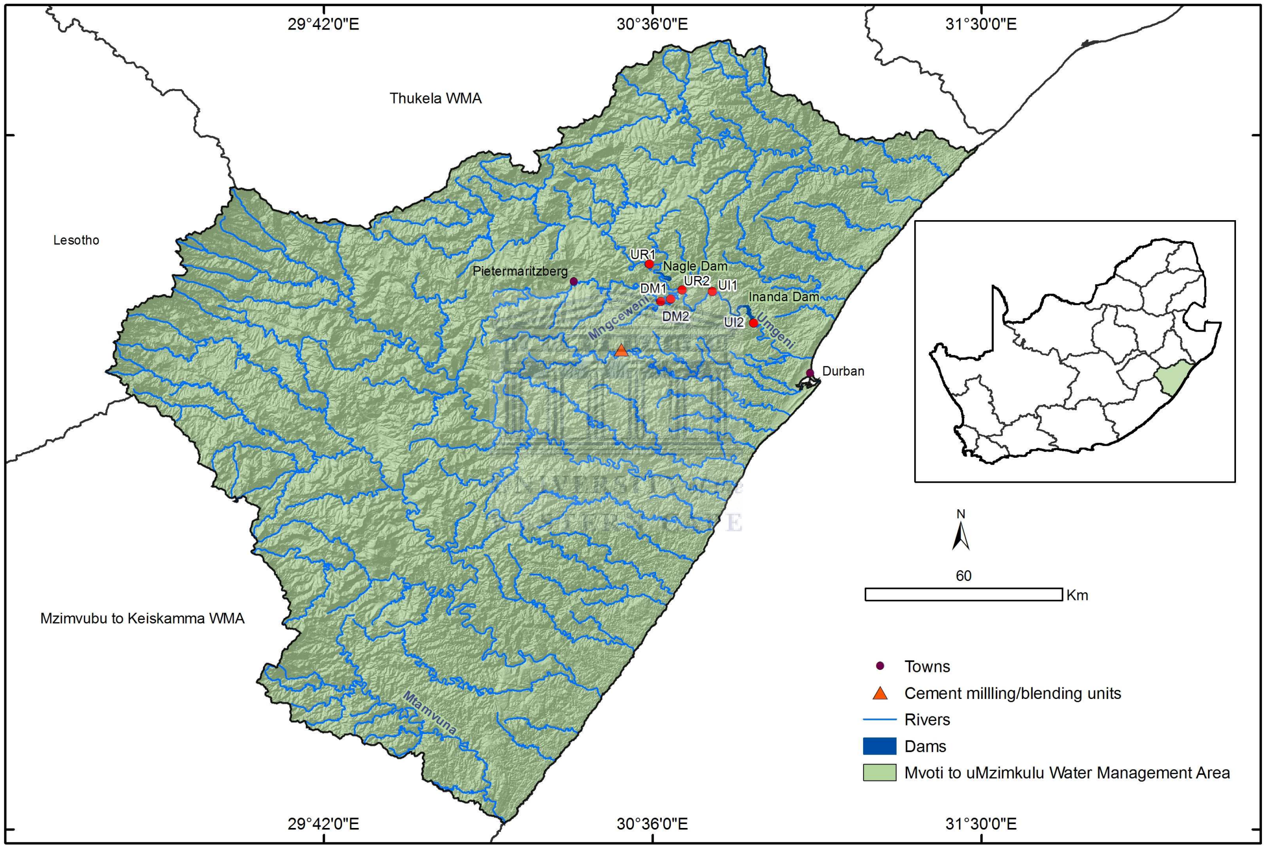
Appendix 9: Sampling sites located in the Middle Vaal WMA (9)



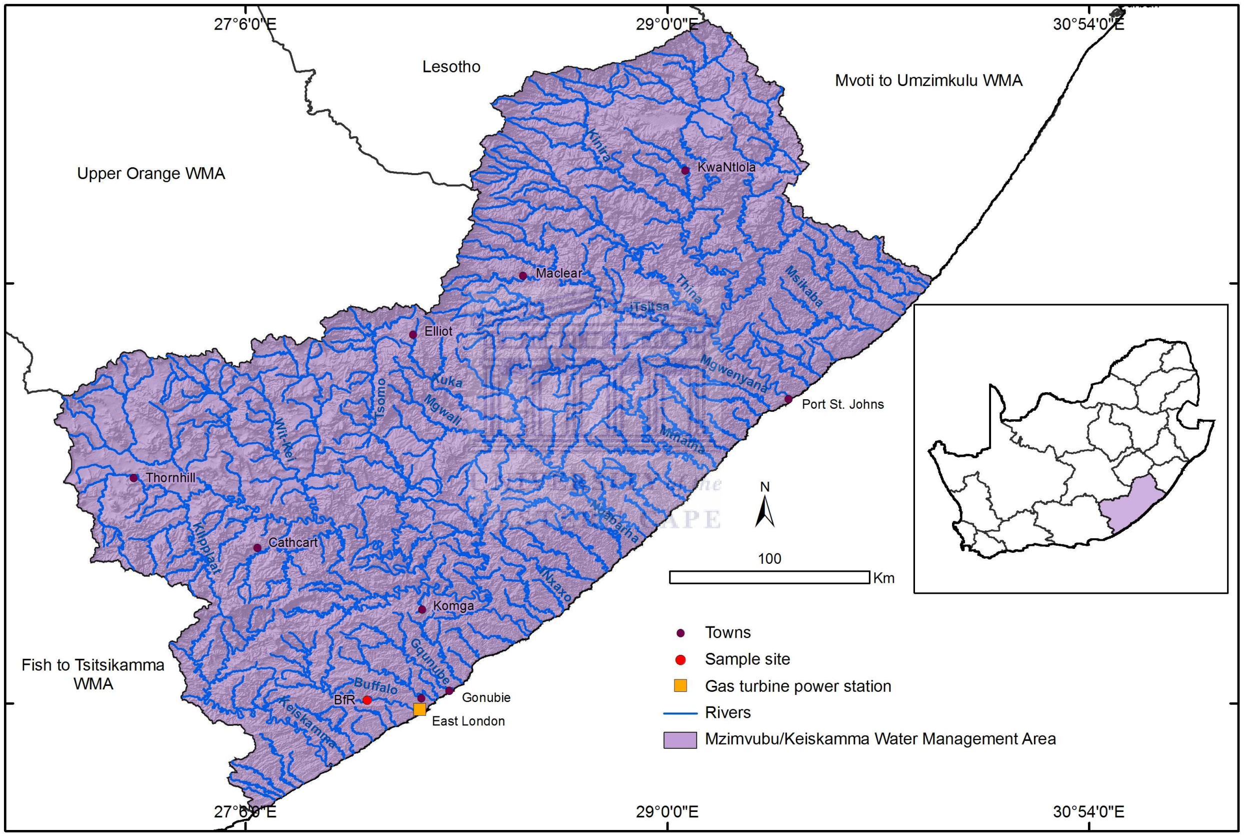
Appendix 10: Sampling sites located in the Lower Vaal WMA (10)



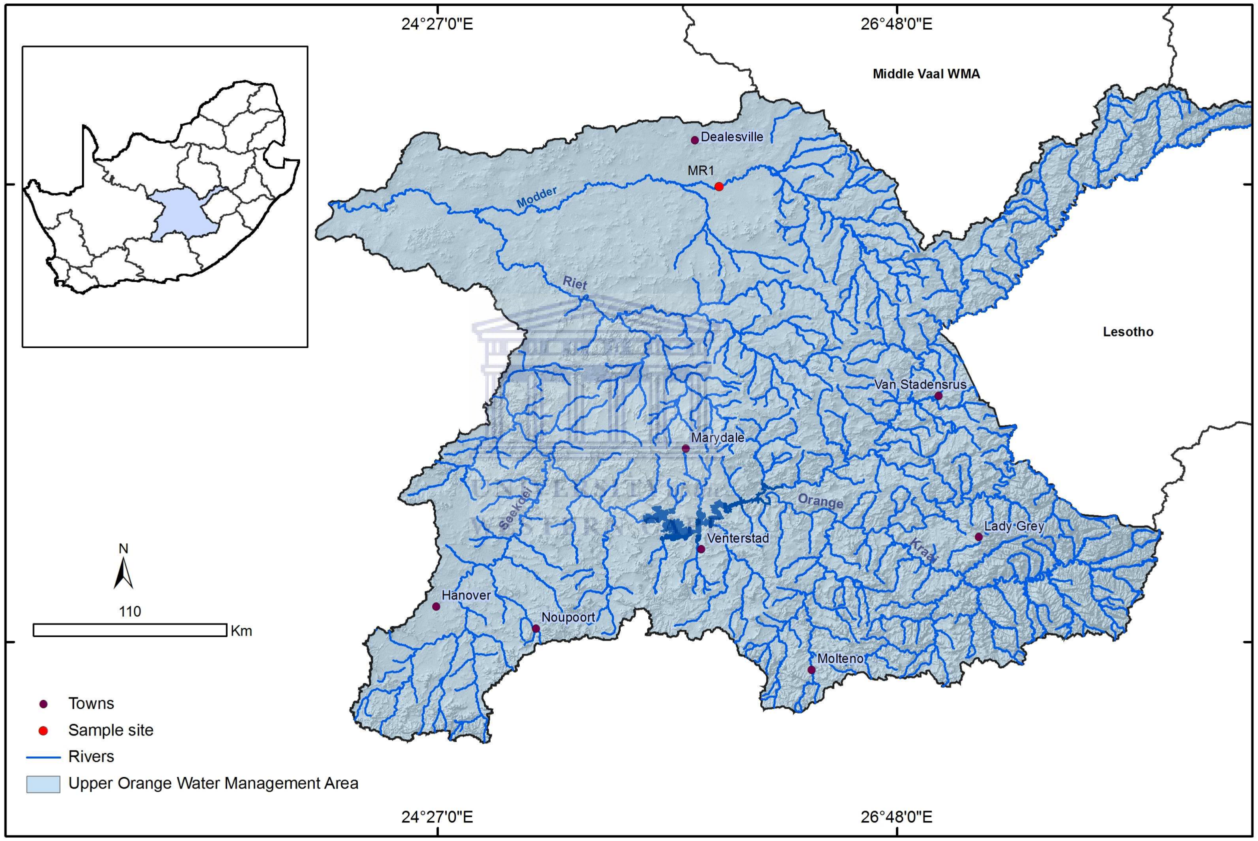
Appendix 11: Sampling sites located in the Mvoti-Umzimkulu WMA (11)



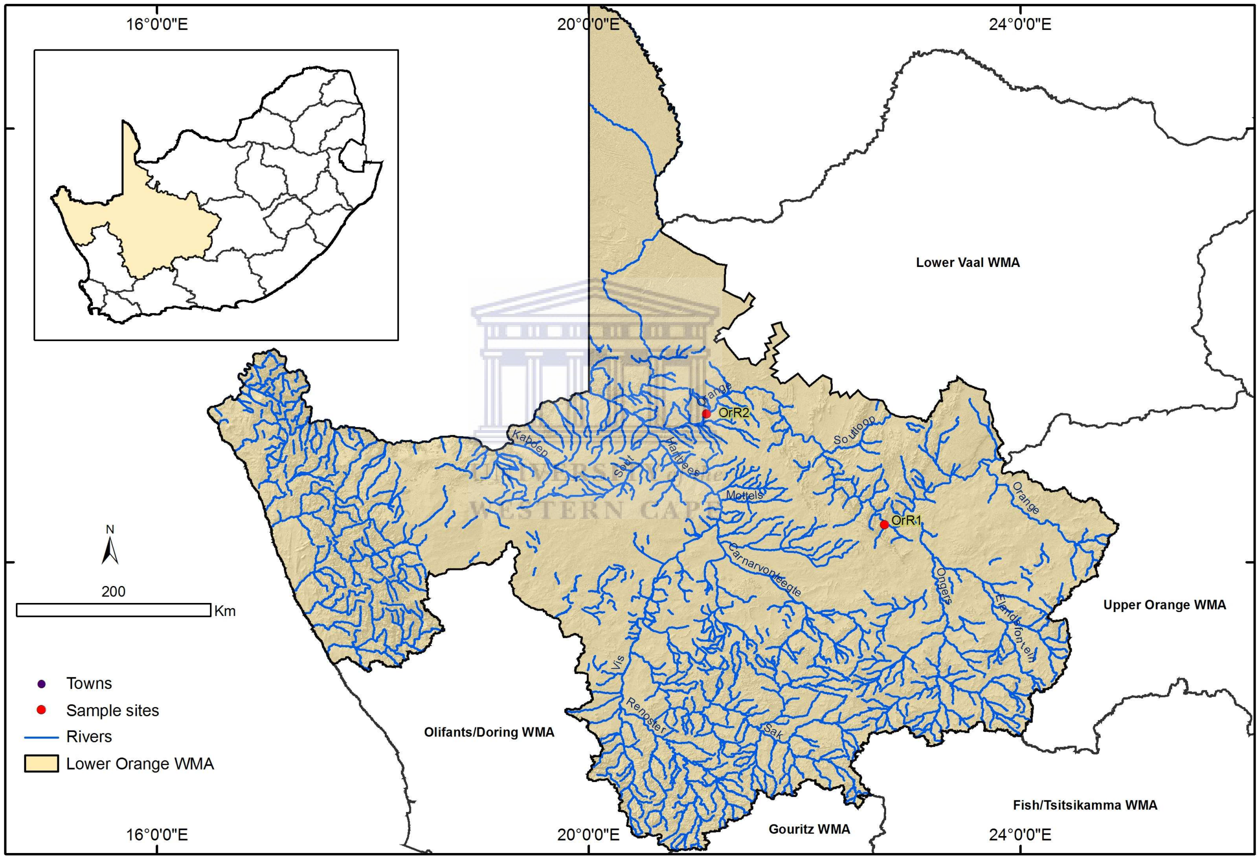
Appendix 12: Sampling sites located in the Mzimvubu- Keiskamma WMA (12)



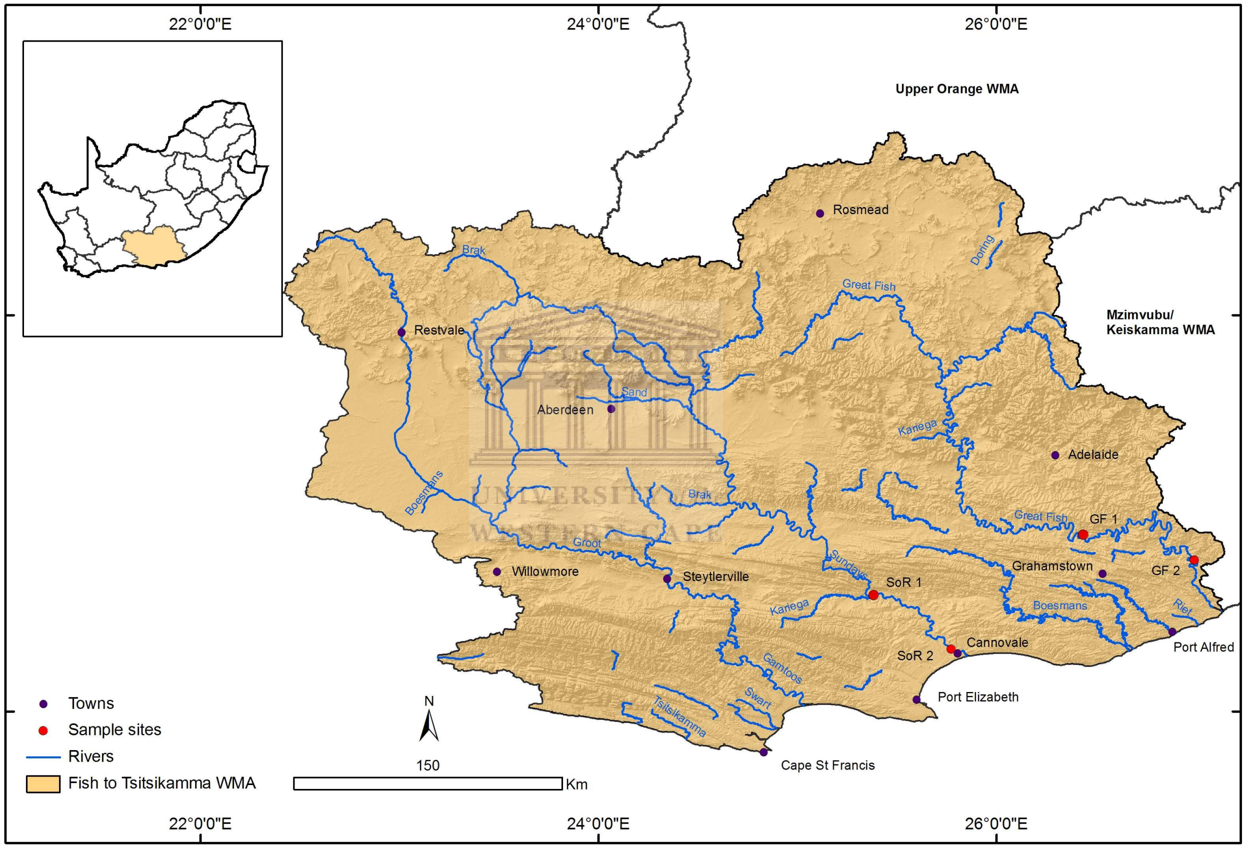
Appendix 13: Sampling sites located in the Upper Orange WMA (13)



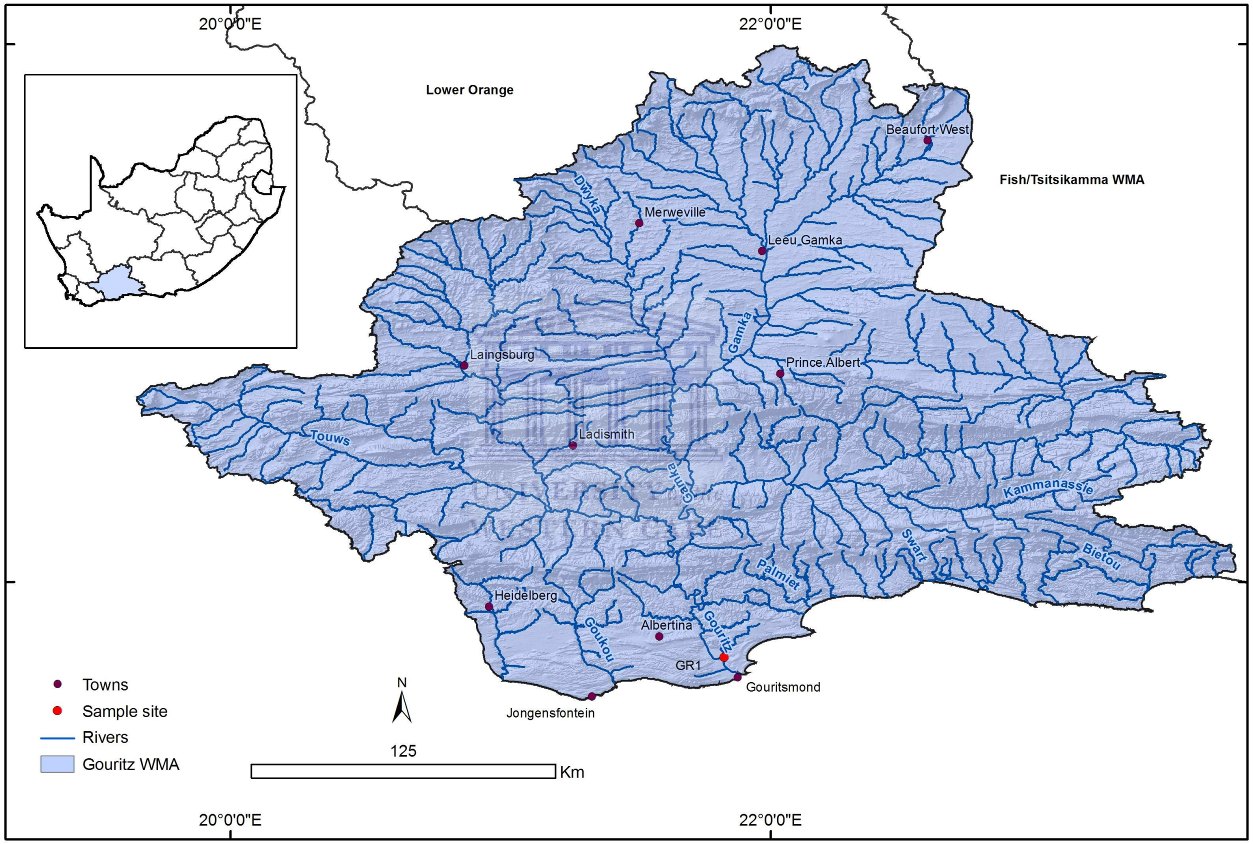
Appendix 14: Sampling sites located in the Lower Orange WMA (14)



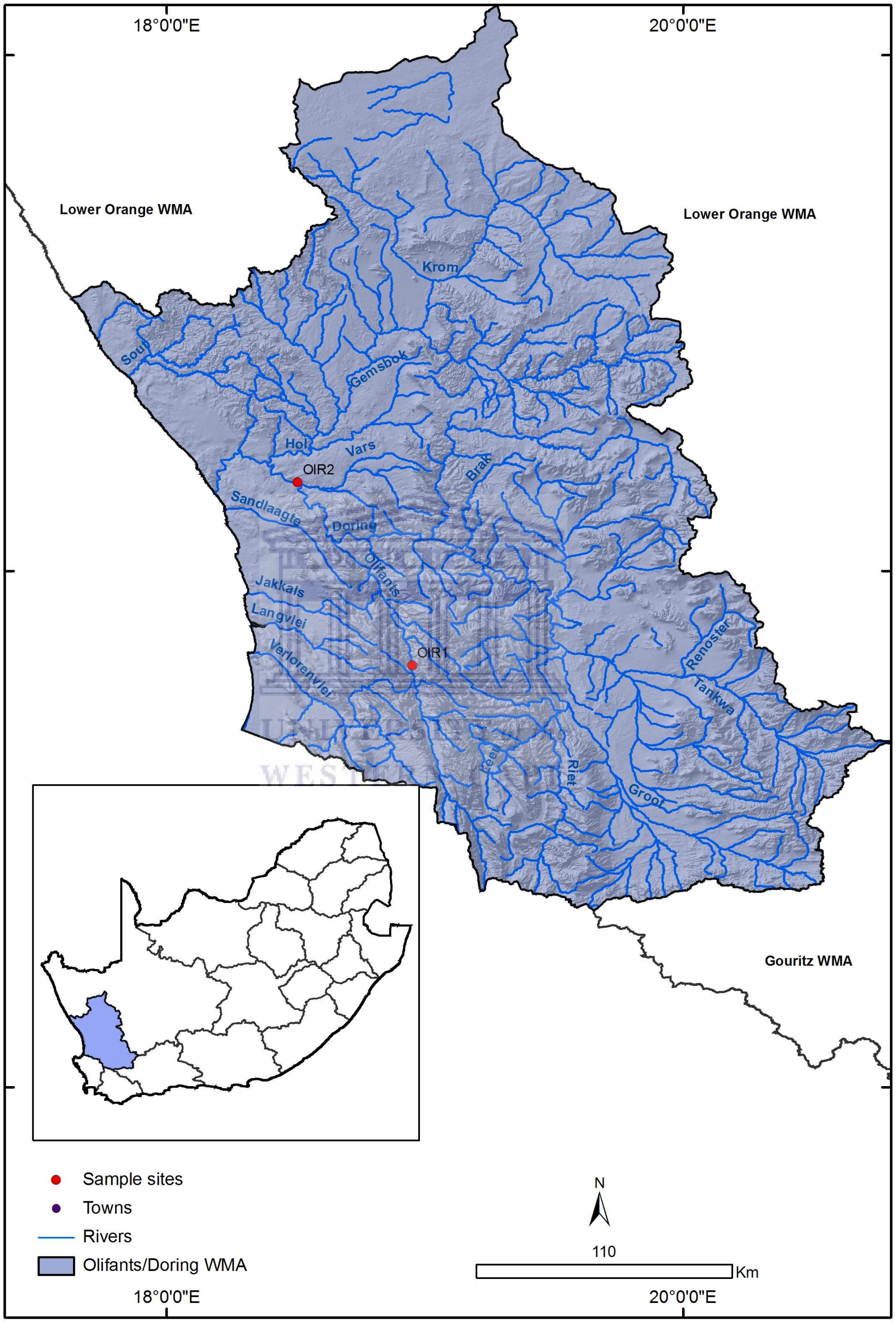
Appendix 15: Sampling sites located in the Fish-Tsitsikamma WMA (15)



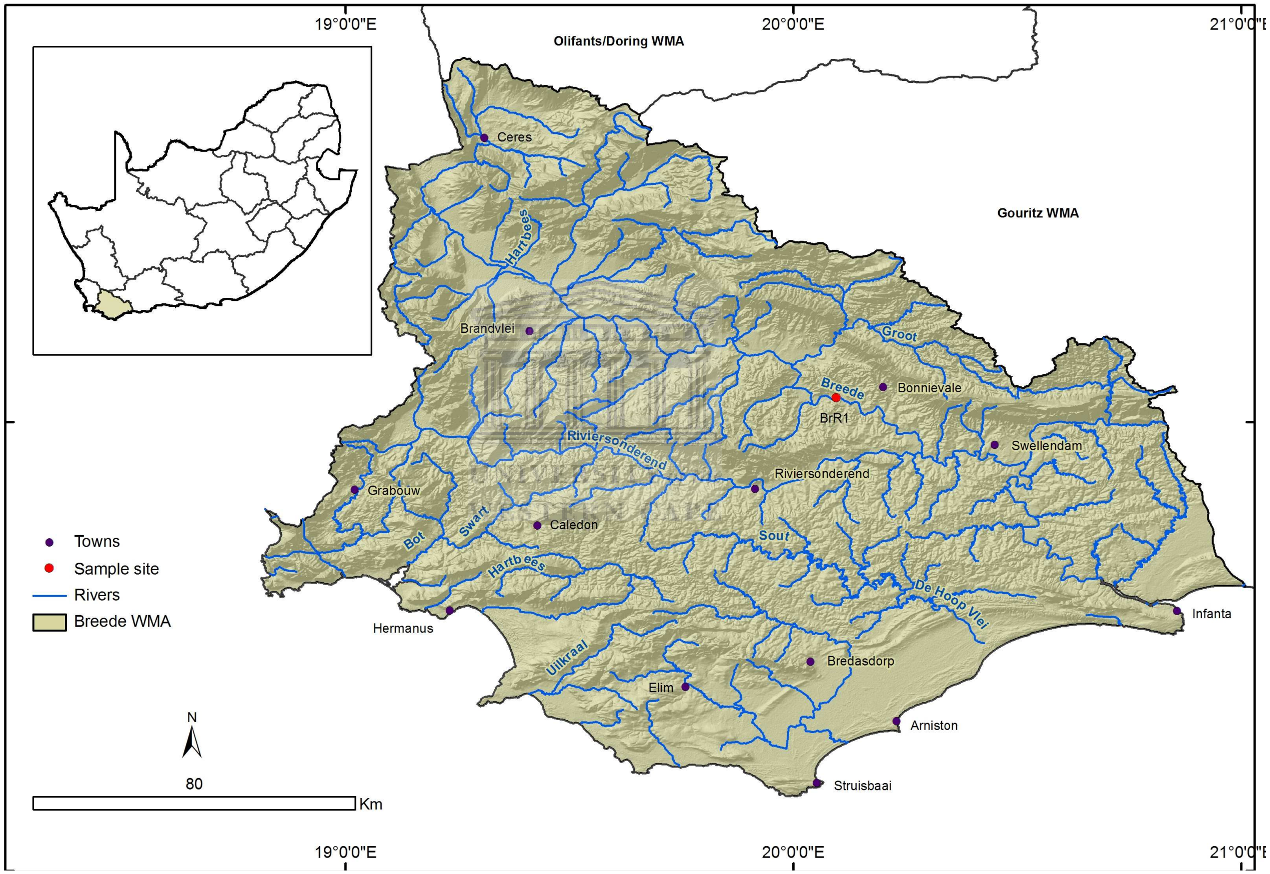
Appendix 16: Sampling sites located in the Gouritz WMA (16)



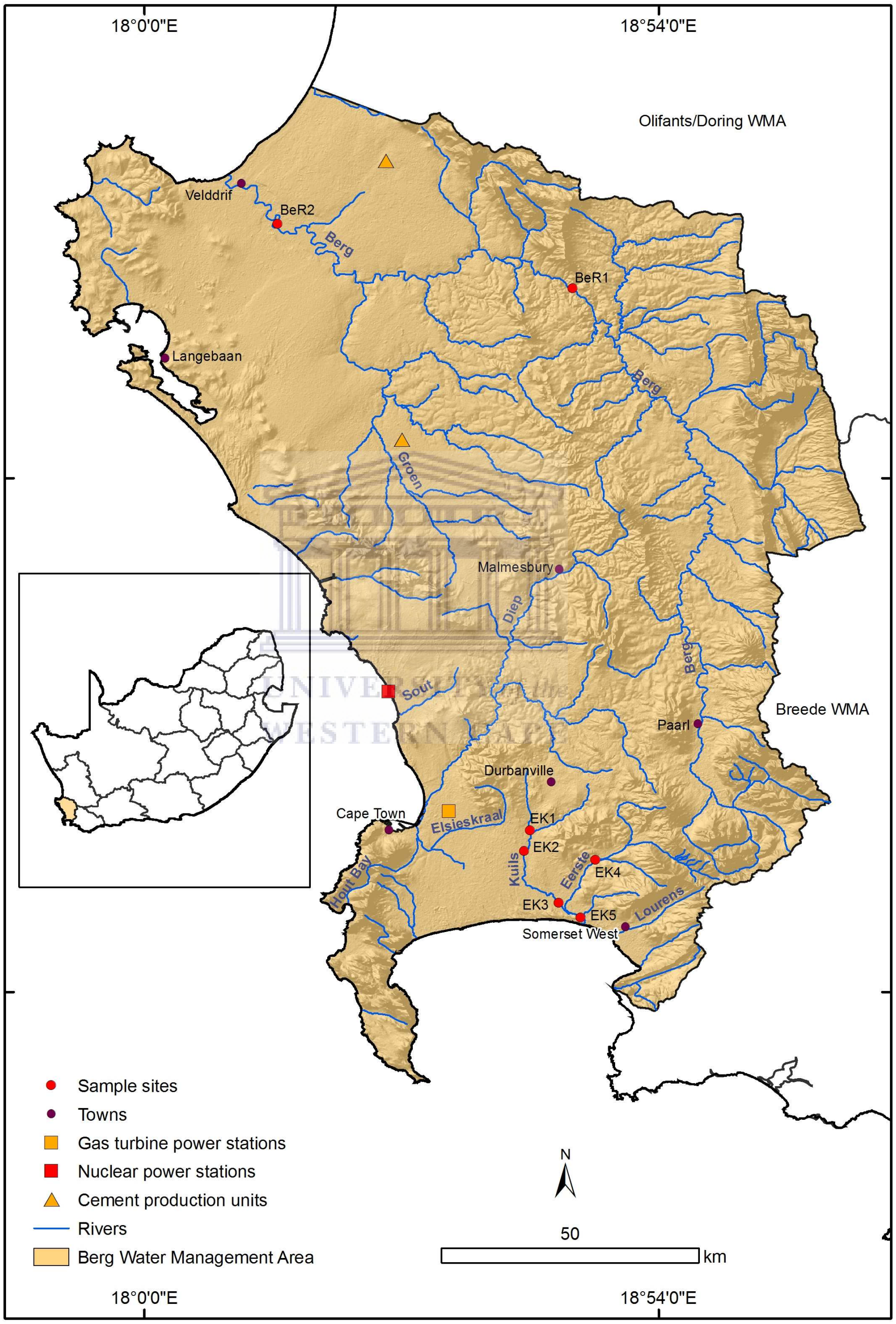
Appendix 17: Sampling sites located in the Olifants/Doorn WMA (17)



Appendix 18: Sampling sites located in the Breede WMA (18)



Appendix 19: Sampling sites located in the Berg WMA (19)

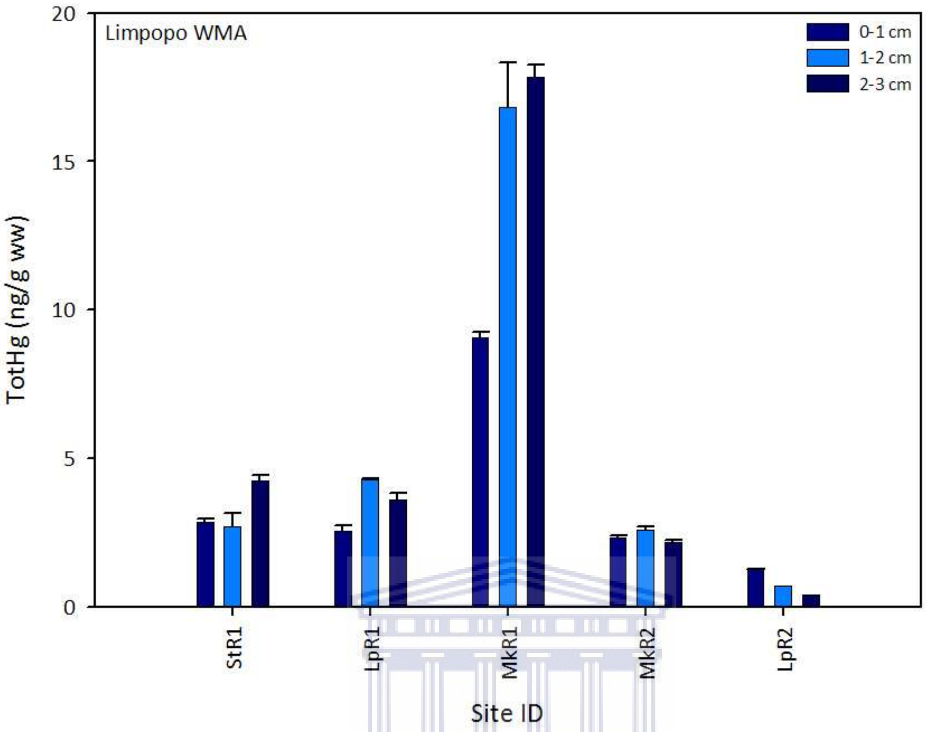


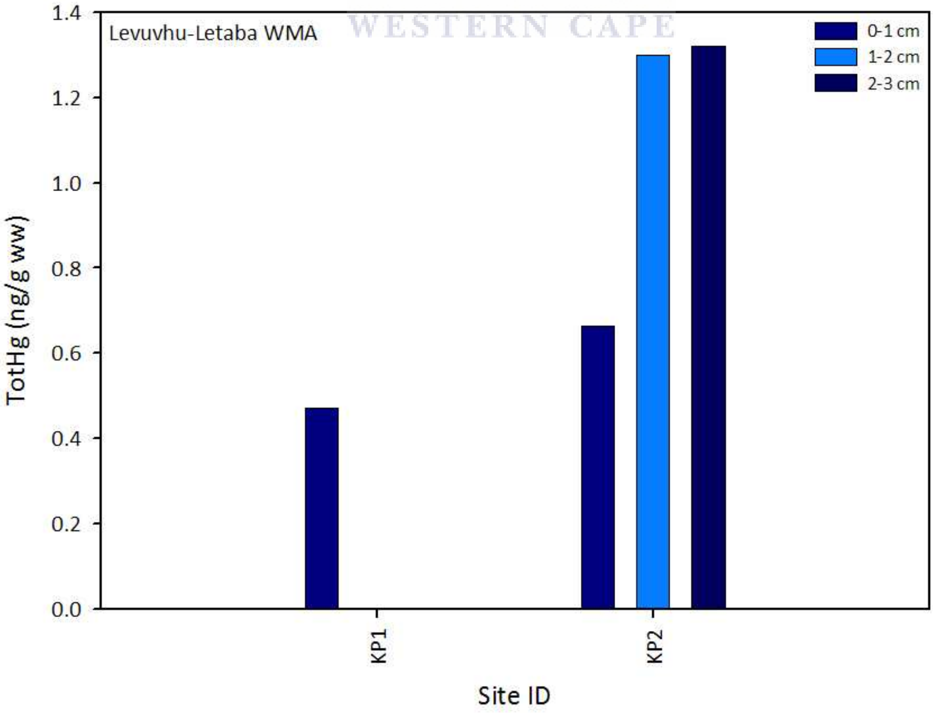
Appendix 20: Chapter 2 - Sampling sites for assessing mercury concentrations in selected water resources of South Africa and their potential anthropogenic mercury sources.

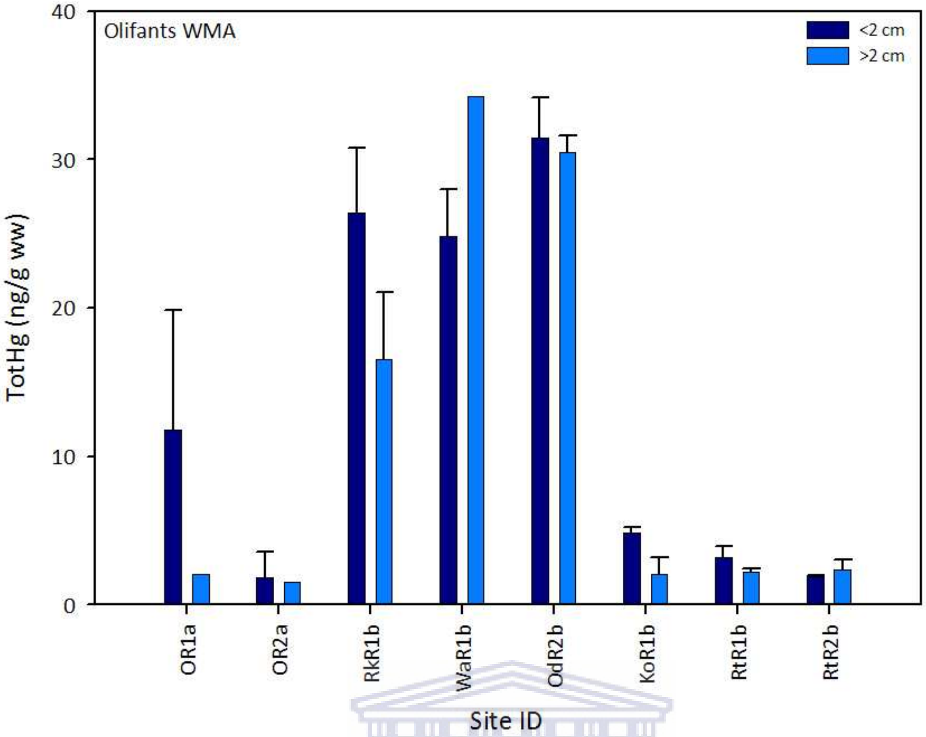
Site ID	Water Resource	Site Description	WMA	Anthropogenic Hg impact	Date(s) Sampled
StR1	Sterkloop River	Upstream of Lefarge (Polokwane)	1. Limpopo	Cement production	July 09
LpR1	Lephalala River	Downstream of Lephalala River	1. Limpopo	Cement production	July 09
MkR1	Mokolo River	Dowstream of Matimba Power	1. Limpopo	Coal-fired power stations	July 09
MkR2	Mokolo River	Upstream of Matimba Power Station	1. Limpopo	Coal-fired power stations	July 09
LpR2	Lephalala River	Upstream of Lephalala River	1. Limpopo	Coal-fired power stations	July 09
KP1	Letabe River	Letabe River	2. Levuvhu-Letaba	Natural/unimpacted	June 07
KP2	Tsende River	Tsende River	2. Levuvhu-Letaba	Natural/unimpacted	June 07
CR1	Crocodile River	At Roosoord Campsite	3. Crocodile (West) Marico	Cement production	June 07
CR2	Crocodile River	Hartebeespoort Dam	3. Crocodile (West) Marico	Cement production	June 07
OR1	Olifants River	At Middelburg	4. Olifants	Coal-fired power stations	June 07
OR2	Olifants River	At Loskop Dam	4. Olifants	Coal-fired power stations	June 07
RkR1	Rietkuil River	Downstream of Arnot Power Station	4. Olifants	Coal-fired power stations	Nov 07
WaR1	Woes-Alleen River	Upstream of Hendrina Power Station	4. Olifants	Coal-fired power stations	Nov 07
KoR1	Klein Olifants River	Downstream of Hendrina Power	4. Olifants	Coal-fired power stations	Nov 07
OdR2	Olifants River	Downstream of Duvha Power Station	4. Olifants	Coal-fired power stations	Nov 07
RtR1	Riet River	Upstream of Kriel Colliery	4. Olifants	Coal-fired power stations	Nov 07
RtR2	Riet River	Downstream of Kriel Colliery	4. Olifants	Coal-fired power stations	Nov 07
BnK1	Noordkaap River	At nature reserve	5. Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BsK1	Suid Kaap River	At bridge on R38	5. Inkomati	Artisanal gold mining	Nov 07(b); July 08(c); Oct 08(d)
KpR1	Kaap River	Kaap River	5. Inkomati	Artisanal gold mining	Nov 07(b)
BK1	Kaap River	Downstream of Barberton	5. Inkomati	Artisanal gold mining	July 08(c)
BK2	Kaap River	At New Consort Mine	5. Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK3	Kaap River	At Eureka	5. Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK4	Kaap River	Downstream of New Consort Mine	5. Inkomati	Artisanal gold mining	July 08(c)
BK5	Kaap River	At Scotia Talc Mine	5. Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BK6	Kaap River	At R38 and N4 crossing (Boulders	5. Inkomati	Artisanal gold mining	July 08(c)
BQ1	Queens River	At R38	5. Inkomati	Artisanal gold mining	July 08(c); Oct 08(d)
BM1	Kaap River	At Olifants Creek (at Barberton Mine	5. Inkomati	Artisanal gold mining	July 08(c)
BF1	Kaap River	At Figtree Creek near Sheba Mine	5. Inkomati	Artisanal gold mining	July 08(c)
PR1	Phongola River	Phongola River	6. Usutu-Mhlatuze	Cement milling / blending	May 09

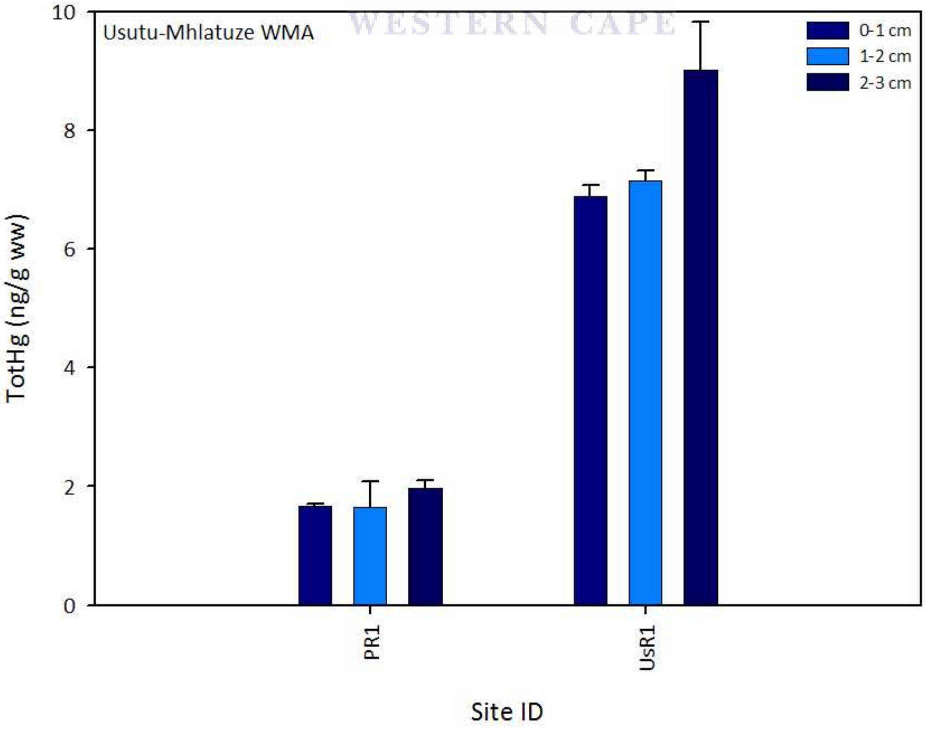
Site ID	Water Resource	Site Description	WMA	Anthropogenic Hg	Date(s) Sampled
UsR1	Usutu River	Usutu River	6. Usutu-Mhlatuze	Cement milling / blending	May 09
TR1	Tugela River	Tugela River	7. Thukela	Cement milling	June 07
BuR1	Buffalo River	At Newcastle	7. Thukela	Cement milling	June 07
VR1	Vaal River	At Parys	8. Upper Vaal	Coal-fired power stations	June 07
KlR1	Klip River	Klip River	8. Upper Vaal	Coal-fired power stations	Nov 07
KlR2	Klip River	Upstream of Sasol	8. Upper Vaal	Coal-fired power stations	Nov 07
ThU1	Vaal River	At Thutuka Power Station	8. Upper Vaal	Coal-fired power stations	Nov 07
VR3	Vaal River	Downstream of Lethabo Power	8. Upper Vaal	Coal-fired power stations	Nov 07
VR2	Vaal River	At River Dew Pub	9. Middle Vaal	Coal-fired power stations	June 07
VR4	Vaal River	At Bloemhof Dam	10. Lower Vaal	Cement production	April 09
UR1	Umgeni River	Upstream of Nagle Dam	11. Mvoti-Umzimkulu	Previously Hg contaminated area	June 07(a); Jul 08(b); Dec 08(c)
UR2	Mngceweni River	Downstream of Nagle Dam	11. Mvoti-Umzimkulu	Previously Hg contaminated area	Jul 08(b); Dec 08(c)
DM1	Mngceweni River	At bridge	11. Mvoti-Umzimkulu	Previously Hg contaminated area	Jul 08(b)
DM2	Mngceweni River	Mngceweni River	11. Mvoti-Umzimkulu	Previously Hg contaminated area	Jul 08(b)
UI1	Umgeni River	Upstream of Inanda Dam	11. Mvoti-Umzimkulu	Previously Hg contaminated area	Jul 08(b); Dec 08(c)
UI2	Umgeni River	Downstream of Inanda Dam	11. Mvoti-Umzimkulu	Previously Hg contaminated area	Jul 08(b); Dec 08(c)
BfR1	Buffalo River	At fish bridge	12. Mzimvubu-Keiskamma	Urban/industrial effluent	May 09
MR1	Modder River	At Krugersdrift Dam	13. Upper Orange	Agricultural/urban effluent	April 09
OrR1	Orange River	At Prieska	14. Lower Orange	Agricultural/urban effluent	Mar 09
OrR2	Orange River	At Kanoneiland	14. Lower Orange	Agricultural/urban effluent	Mar 09
GF1	Great Fish River	Upstream of the Great Fish River	15. Fish-Tsitsikamma	Agricultural effluent	Dec 08
GF2	Great Fish River	Downstream of the Great Fish River	15. Fish-Tsitsikamma	Agricultural effluent	Dec 08
SoR2	Sondays River	Downstream of the Sondays River	15. Fish-Tsitsikamma	Agricultural effluent	Dec 08
SoR1	Sondays River	Upstream of the Sondays River	15. Fish-Tsitsikamma	Agricultural effluent	Dec 08
GoR1	Gouritz River	Gouritzmond	16. Gourtiz	Agricultural effluent	Mar 09
OlR1	Olifants River	Upstream of Clanwilliam Dam	17. Olifants/Doorn	Agricultural effluent	Mar 09
OlR2	Olifants River	At Vredendal	17. Olifants/Doorn	Agricultural effluent	Mar 09
BrR1	Breede River	Breede River	18. Breede	Agricultural effluent	Mar 09
EK1	Kuils River	At Hospital	19. Berg	Wastewater treatment works	June 07
EK2	Kuils River	Westbank	19. Berg	Wastewater treatment works	Aug 08
EK3	Eerste River	At Baden Powell	19. Berg	Wastewater treatment works	Aug 08
EK4	Eerste River	At Spier	19. Berg	Wastewater treatment works	Aug 08
EK5	Eerste River	At Macassar	19. Berg	Wastewater treatment works	Aug 08

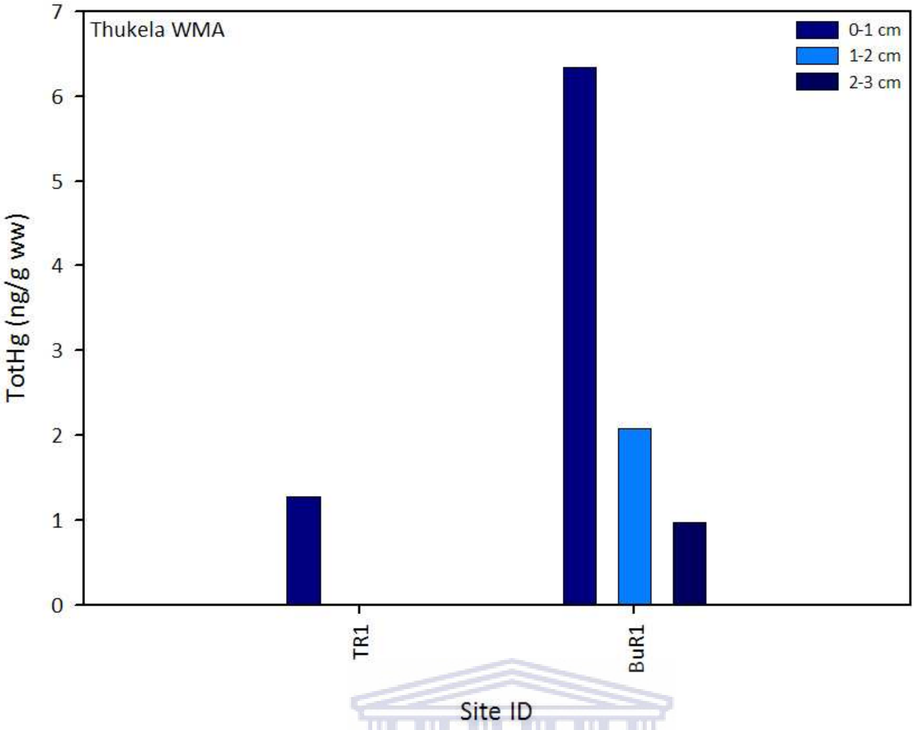
Appendix 21: Chapter 2 - Total mercury (TotHg) concentrations in surface sediment

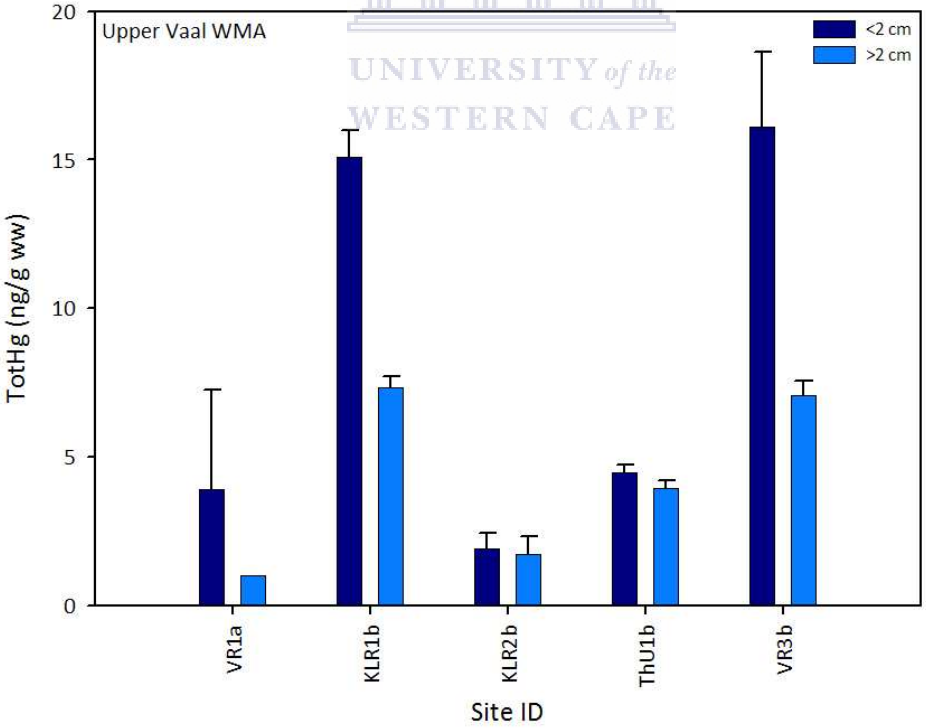


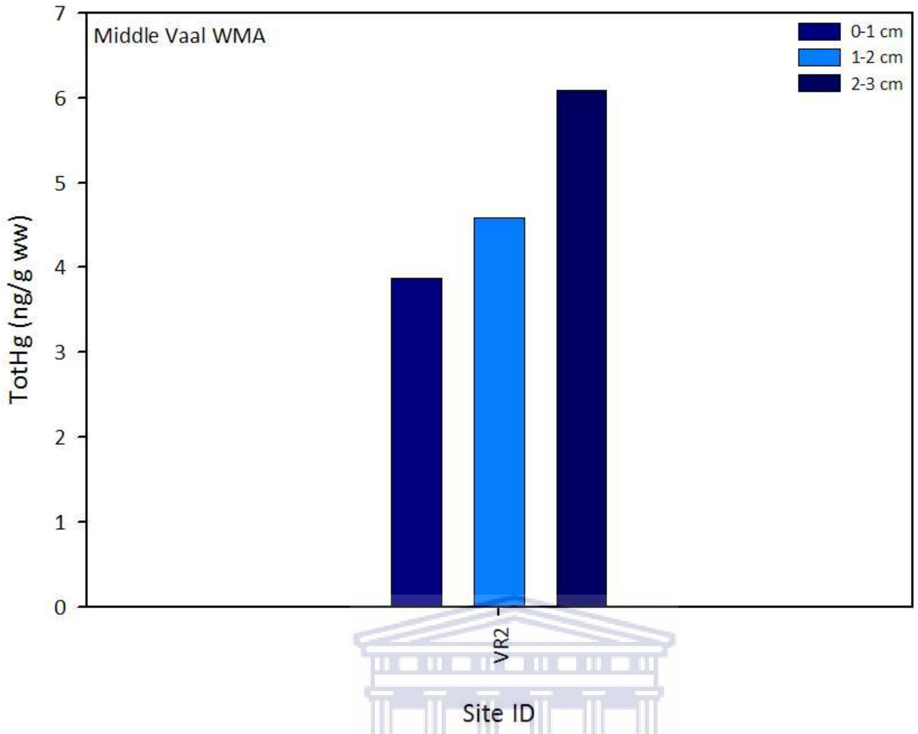


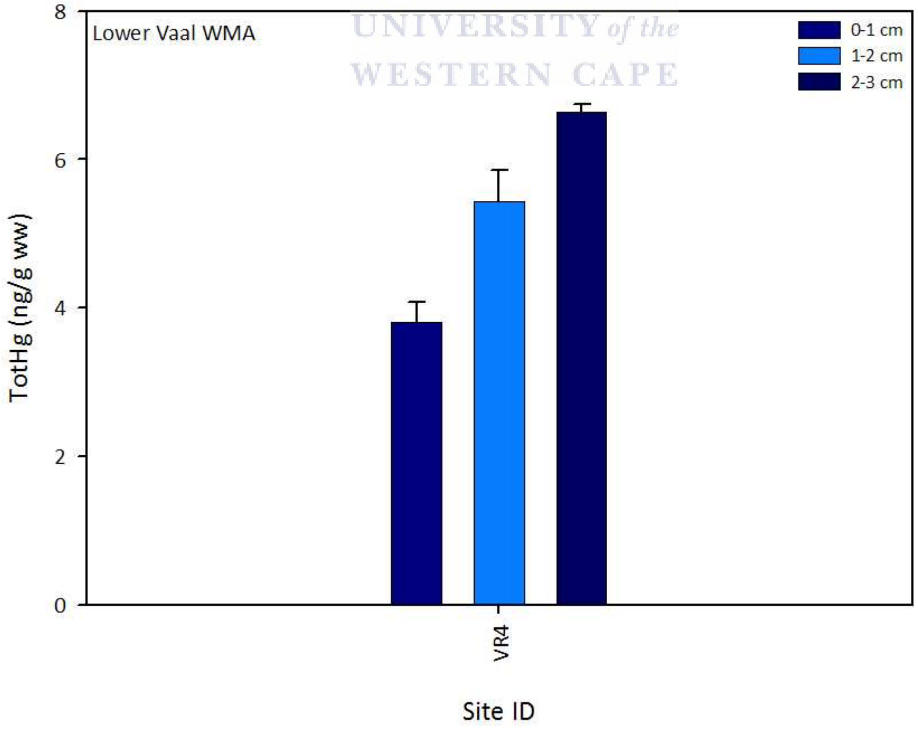

Olifants WMA
<2 cm
>2 cm
TotHg (ng/g ww)
0
10
20
30
40
OR1a
OR2a
RkR1b
WaR1b
OdR2b
KoR1b
RtR1b
RtR2b
Site ID

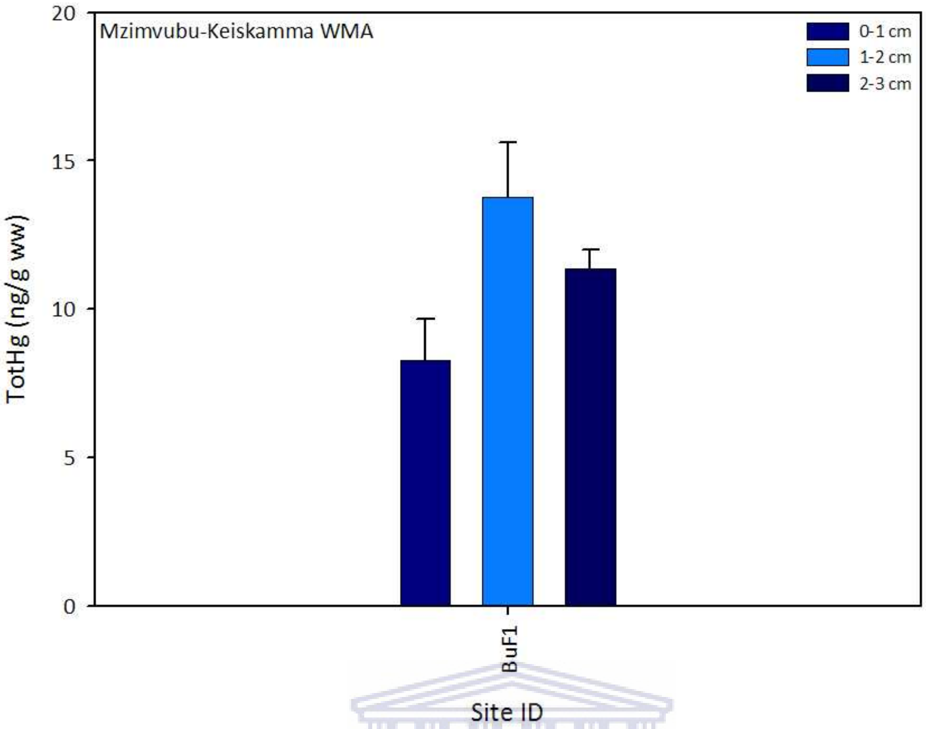

Usutu-Mhlatuze WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
2
4
6
8
10
PR1
UsR1
Site ID

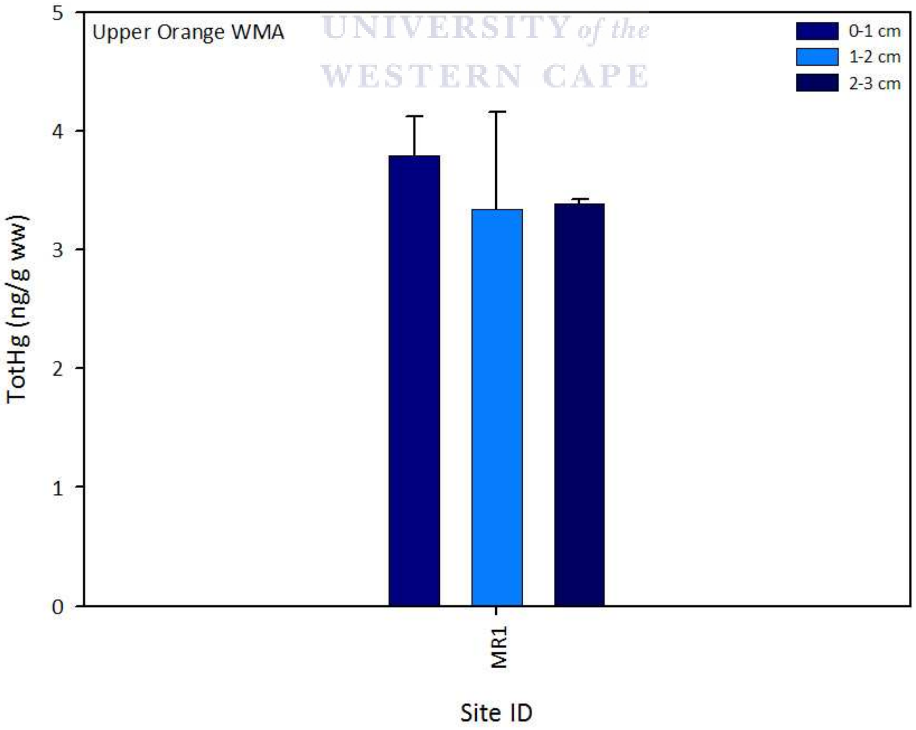

Thukela WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
1
2
3
4
5
6
7
TR1
BuR1
Site ID

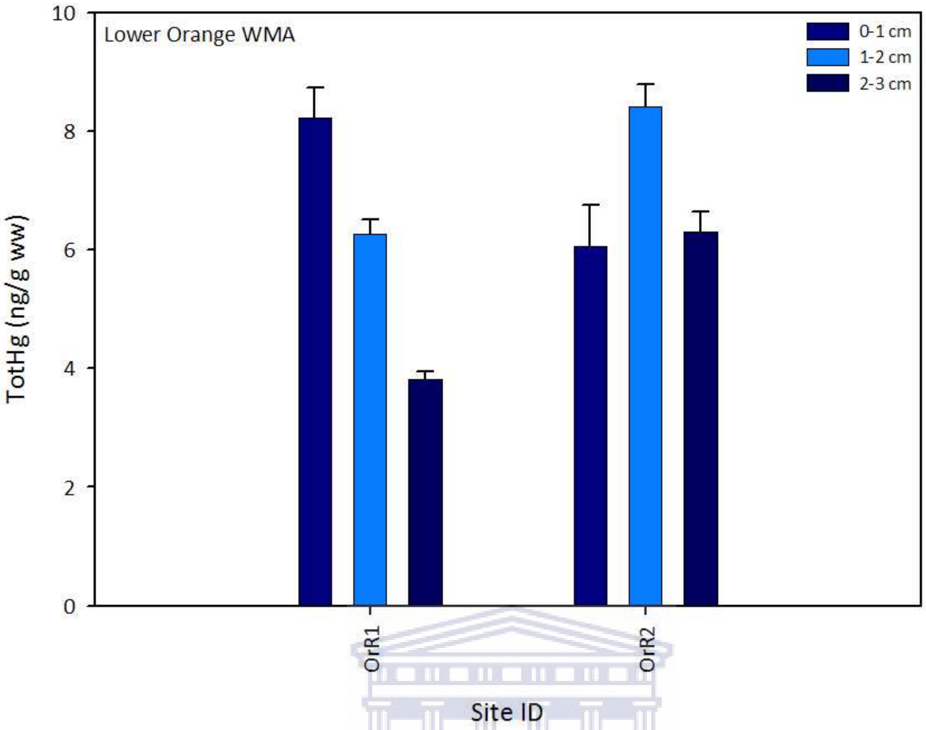

Upper Vaal WMA
<2 cm
>2 cm
TotHg (ng/g ww)
0
5
10
15
20
VR1a
KLR1b
KLR2b
ThU1b
VR3b
Site ID

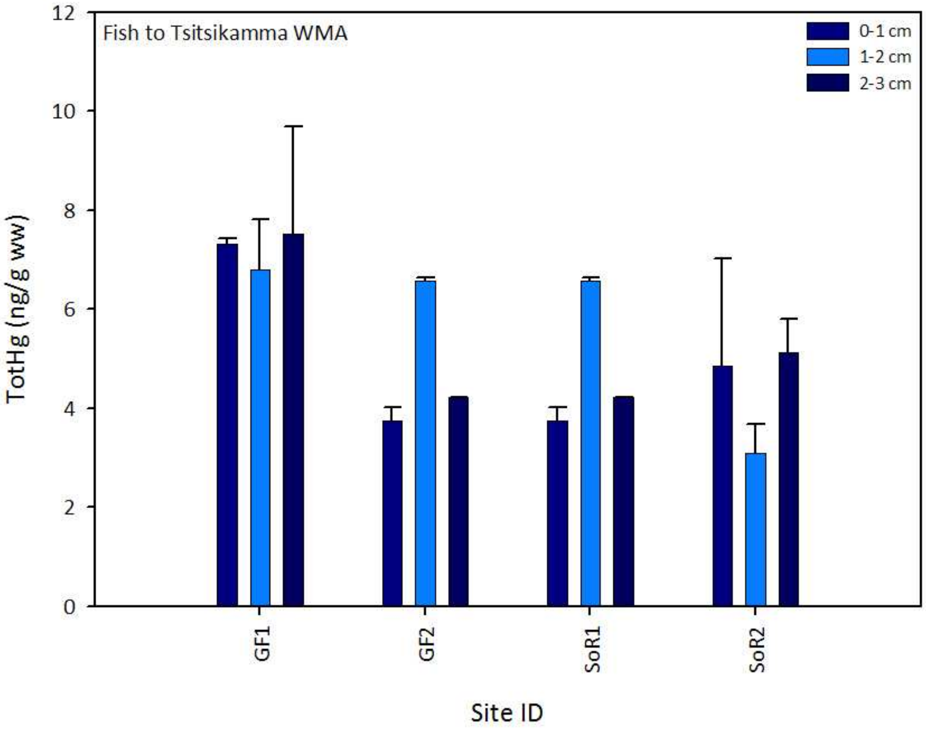

Middle Vaal WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
1
2
3
4
5
6
7
VR2
Site ID

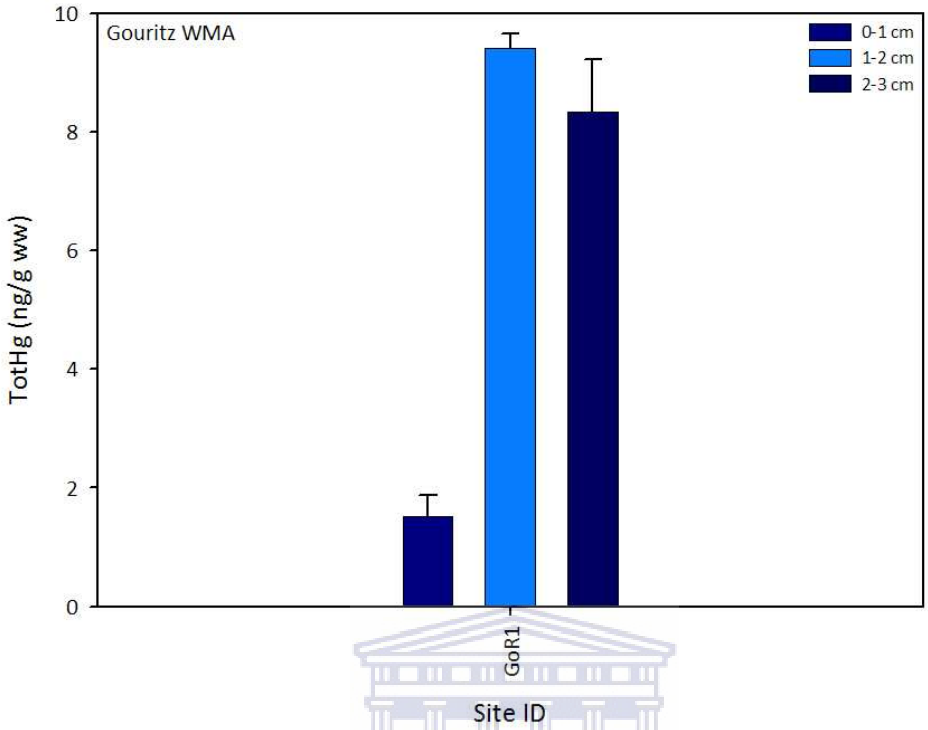

Lower Vaal WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
2
4
6
8
VR4
Site ID

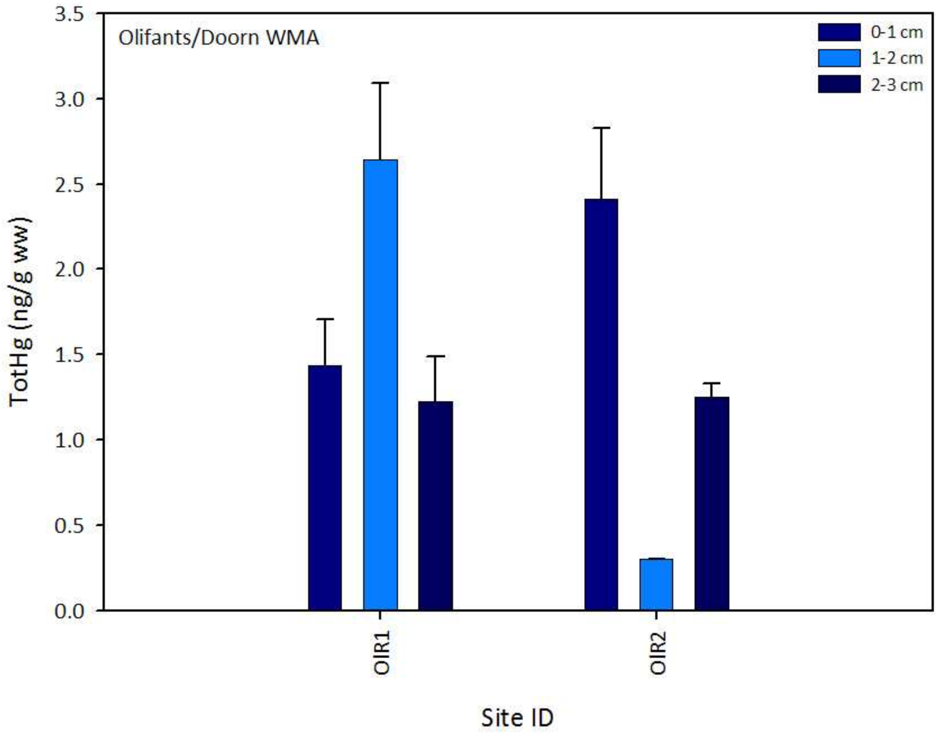

Mzimvubu-Keiskamma WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
5
10
15
20
BuF1
Site ID

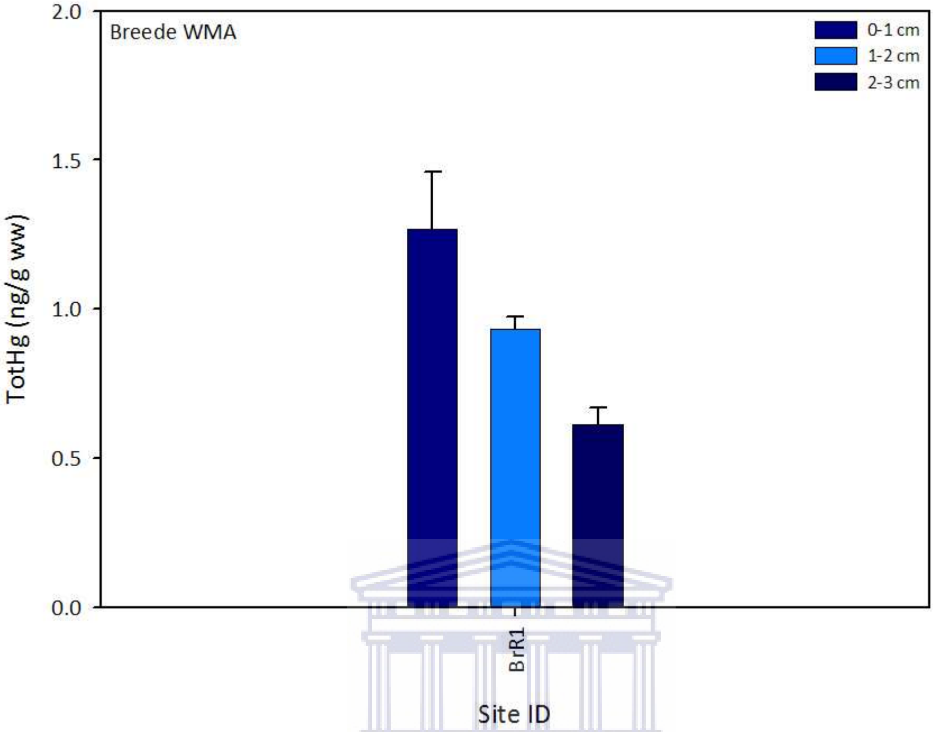

Upper Orange WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
1
2
3
4
5
MR1
Site ID

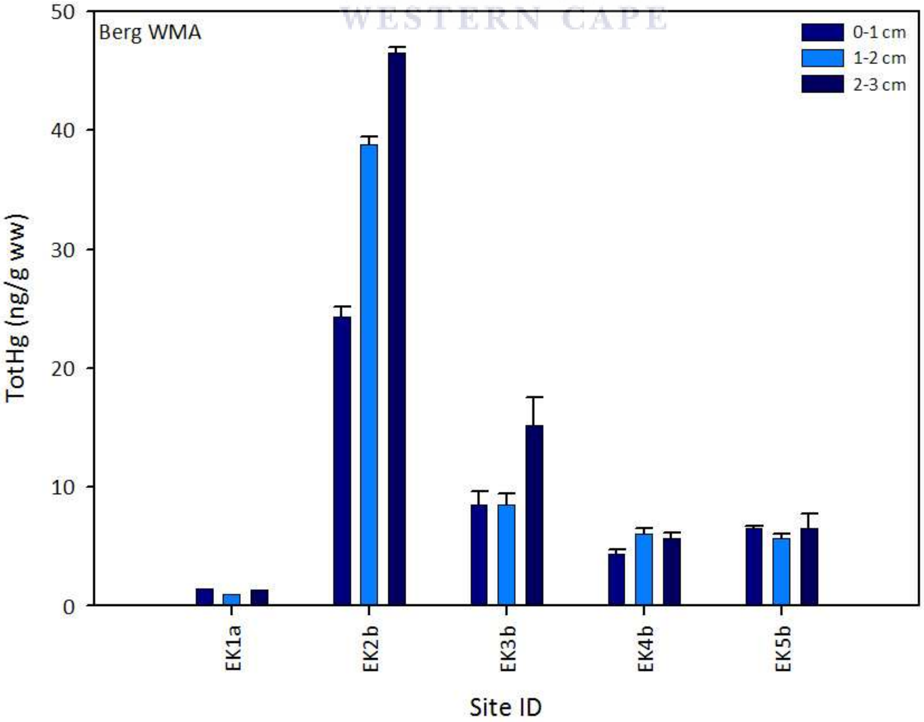

Lower Orange WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
2
4
6
8
10
OrR1
OrR2
Site ID


Fish to Tsitsikamma WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
2
4
6
8
10
12
GF1
GF2
SoR1
SoR2
Site ID

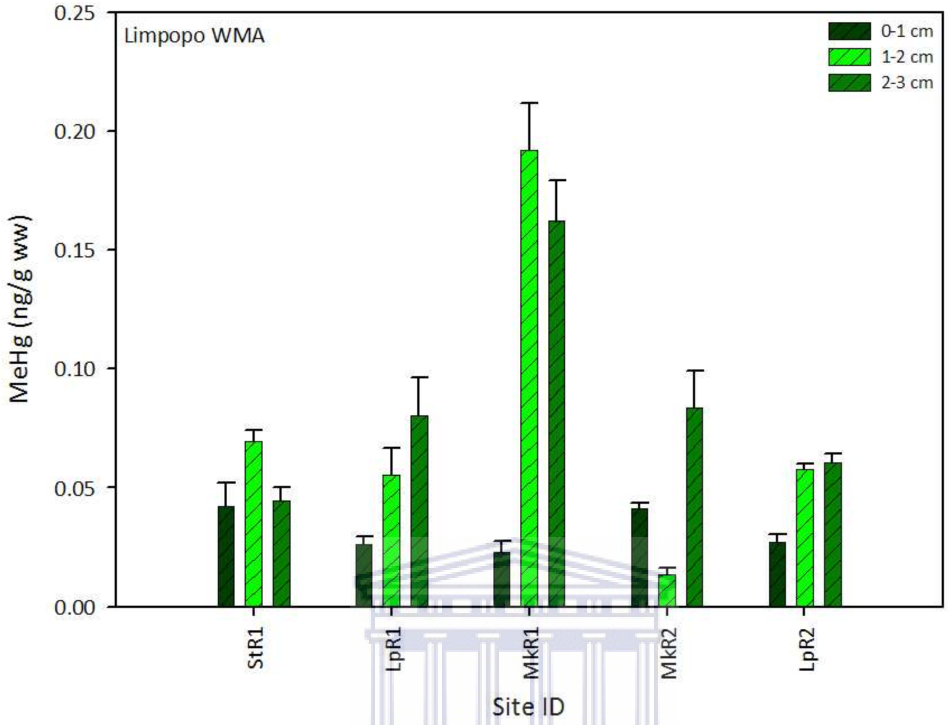

Gouritz WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0
2
4
6
8
10
GoR1
Site ID

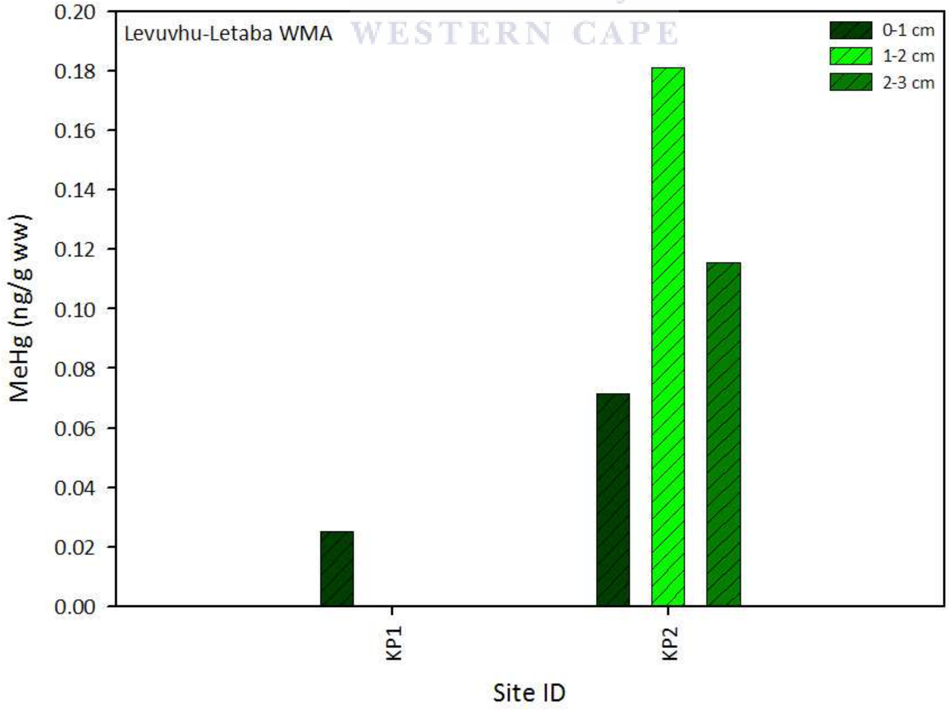

Olifants/Doorn WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
OlR1
OlR2
Site ID

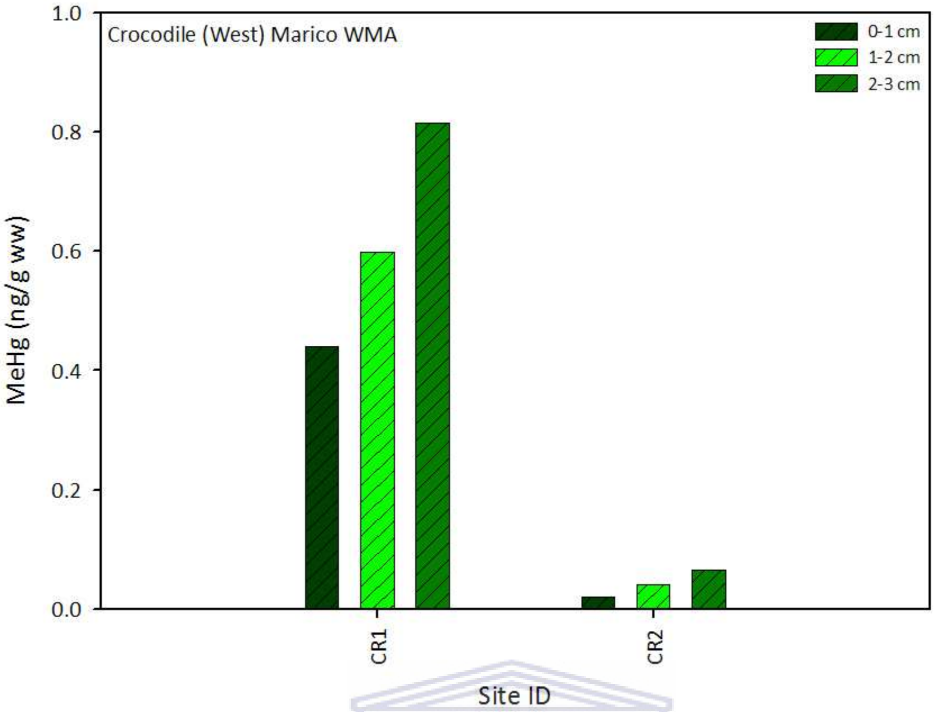

Breede WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
2.0
1.5
1.0
0.5
0.0
BrR1
Site ID

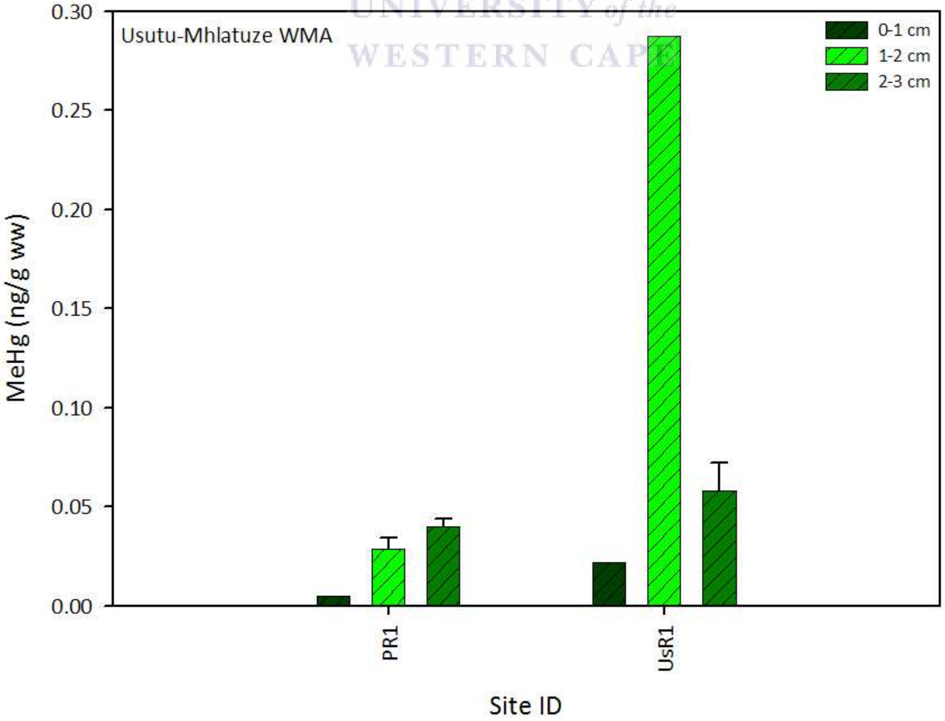

Berg WMA
0-1 cm
1-2 cm
2-3 cm
TotHg (ng/g ww)
50
40
30
20
10
0
EK1a
EK2b
EK3b
EK4b
EK5b
Site ID

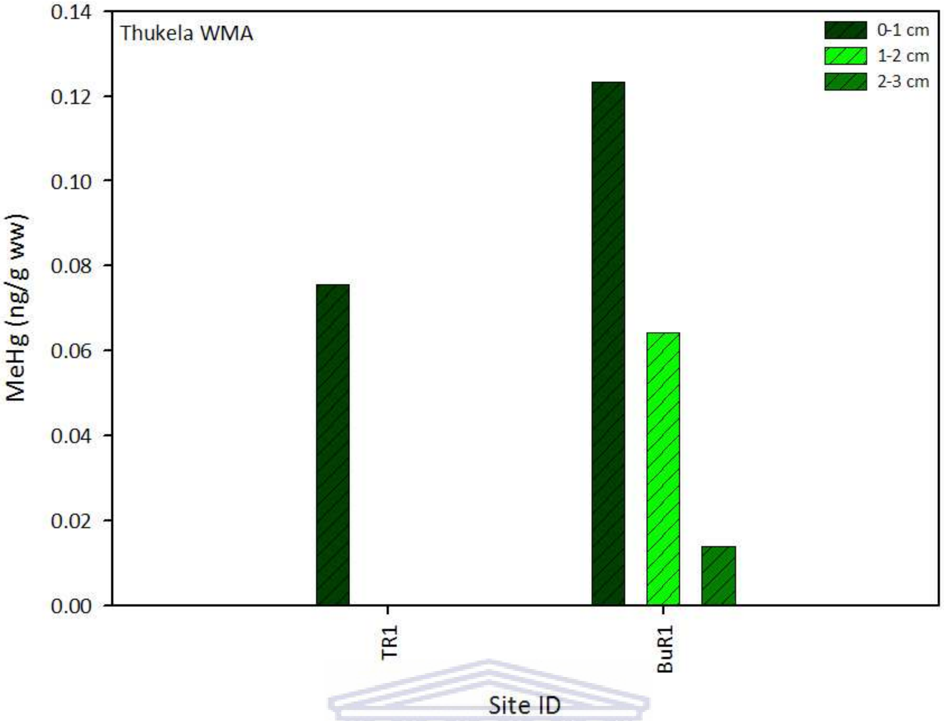
Appendix 22: Chapter 2 - Methylmercury (MeHg) concentrations in surface sediment

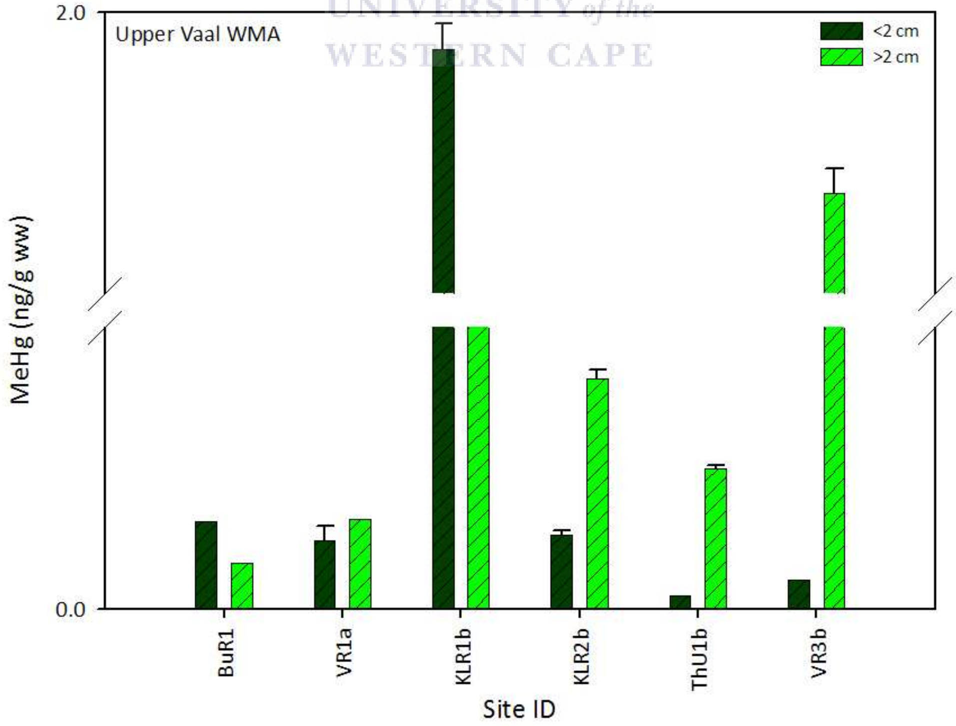


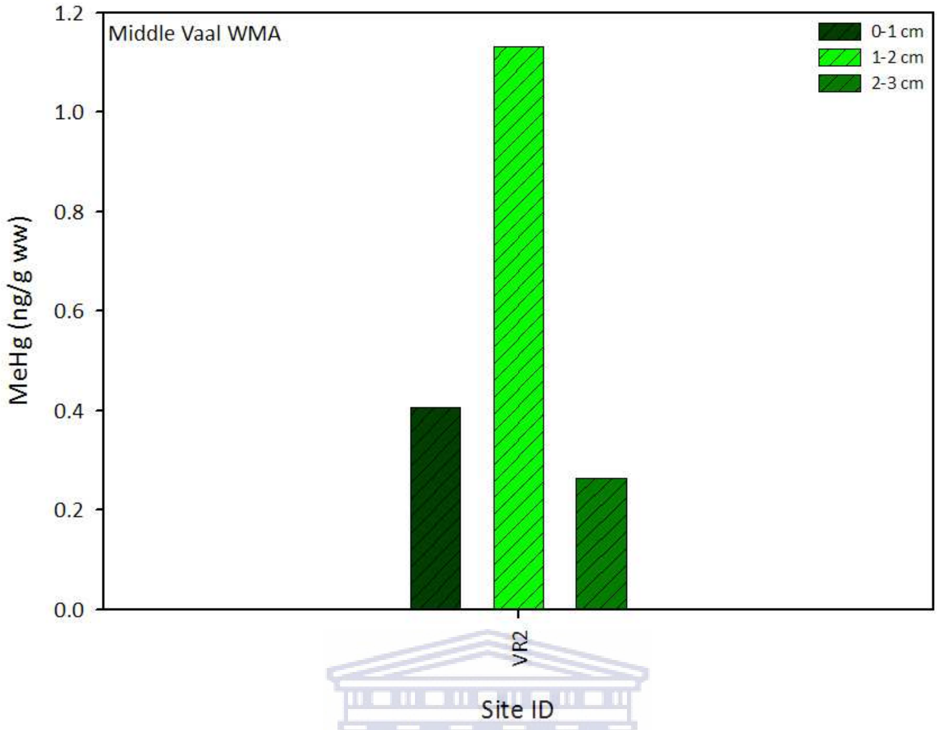


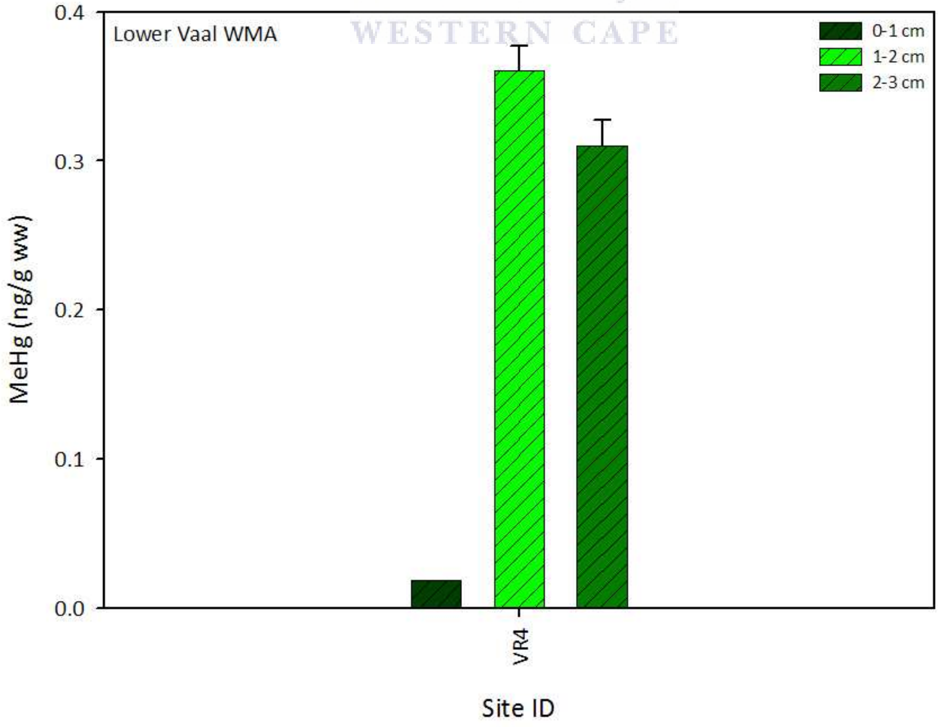

Crocodile (West) Marico WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
1.0
0.8
0.6
0.4
0.2
0.0
CR1
CR2
Site ID

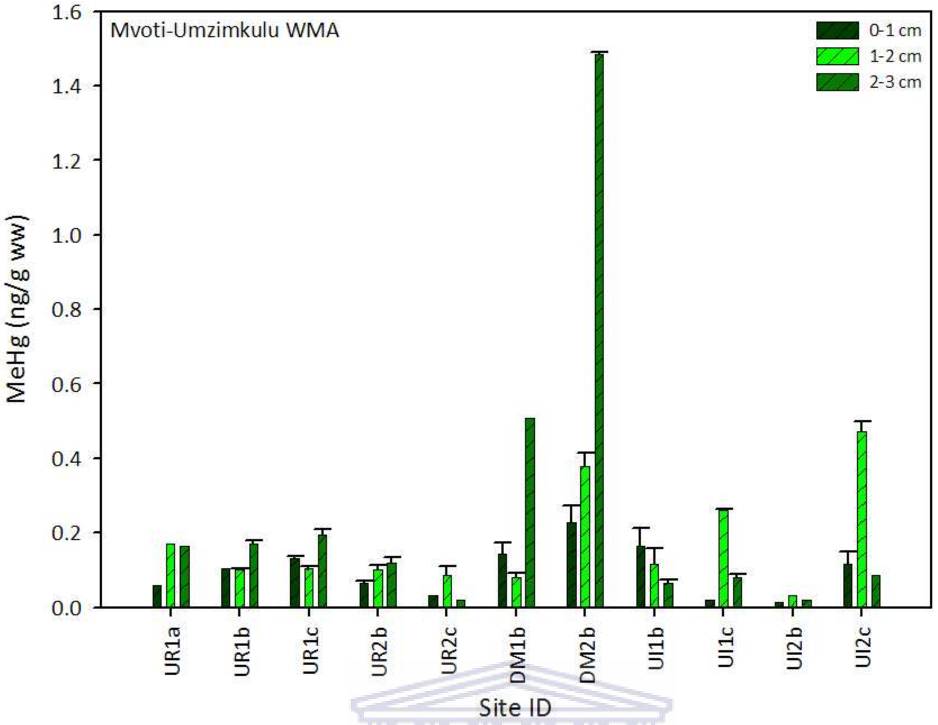

Usutu-Mhlatuze WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
PR1
UsR1
Site ID

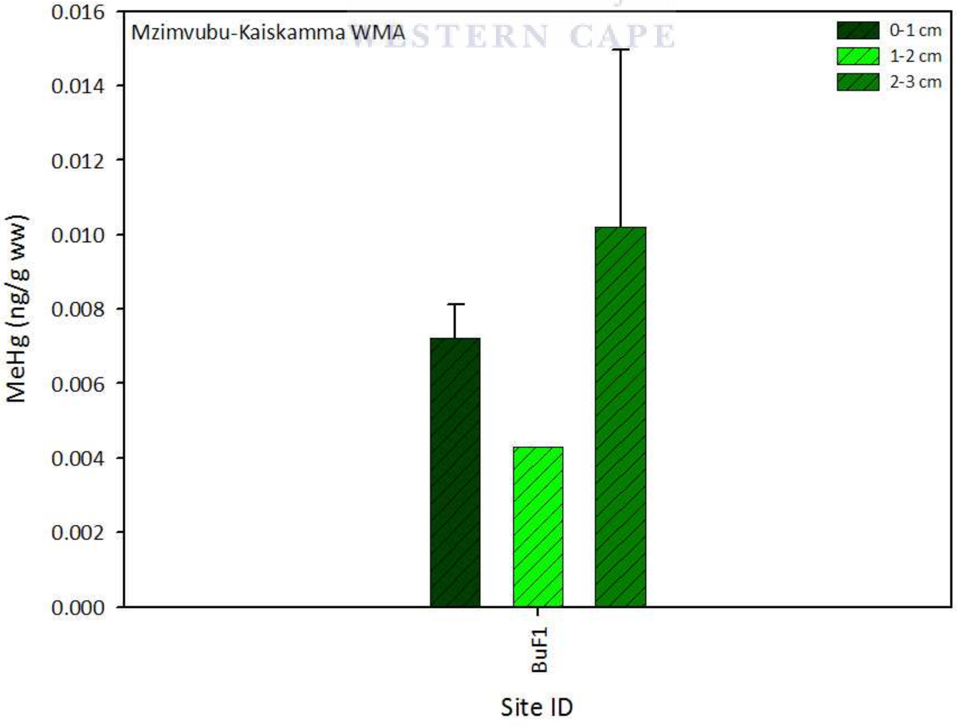

Thukela WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
TR1
BuR1
Site ID

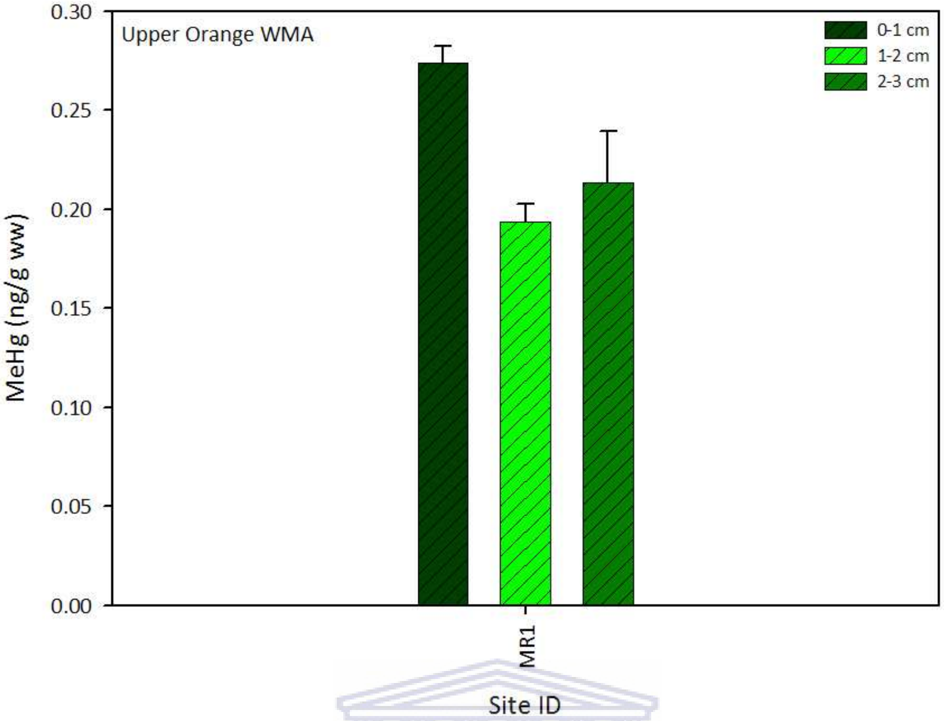

Upper Vaal WMA
<2 cm
>2 cm
MeHg (ng/g ww)
2.0
0.0
BuR1
VR1a
KLR1b
KLR2b
ThU1b
VR3b
Site ID

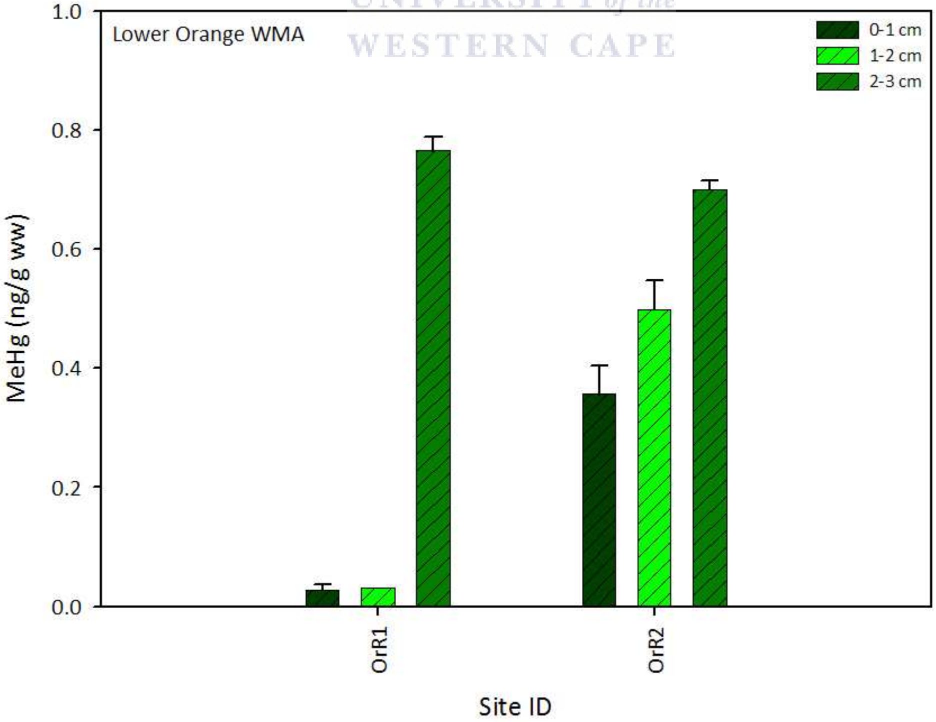

Middle Vaal WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
VR2
Site ID

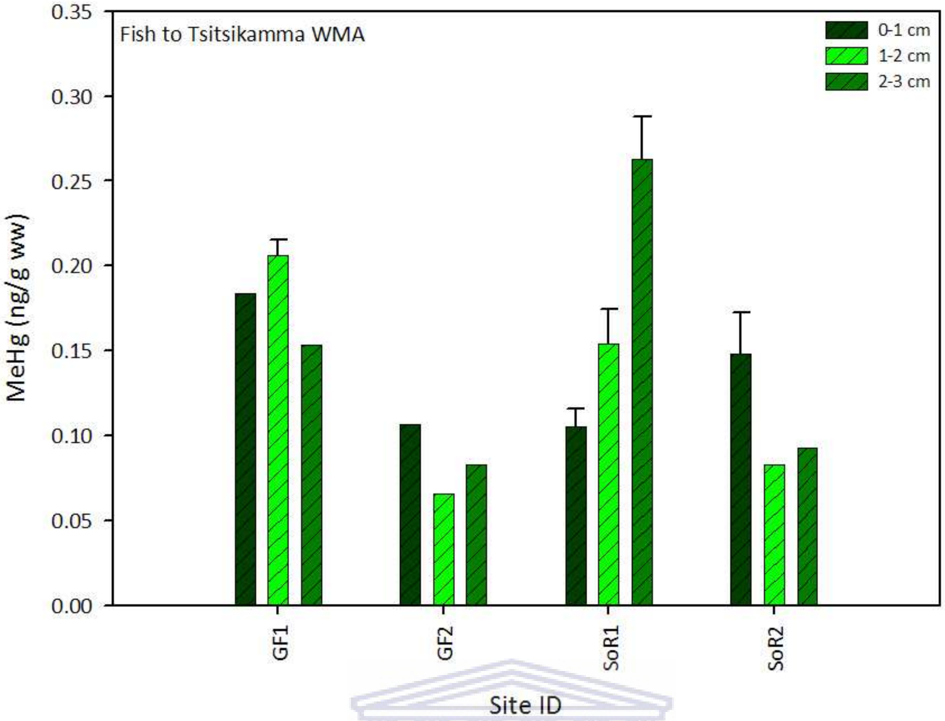

Lower Vaal WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.0
0.1
0.2
0.3
0.4
VR4
Site ID

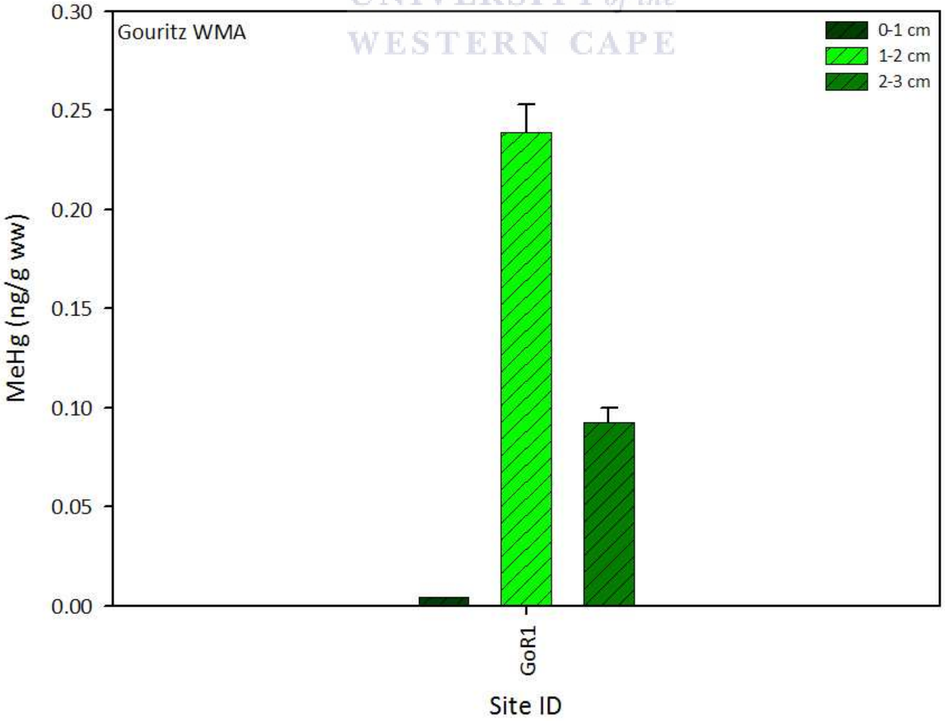

Mvoti-Umzimkulu WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
UR1a
UR1b
UR1c
UR2b
UR2c
DM1b
DM2b
UI1b
UI1c
UI2b
UI2c
Site ID

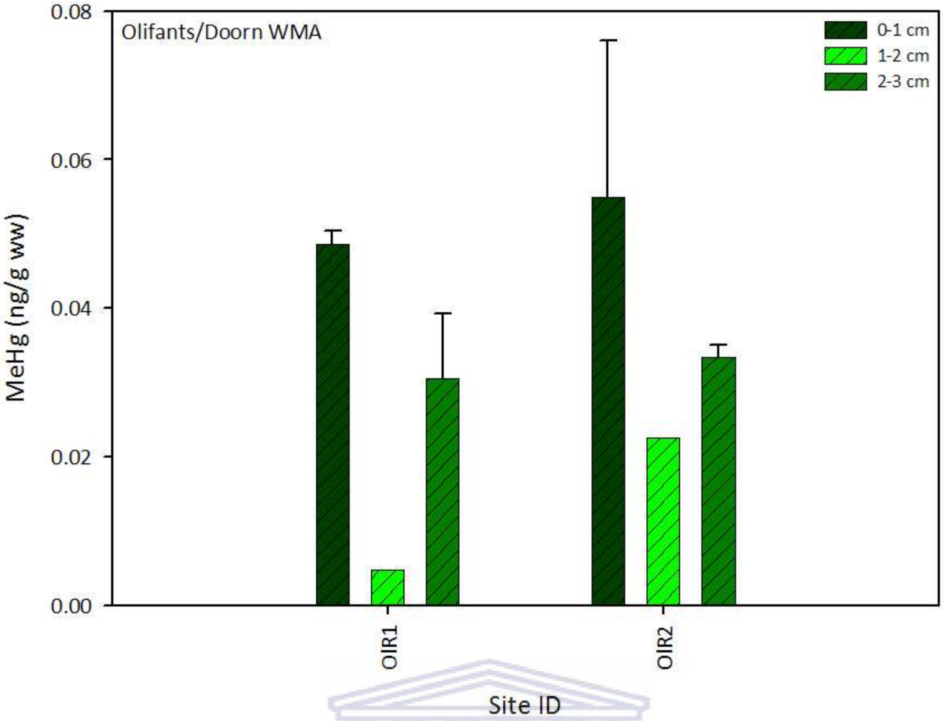

Mzimvubu-Kaiskamma WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.000
0.002
0.004
0.006
0.008
0.010
0.012
0.014
0.016
BuF1
Site ID

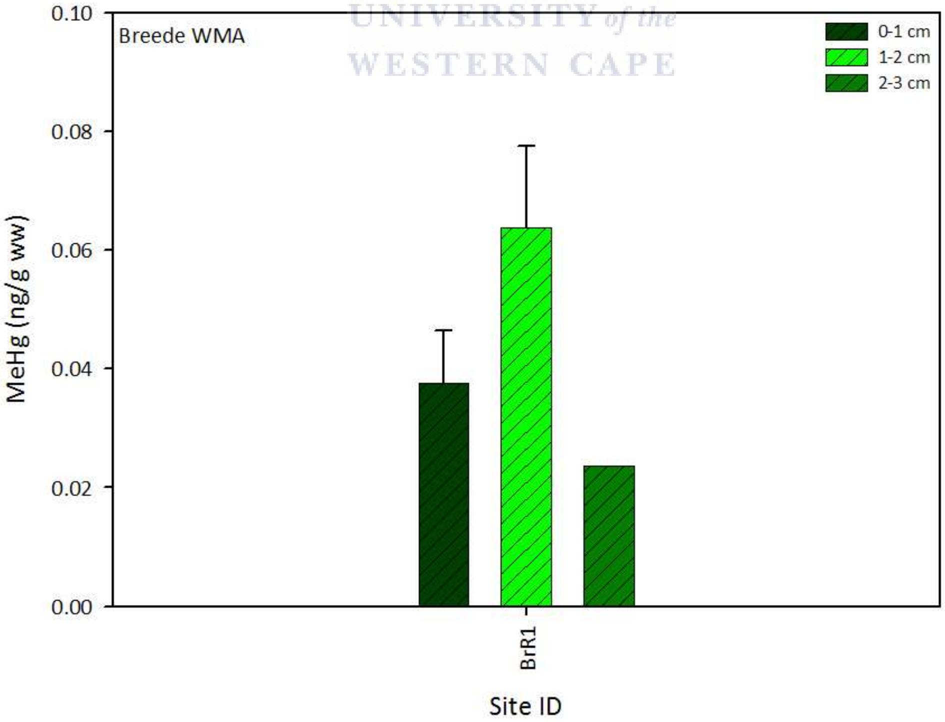

Upper Orange WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
MR1
Site ID

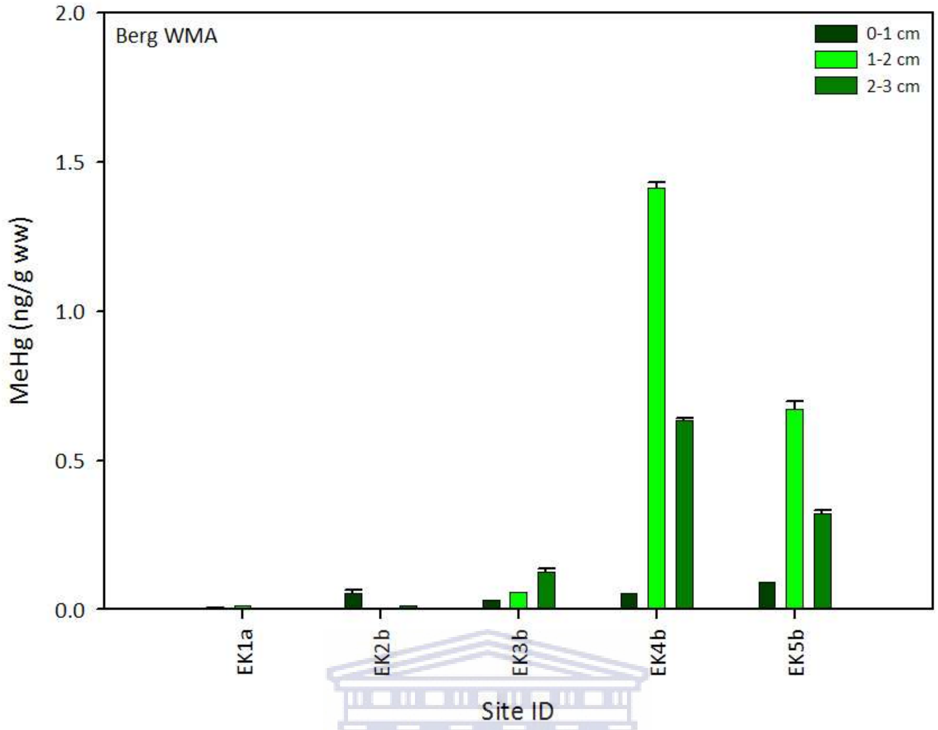

Lower Orange WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
1.0
0.8
0.6
0.4
0.2
0.0
OrR1
OrR2
Site ID


Fish to Tsitsikamma WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
GF1
GF2
SoR1
SoR2
Site ID


Gouritz WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.00
0.05
0.10
0.15
0.20
0.25
0.30
GoR1
Site ID


Olifants/Doorn WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.00
0.02
0.04
0.06
0.08
OlR1
OlR2
Site ID

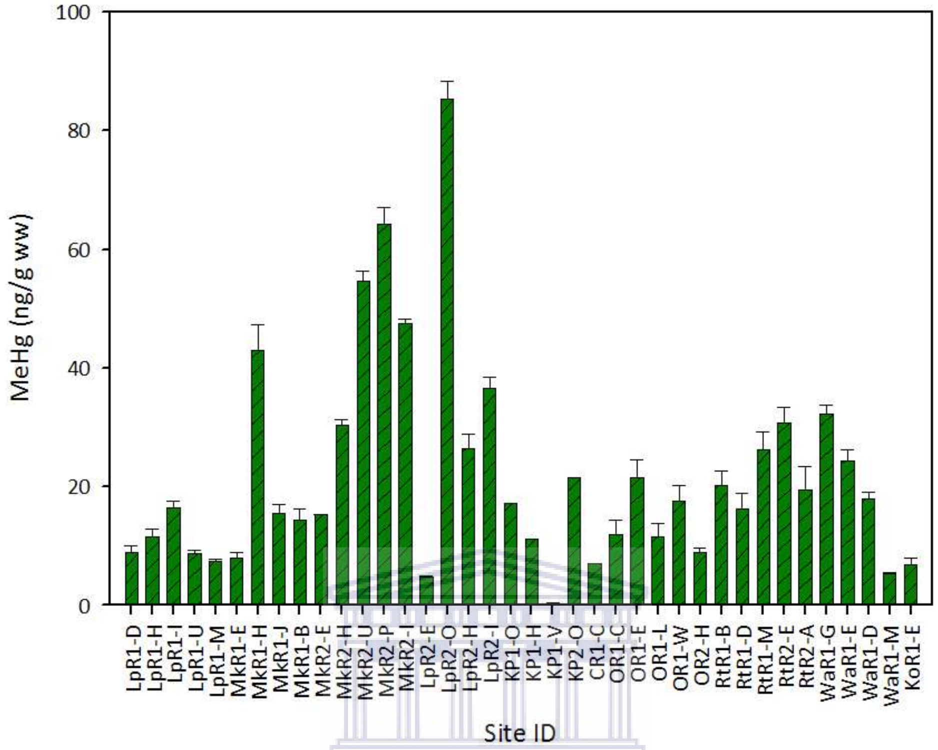

Breede WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
0.00
0.02
0.04
0.06
0.08
0.10
BrR1
Site ID

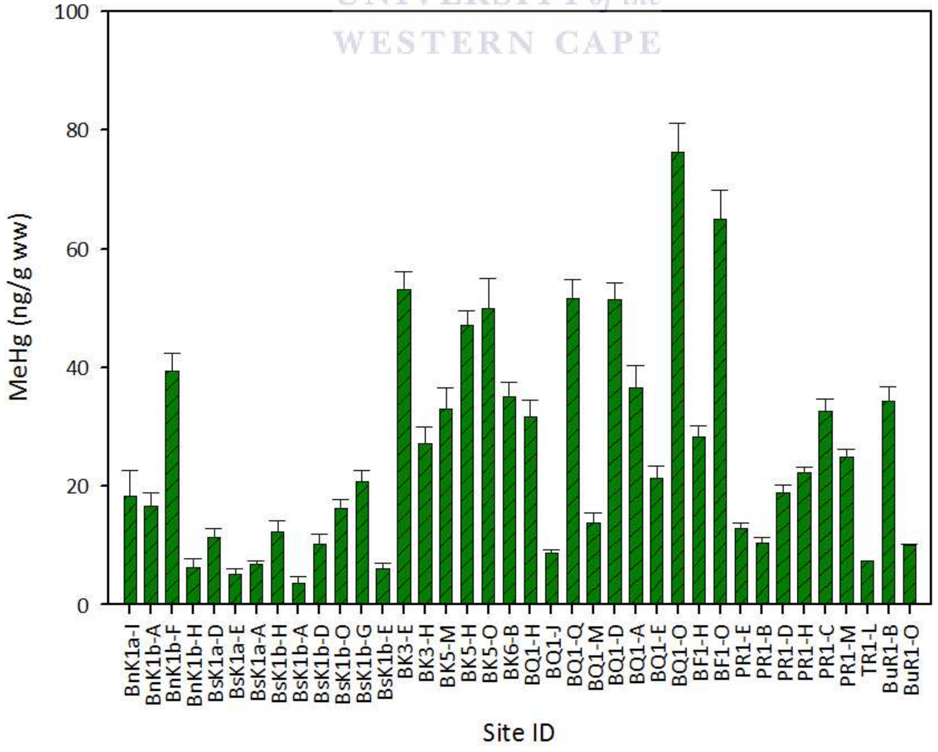

Berg WMA
0-1 cm
1-2 cm
2-3 cm
MeHg (ng/g ww)
2.0
1.5
1.0
0.5
0.0
EK1a
EK2b
EK3b
EK4b
EK5b
Site ID

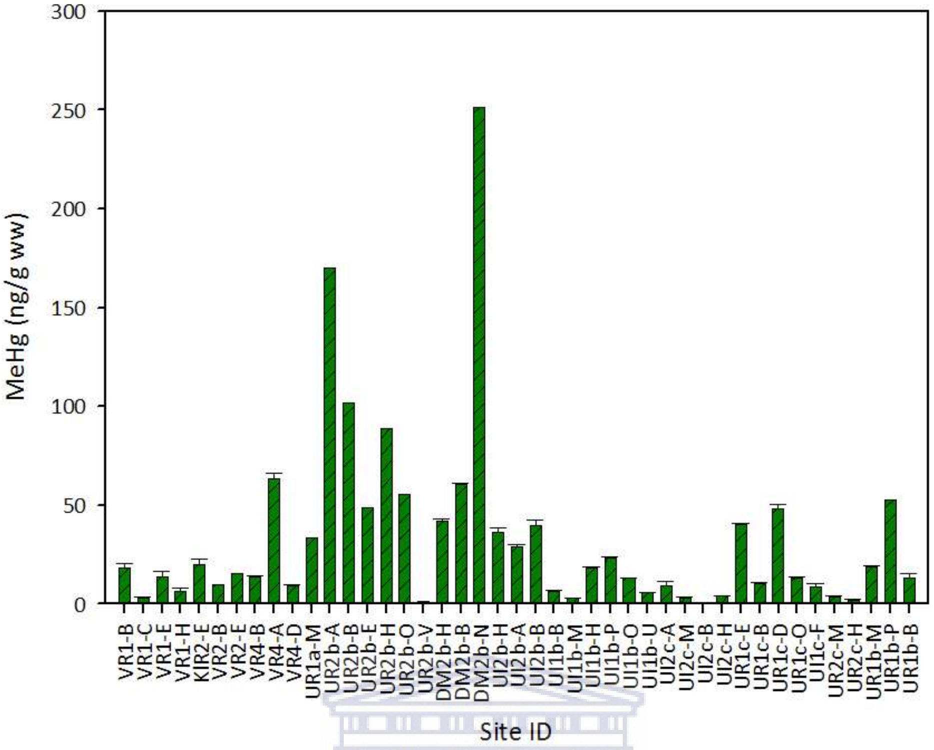
Appendix 23: Chapter 2 - List of biota collected, species code and diet.

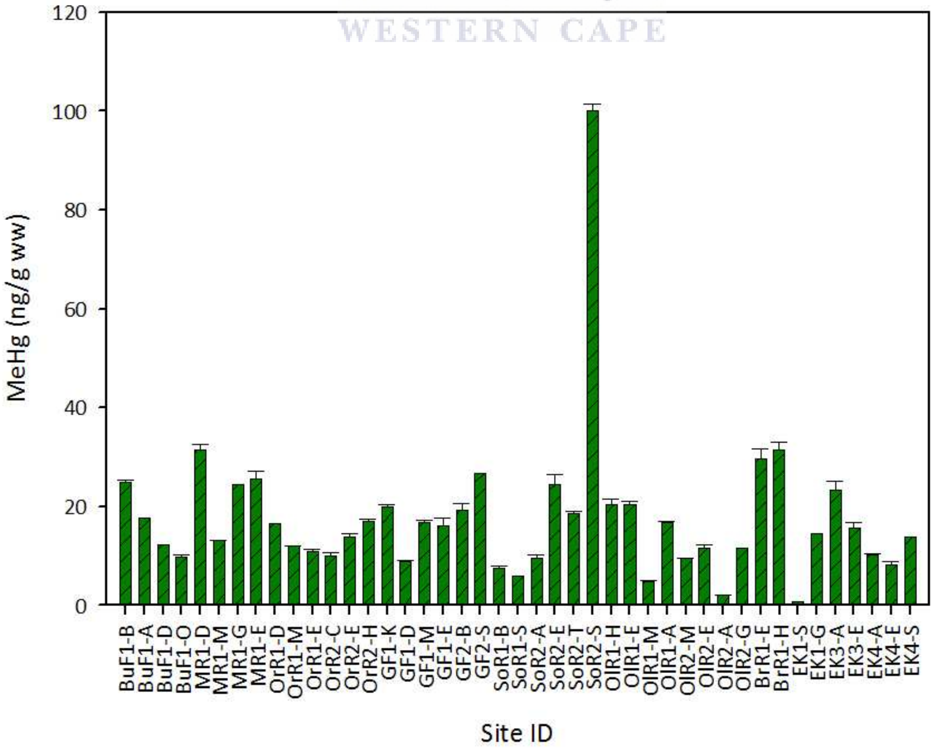
ID	Species Name	Common Name	Diet
Invertebrates			
A	*Aeshnidae*	Dragonfly	Insects; small fish
B	*Atyidae*	Freshwater shrimp	Aquatic plants; invertebrates (benthic)
C	*Baetidae*	Small minnow mayfly	Aquatic plants
D	*Belastomatidae*	Giant waterbug	Crustaceans, amphibians, fish
E	*Coenagrionidae*	Damselfly	Daphnia, mosquito larvae
F	*Corixidae*	Water boatmen	Insects, tadpoles, small fish
G	*Dysticidae*	Predacious diving beetle	Tadpoles; glassworms; other small invertebrates
H	*Gomphidae*	Dragonfly	Daphnia, mosquito larvae, small aquatic organisms
I	*Gyrinidae*	Whirligig beetle	Benthic invertebrates
J	*Heptagenidae*	Flat-headed mayfly	Small invertebrates
K	*Hirudinea*	Leech	Small invertebrates
L	*Hydropsyches*	Caseless caddisfly	Algae; detritus, organic matter
M	*Libellulidae*	Dragonfly	Daphnia, mosquito larvae, small aquatic organisms
N	*Naucoridae*	Creeping waterbug	Insects, snails
O	*Nepidae*	Water scorpion	Aquatic invertebrates
P	*Notonectidae*	Backswimmer	Tadpoles; small fish
Q	*Perlidae*	Stonefly	Aquatic invertebrates
R	*Planorbidae*	Orb snail	Algae, diatoms; detritus
S	*Potamonautes*	Crab	Small fish
T	*Physidae*	Cony snail	Algae, diatoms; detritus
U	*Tabanidae*	Horsefly	Males: nectar/pollen; females: blood
V	*Thiaridae*	Snail	Aquatic plants
W	*Simuliidae*	Blackfly	Males: nectar/pollen; females: blood
Fish			
A	*Tilapia sparrmanii*	Banded tilapia	Aquatic plants, small invertebrates
B	*Amphilius spp.*	Catfish	Benthic invertebrates
D	*Gambusia affinis*	Mosquitofish	Small aquatic organisms
E	*Labeobarbus*	Yellowfish	Detritus; invertebrates
F	*Labeo ruddi*	Silver labeo	Organic sediments
G	*Tilapia rendalli*	Red-breasted tilapia	Aquatic plants, small invertebrates

Appendix 24: Chapter 2 - Methylmercury (MeHg) concentrations in invertebrates

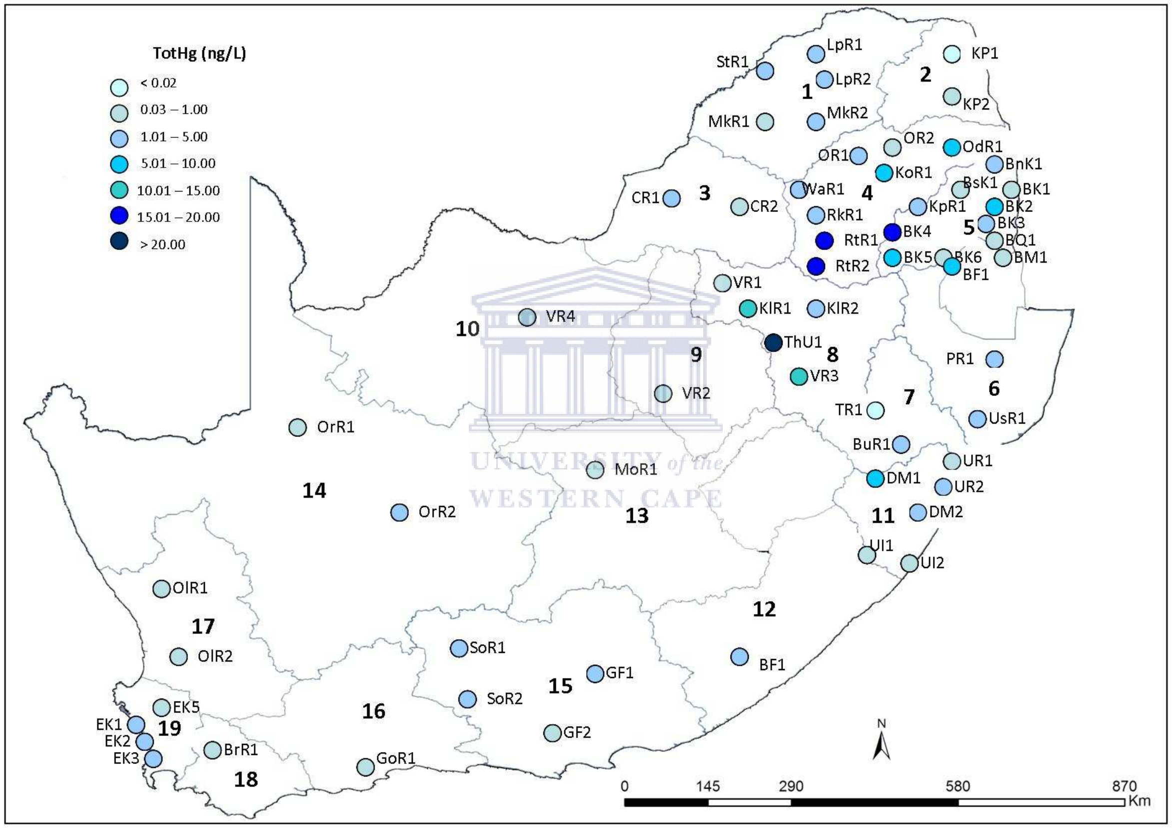





MeHg (ng/g ww)
0
50
100
150
200
250
300
Site ID
VR1-B
VR1-C
VR1-E
VR1-H
KIR2-E
VR2-B
VR2-E
VR4-B
VR4-A
VR4-D
UR1a-M
UR2b-A
UR2b-B
UR2b-E
UR2b-H
UR2b-O
UR2b-V
DM2b-H
DM2b-B
DM2b-N
UI2b-H
UI2b-A
UI2b-B
UI1b-B
UI1b-M
UI1b-H
UI1b-P
UI1b-O
UI1b-U
UI2c-A
UI2c-M
UI2c-B
UI2c-H
UR1c-E
UR1c-B
UR1c-D
UR1c-O
UI1c-F
UR2c-M
UR2c-H
UR1b-M
UR1b-P
UR1b-B

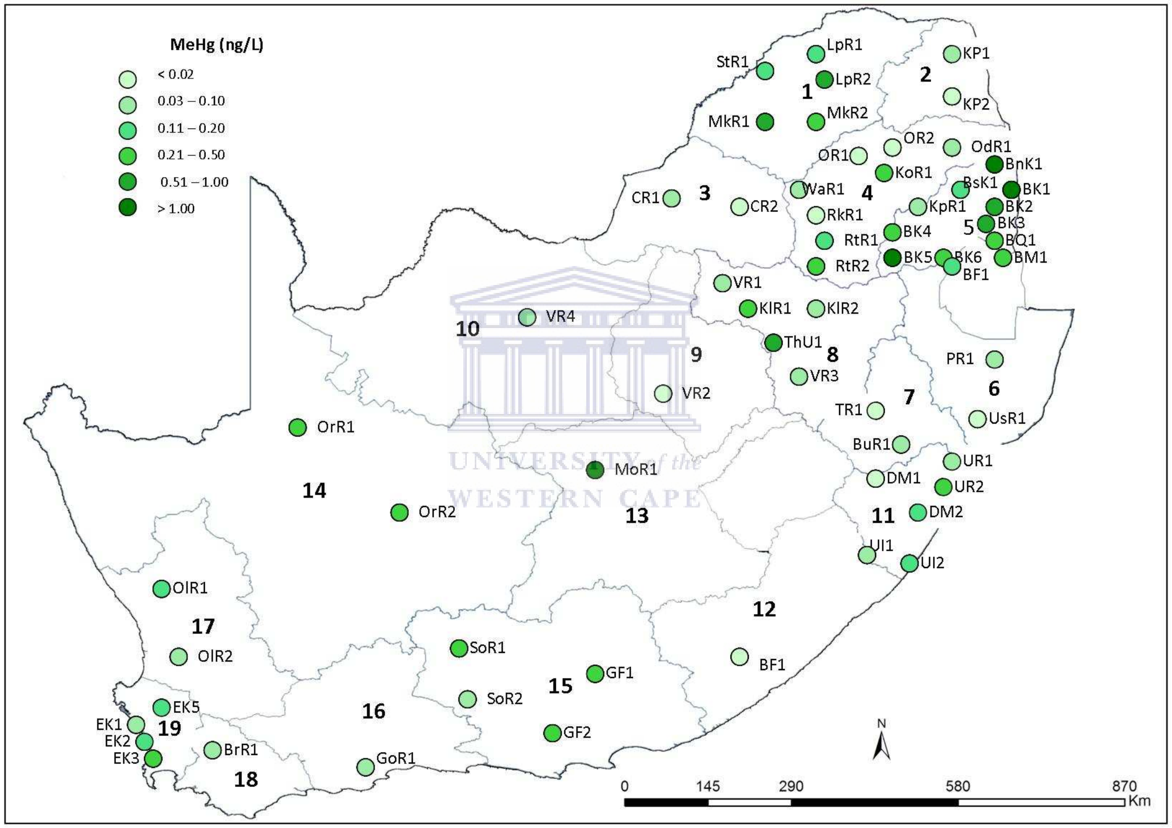

MeHg (ng/g ww)
0
20
40
60
80
100
120
Site ID
BuF1-B
BuF1-A
BuF1-D
BuF1-O
MR1-D
MR1-M
MR1-G
MR1-E
OrR1-D
OrR1-M
OrR1-E
OrR2-C
OrR2-E
OrR2-H
GF1-K
GF1-D
GF1-M
GF1-E
GF2-B
GF2-S
SoR1-B
SoR1-S
SoR2-A
SoR2-E
SoR2-T
SoR2-S
OlR1-H
OlR1-E
OlR1-M
OlR1-A
OlR2-M
OlR2-E
OlR2-A
OlR2-G
BrR1-E
BrR1-H
EK1-S
EK1-G
EK3-A
EK3-E
EK4-A
EK4-E
EK4-S

Appendix 25: Chapter 5 - Spatial distribution of average aqueous total mercury (TotHg) concentrations in South Africa's 19 WMAs



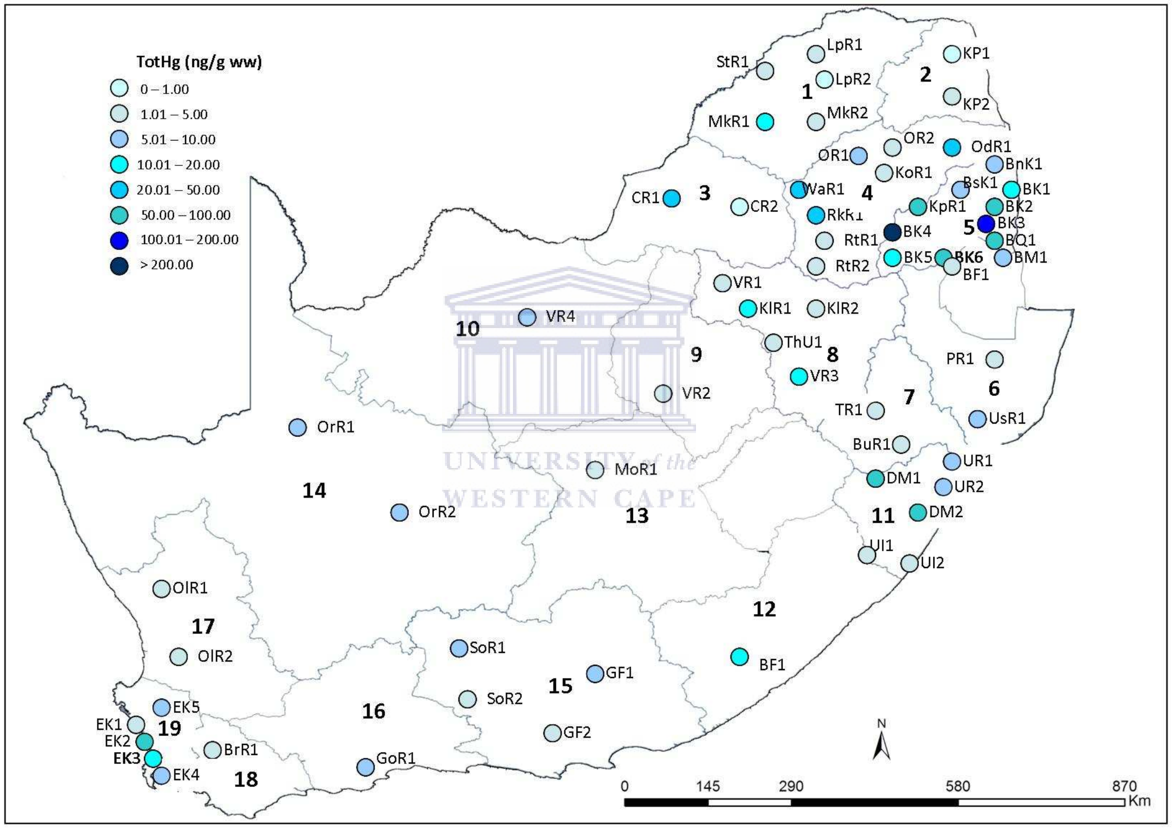
*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 26: Chapter 5 - Spatial distribution of average aqueous methylmercury (MeHg) concentrations in South Africa's 19 WMAs



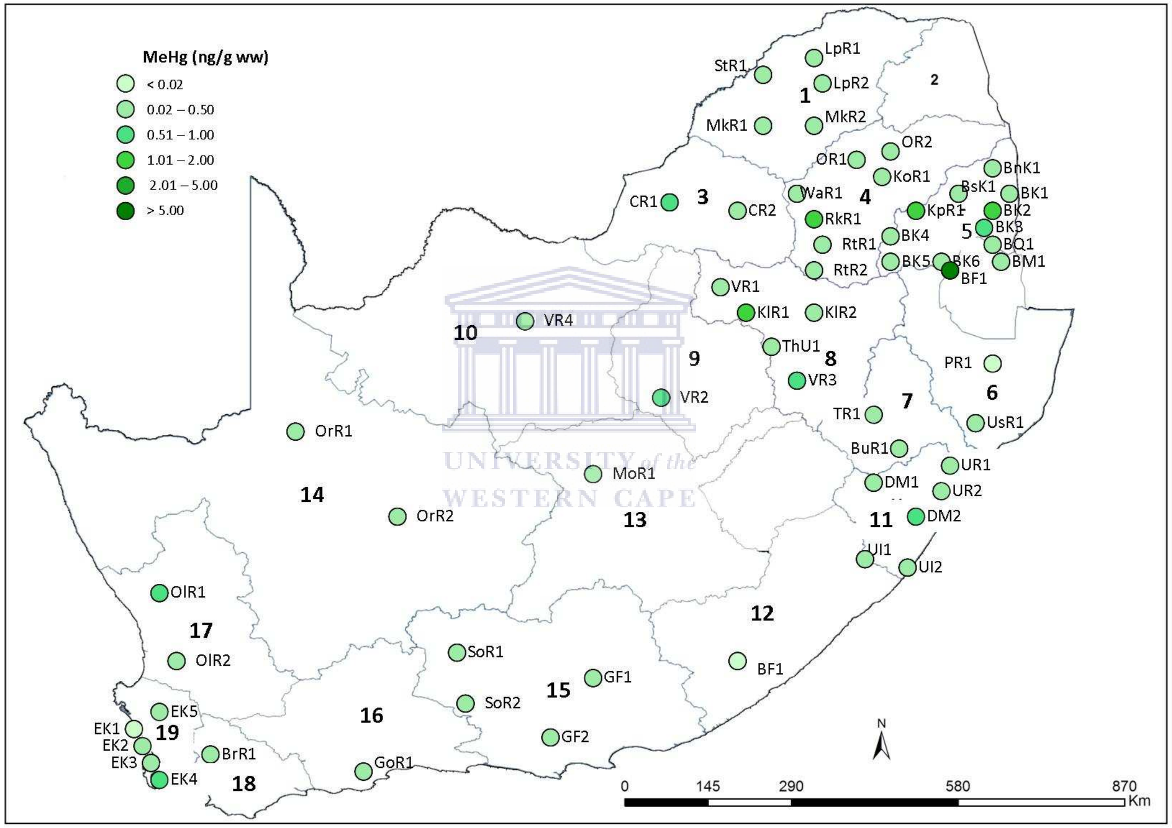
*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 27: Chapter 5 - Spatial distribution of average sediment total mercury (TotHg) concentrations in South Africa's 19 WMAs



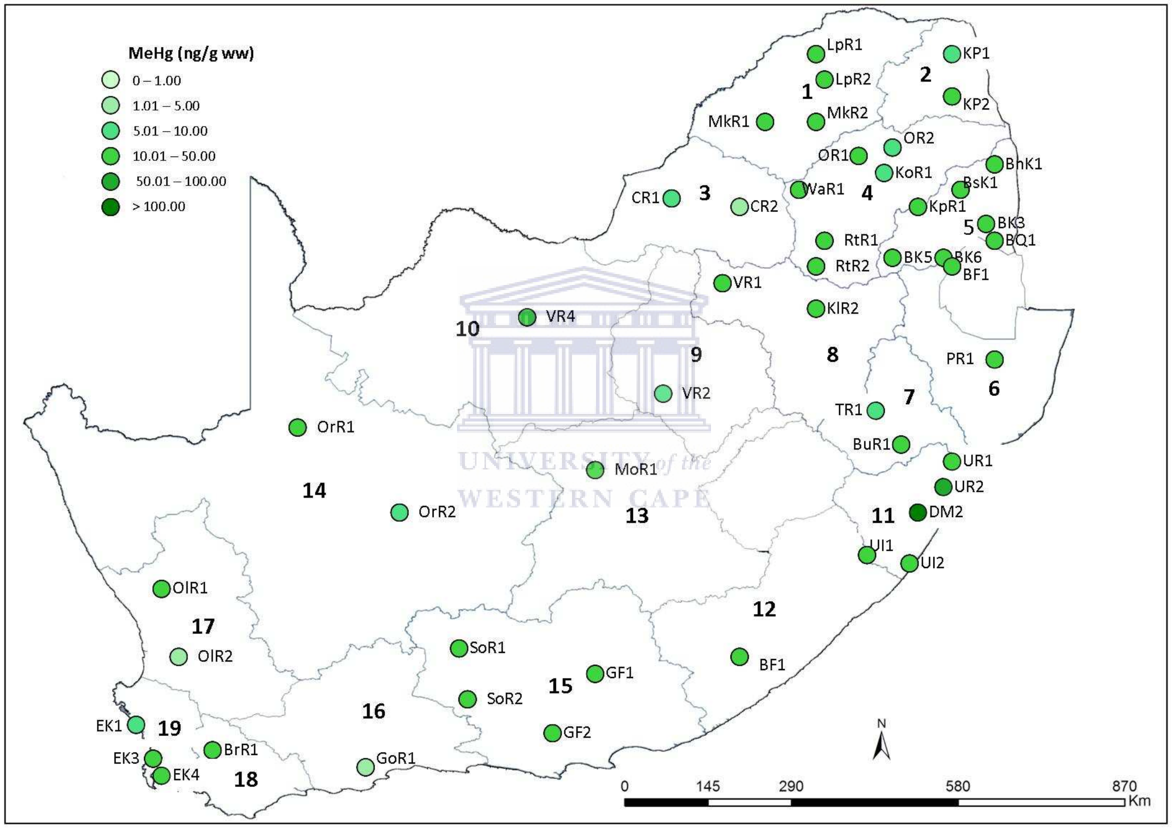
*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 28: Chapter 5 - Spatial distribution of average sediment methylmercury (MeHg) concentrations in South Africa's 19 WMAs



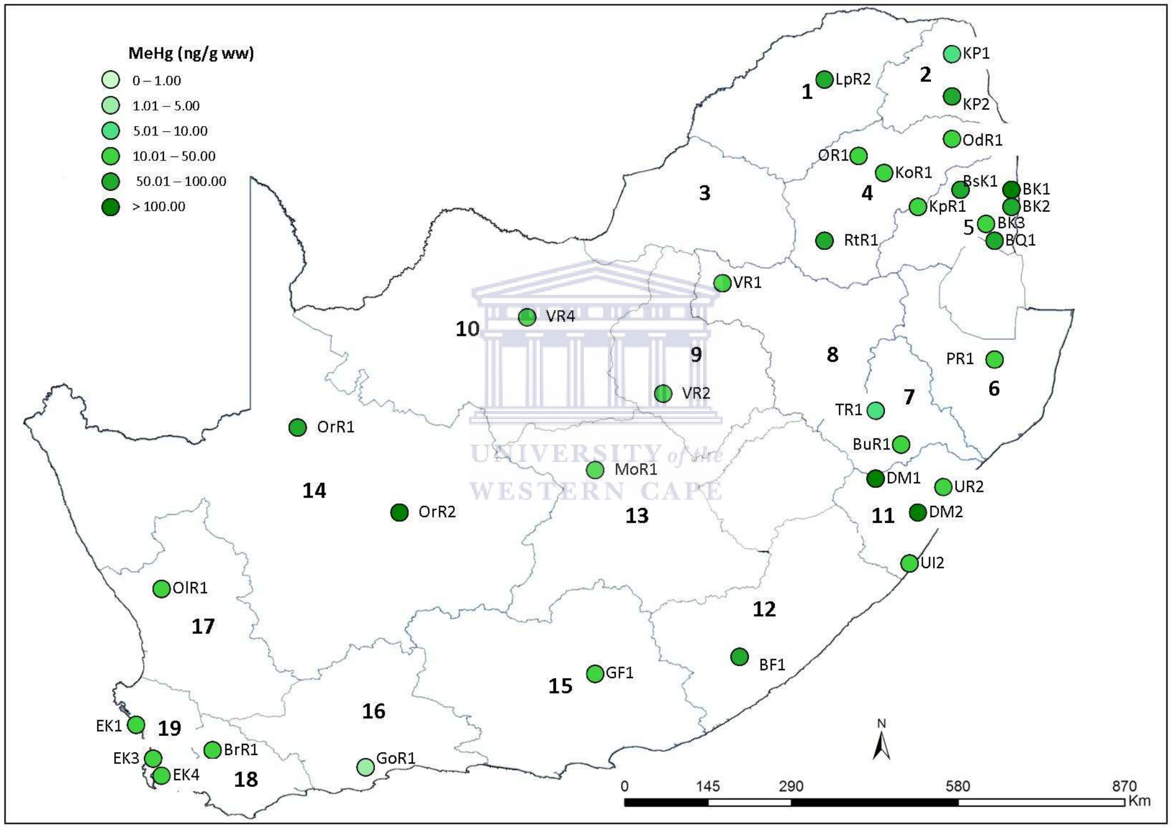
*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 29: Chapter 5 - Spatial distribution of average invertebrate methylmercury (MeHg) concentrations in South Africa's 19 WMAs



*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 30: Chapter 5 - Spatial distribution of average fish methylmercury (MeHg) concentrations in South Africa's 19 WMAs



*The position of the sampling locations indicating average concentrations and sample ID are not representative of the actual sampling location, but serve merely to indicate in which WMA each sampling site occurred.

Appendix 31: Ancillary water quality parameters

(NR = Not Recorded)

Site ID	pH	T (ºC)	EC (mS/cm)	TDS (ppt)	DO (ppm)	Eh (mV)	SO_4 (ppm)	Cl^- (ppm)	NO_3^- (ppm)	PO_3^{4-} (ppm)	DOC (ppm)
StR1	8.15	14.10	0.74	0.37	8.55	189.30	19.20	18.50	0.08	< 0.05	2.26
LpR1	6.75	13.00	0.15	0.07	7.47	192.30	6.37	15.30	0.42	< 0.05	0.94
MkR1	6.85	16.10	0.05	0.02	6.45	201.50	3.97	4.75	< 0.05	1.70	5.09
MkR2	7.18	16.50	0.09	0.04	8.11	255.80	6.30	6.04	0.20	< 0.05	1.95
LpR2	6.88	10.40	0.03	0.01	7.64	187.50	3.39	2.57	0.06	< 0.05	0.59
KP1	7.82	16.50	0.61	0.31	NR	NR	12.00	63.00	0.06	0.09	4.79
KP2	8.70	21.00	1.97	0.99	NR	NR	12.00	223.00	0.08	0.16	10.00
CR1	6.94	13.40	0.58	0.29	11.30	NR	49.14	66.18	0.80	2.74	8.68
CR2	8.82	13.30	054	0.27	8.00	NR	45.69	69.12	1.20	0.76	7.65
OR1	7.48	10.50	0.66	0.33	7.50	NR	163.41	29.17	1.67	0.85	10.94
OR2	7.40	16.80	0.47	0.24	10.00	NR	145.35	15.34	0.25	< 0.05	6.91
RkR1	8.08	18.60	0.24	0.12	43.60	NR	468.00	27.30	1.94	0.47	3.62
WaR1	8.50	20.40	0.84	0.42	53.00	NR	114.00	8.90	< 0.05	0.11	10.51
KoR1	7.92	16.20	0.31	0.15	93.10	NR	43.80	13.90	< 0.05	0.13	10.20
OdR2	8.40	22.30	0.46	0.23	52.30	NR	40.90	17.80	0.29	0.11	11.53
RtR1	8.08	18.60	0.24	0.12	43.60	NR	24.10	34.80	< 0.05	0.12	11.12
RtR2	7.88	19.40	0.31	0.18	49.90	NR	12.30	4.80	0.66	0.12	10.00
BnK1b	8.00	11.10	0.14	0.07	10.82	-87.70	3.75	2.08	< 0.05	NR	2.20
BnK1c	8.18	21.50	0.18	0.09	11.45	46.70	7.74	5.08	0.17	0.11	2.60
BsK1a	7.91	23.20	0.16	0.08	442.80	-72.40	10.60	6.16	0.22	0.11	2.22
BsK1b	7.80	12.10	0.15	0.07	6.60	-71.40	46.00	26.00	0.25	0.10	4.37
BsK1c	7.12	31.00	0.17	0.08	11.75	91.20	5.34	4.95	0.08	NR	2.47
KpR1a	8.22	24.10	0.35	0.17	NR	-80.20	46.00	26.00	0.25	0.10	4.37

Site ID	pH	T (ºC)	EC (mS/cm)	TDS (ppt)	DO (ppm)	Eh (mV)	SO_4 (ppm)	Cl^- (ppm)	NO_3^- (ppm)	PO_3^{4-} (ppm)	DOC (ppm)
BK1b	8.10	17.40	0.41	0.20	11.53	-70.70	5.34	4.95	0.08	NR	2.47
BK2b	7.65	16.40	0.43	0.21	9.25	-44.80	72.80	15.30	0.79	0.11	2.20
BK2c	7.23	25.40	0.50	0.25	8.65	-79.50	5.91	5.18	0.06	NR	2.68
BK3a	8.71	16.20	0.42	0.21	10.59	-82.90	68.75	20.83	0.56	< 0.05	7.65
BK3c	7.28	26.40	0.47	0.23	11.82	-80.20	3.75	2.08	< 0.05	NR	2.20
BK4b	8.22	17.10	0.41	0.20	0.31	-86.10	68.75	18.75	0.52	NR	6.76
BK5b	6.80	16.00	0.43	0.21	7.31	128.30	74.22	18.75	0.54	NR	6.62
BK5c	7.12	27.00	0.48	0.24	8.56	-72.40	69.53	32.81	0.79	NR	3.57
BK6b	6.80	20.00	0.64	0.32	9.87	96.80	69.53	32.81	0.79	NR	3.57
BQ1b	8.29	14.50	0.35	0.17	8.50	-76.30	37.00	8.92	0.54	0.10	1.00
BQ1c	7.12	25.00	0.30	0.15	9.26	4.10	92.00	12.00	0.92	0.09	5.38
BM1b	8.29	22.80	0.53	0.26	8.29	-82.70	92.00	12.00	0.92	0.09	5.38
BF1b	6.79	13.70	0.33	0.16	9.39	186.30	68.75	18.75	0.52	NR	6.76
PR1	7.36	18.30	0.33	0.17	7.69	174.50	10.00	16.7	0.32	0.09	1.38
UsR1	5.94	18.70	0.06	0.03	6.08	204.60	7.26	3.64	0.08	0.09	5.13
TR1	7.76	8.20	0.07	0.04	NR	NR	0.89	1.15	3.74	< 0.05	1.13
BuR1	8.28	13.50	0.42	0.21	NR	NR	69.44	20.00	1.88	1.90	4.85
VR1	7.45	10.50	0.65	0.32	10.20	<0.05	130.23	88.24	8.21	1.08	8.24
KlR1	8.35	19.00	0.63	0.30	122.80	0.30	85.90	29.10	1.08	0.19	7.50
KlR2	8.52	19.00	0.55	0.27	58.20	0.27	37.20	11.40	< 0.05	0.11	7.13
ThU1	7.60	19.70	0.31	0.14	4.70	0.14	134.00	54.40	0.56	0.26	14.59
VR3	8.18	25.40	0.78	0.39	5.88	0.39	428.00	173.00	1.70	0.44	5.13
VR2	8.65	13.40	0.76	0.38	11.60	NR	170.73	61.76	2.02	0.48	7.65
VR4	7.12	25.10	0.38	0.17	5.09	224.40	40.00	12.80	0.32	0.15	5.13
UR1a	7.75	14.50	95.00	0.05	NR	NR	1.79	9.47	2.48	< 0.05	6.76
UR1b	9.75	17.20	0.09	0.04	6.65	171.40	7.50	4.17	0.07	< 0.05	9.41

Site ID	pH	T (ºC)	EC (mS/cm)	TDS (ppt)	DO (ppm)	Eh (mV)	SO_4 (ppm)	Cl^- (ppm)	NO_3^- (ppm)	PO_3^{4-} (ppm)	DOC (ppm)
UR1c	6.84	29.00	0.12	0.06	10.96	138.00	5.00	4.17	0.14	0.06	3.38
UR2b	8.80	15.60	0.34	0.17	8.30	130.60	15.38	83.82	0.02	4.04	4.46
UR2c	7.12	26.00	1.19	0.72	9.01	221.30	37.10	41.70	2.81	0.23	4.65
DM1	8.80	17.00	0.61	0.32	10.22	148.00	5.00	29.69	1.74	< 0.05	14.81
DM2	7.68	17.50	0.57	0.29	6.84	205.10	26.52	111.11	1.31	0.89	9.56
UI1b	8.60	12.50	0.12	0.04	9.27	200.70	15.83	100.00	1.22	0.97	3.10
UI1c	7.21	25.00	0.28	0.14	5.98	161.60	17.50	32.81	1.81	< 0.05	13.65
UI2b	8.95	17.50	0.26	0.13	11.60	221.70	3.75	14.58	0.29	0.05	7.65
UI2c	7.08	25.00	1.38	0.71	9.24	65.70	18.33	34.38	0.52	< 0.05	9.85
BfR1	7.15	21.00	19.88	9.98	7.43	181.30	1250.00	9440.00	0.12	0.13	0.70
MR1	7.21	24.40	0.42	0.20	5.63	199.10	12.00	31.30	< 0.05	0.10	3.53
OrR1	7.08	23.10	0.14	0.07	6.31	176.30	20.30	8.51	0.13	0.11	2.50
OrR2	7.25	25.10	2.33	1.18	5.47	187.10	22.00	15.00	0.06	0.09	3.00
GF1	7.14	24.90	1.12	0.56	6.70	135.20	83.00	126.00	1.24	0.39	2.30
GF2	7.24	20.70	19.58	9.24	4.97	119.70	25700.00	10400.00	0.22	0.16	< 1.00
SoR2	7.08	24.80	7.38	3.69	7.38	75.10	630.00	2220.00	0.46	0.17	< 1.00
SoR1	7.12	24.30	5.23	2.61	3.25	109.20	77.90	193.00	0.40	0.16	0.53
GoR1	8.05	21.60	> 20.00	> 10.00	8.83	NR	100.00	493.00	0.44	< 0.05	< 1.00
OlR1	7.08	23.10	0.14	0.07	6.31	176.30	6.79	38.60	0.06	0.11	1.60
OlR2	7.25	25.10	2.33	1.18	5.47	187.10	293.00	388.00	0.22	0.12	0.53
BrR1	6.59	22.20	1.63	81.00	5.09	184.60	94.60	315.00	< 0.05	0.12	1.40
EK1	6.95	13.20	1.11	0.55	NR	NR	81.82	159.38	2.35	0.17	13.36
EK2	7.04	14.00	1.21	0.57	1.80	188.70	78.00	154.00	3.71	1.88	17.67
EK3	7.08	13.80	1.14	0.57	4.19	1.14	79.00	179.00	2.17	1.57	17.67
EK4	7.08	13.60	0.35	0.17	10.38	194.80	43.10	61.77	3.01	1.89	6.77
EK5	7.10	16.90	0.78	0.39	5.76	218.80	52.00	128.00	2.76	1.61	10.10