# HEAVY METAL CONTAMINATION IN THE BLACK RIVER, CAPE TOWN


## LUCY GILBERT

**Supervised by Dr Kevin Winter**





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Department of Environmental and Geographical Science
University of Cape Town


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# ABSTRACT

Urban river sediments are often contaminated as a result of development and anthropocentric activity, and the Black River in Cape Town is a prime example of a river system suffering from unsustainable development. Methods of determining total and background concentrations of selected heavy metals were researched and utilized in the effort to quantify heavy metal concentrations derived from anthropogenic sources in the Black River. The findings were intended for use in the aim of producing sediment quality guidelines (SQG) for South Africa as described in the Water Research Commission Phase I Report; Developing Sediment Quality Guidelines (Gordon and Muller, 2010). The ability of the invasive *Eichhornia crassipes* (water hyacinth) to uptake and store heavy metals was also briefly investigated to identify its potential as a phyto-remediator in the Black River.

Toxicity of the sediment was quantified using the consensus-based mechanistic approach (Gordon & Muller, 2010) whereby assuming that total concentration of a heavy metal is the critical factor in its hazardousness. Sediment samples were divided into grain size and measured by X-Ray Fluorescence and concentrations of the focus elements antimony, arsenic, cadmium, chromium, copper, nickel, lead, and zinc in the mud fraction were compared with Consensus Based Sediment Quality Guidelines (McDonald et al., 2002). Based on guideline exceedances, the most toxic sample was collected from anoxic sediment conditions at the point where the N2 Highway crosses the Black River. The succeeding high toxicity risk locations were all within areas slightly downstream of a river convergence or within 50 m of one, specifically the Vygekraal, Jakkelsvlei, Esliekraal and Kromboom rivers. Exceedances were most common for chromium, copper, lead, nickel and zinc. The least toxic sample was collected 160 m downstream of the Athlone wastewater treatment works, with the one sample collected between these two points also holding relatively low toxicity risk. Concentrations of the selected analytes were also compared to results from a previous study conducted in 2002 on the Black River sediment (Haniff). The comparison suggested contamination has generally worsened in the past 13 years however due to potentially large analytical error from the differences in sample analyses in 2002 and in this investigation; the reliability of the comparative study is limited to general observation. The data implies that the Athlone wastewater treatment works was contributing to heavy metal concentrations in the sediment in 2002, but now in 2015 appears to improve sediment quality.

The Water Research Commission Phase I report identifies four ways to assess sediment quality to produce SQG; one of which is to establish normal background concentrations. In this investigation, background concentrations of heavy metals from natural sediment input to the Black River was estimated using two methods, the first was by combining globally recognized average shale values (Turekian and Wedepohl, 1961; USGS, 2000) with results obtained from studies undertaken on virgin soils of the Black River catchment area (Soderberg, 2003; Herselman, 2007) to form what is referred to as Estimated Background Values (EBV). The second method was to measure element concentrations of weakly-acid rinsed and milled coarse grain fraction of the Black River sediments. This was to see whether concentrations of the coarse fraction reflect those of the EBV, and to establish whether this would be a feasible method of estimating background concentrations which takes into account the multiple inputs of natual sediment across the river catchment. It was concluded from the application of the t-test that the coarse grain fraction held similar concentrations to 19 major and trace elements of the EBV with 95% certainty, and were comparable for all the focus elements accept antimony and arsenic.

The mud fraction heavy metal concentrations were then applied to three statistical indicators; the Pollution Load Index (PLI), the Geo-accumulation Index (I-Geo) and the Enrichment Factor (EF) in the objective to quantify anthropogenic input using both the EBV and coarse grain fraction results as reference values. All statistical indicators suggest the river is most enriched with cadmium, copper, lead and zinc, which most likely derive from roadside deposit/stormwater drainage and industries. The application of EBV to the statistical indicators revealed relatively little pollution enrichment, whereas the coarse grain results suggested much higher levels of pollution enrichment in the Black River. This disparity verifies the importance in selecting/obtaining suitable data sets as screening values for investigating heavy metal enrichment (Gałuszka & Migaszewski, 2012).

It was concluded that the coarse grain fraction element concentrations would not be feasible for use as EBV in the case of the Black River. This is due to the large assumptions made whilst using this method, namely that the coarse grain fraction is assumed to derive from the same source as the mud fraction. Due to the known disturbances to natural sedimentation in the Black River, it is doubtful that the fractions come from the same source. Also given the relatively low heavy metal concentration in the coarse grain fraction, it is likely that the majority of the sand in the sediment of the Black River derives from the coastline.

Heavy metal concentrations in the water hyacinth and sediments were applied to the Bio-accumulation Factor to identify the potential of the species as a phyto-remediating agent in the Black River. All four water hyacinth samples contained high concentrations of cadmium, and high concentrations of arsenic, nickel and antimony in three samples. Mercury was present (albeit at low concentrations) in three out of the four plant samples, yet was not detected in any of the 32 sediment samples, supporting the conclusions of Buta et al (2011) that the plant has a very strong affiliation to mercury, and that the element has a high affinity to bind with dissolved organic carbon and suspended sediment. The Bio-accumulation Factor revealed the phyto-remediation potential of the water hyacinth is high for antimony, arsenic, cadmium, mercury, lead and nickel. Water hyacinth could therefore be utilized more effectively (with the use of controlled growth) to remediate sediments indirectly by removing heavy metals from the water and preventing them settling into the sediment.

Short-term fluctuations in heavy metal presence and kinetic components cannot be conservatively evaluated due to sediment disturbances, complexities within river system inputs and the ever changing environmental conditions. The findings are based on equilibrium status and the conditions at the time of sampling, and are limited to confinements of the reliability of data generated from sample collection, preparation methods and sample analysis.

The distribution of metals in sediments of the Black River if not controlled by dredging is generally controlled by the association of heavy metals with very fine grained, organic-rich sediment. In addition, locations of high element enrichment reflect other river inputs which drain from various areas of the Cape Flats, with the most significant being the Esliekraal convergence.

Conclusions from the investigation suggest the method of establishing background concentration from the coarse grain fraction could be applicable only to urban rivers which have seen few sedimentation disturbances and are relatively isolated from external sources away the local catchment. This method could reduce sampling costs and be used along with the application of other means available mentioned in the Water Research Commission Phase I report to create South African sediment quality guidelines.

**DECLARATION**

I hereby declare that all the work presented in this thesis is my own, except where otherwise stated.

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*Lucy Gilbert*

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# ABBREVIATIONS

| | |
|---|---|
| **AMIS** | African Mineral Standards |
| **ASTM** | American Society for Testing and Materials |
| **ASV** | Average Shale Values |
| **BAF** | Bioaccumulation Factor |
| **CBSQG** | Consensus Based Sediment Quality Guidelines |
| **CRM** | Certified Reference Material |
| **EF** | Enrichment Factor |
| **EPA** | Environmental Protection Authority (Australia) |
| **I-Geo** | Geo-accumulation Index |
| **MEL** | Midpoint Effect Level |
| **NEM: ICMA** | National Environmental Management: Integrated Coastal Management Act (24 of 2008) |
| **NBC** | Normal Background Concentration |
| **PEL** | Probable Effect Level |
| **PLI** | Pollution Load Index |
| **ppm** | Parts per million/ mg/kg |
| **RDS** | Road drainage systems |
| **SQG** | Sediment Quality Guidelines |
| **TEL** | Threshold Effects Level |
| **Wt %** | Weight Percent/ percent gram per gram |
| **WWTW** | Wastewater treatment works |
| **XRD** | X-Ray Diffraction |
| **XRF** | X-Ray Fluorescence |

# 1. INTRODUCTION

Artificial, impervious surfaces in urban environments combined with heavily engineered drainage systems have transformed hydrological pathways and increased the quantity and speed at which pollution enters a river. In order to protect the environment some anthropogenic activities are lawfully obligated to limit the discharge of pollution, however some land-based activities cannot be controlled as easily, such as accidental industrial spills and vehicles producing roadside dust and so pollution continues to enter the environment at an alarming rate. Typical impurities include hydrocarbons, excessive nutrients, thermal pollution and heavy metals. Some forms of pollution such as heavy metals do not dilute and flow away, but settle out of the water column and accumulate in river beds along with natural sediment.

River sediment provides an essential habitat for organisms and plays a crucial role in the functioning of a 'healthy' ecosystem (MacDonald et al., 2000: Department of Environmental Affairs, 2011). Recent water quality management plans include the improvement of river sediments, such as the State of Rivers Report on Greater Cape Town's River Health Programme (City of Cape Town, 2005), the Water Research Commission (WRC) Phase 1 Report for Developing Sediment Quality Guidelines for South Africa (Gordon & Muller, 2010) and the Revision of National Action List for the Screening of Dredged Material (Department of Environmental Affairs, 2011). Such documents are contributing towards new thinking and practice in the restoration of river systems in South Africa.

Investigating the quality of sediment requires an understanding of normal background concentration (NBC) in order to identify whether elements are enriched and if so, the level of enrichment. Natural heavy metal concentration is dependent on the geochemical composition of the underlying bedrock, superficial deposits and the environmental conditions affecting mineral erosion (Environmental Protection Authority, 2008) and so NBC can vary dramatically between regions. The NBC are also used in the formation of Sediment Quality Guidelines (SQG) which are screening tools used to anticipate toxicity risk of sediments caused by abnormal contaminant concentrations.

South Africa does not have its own set of SQG for aquatic ecosystems, and instead uses those developed in America and Canada as stated in the National Environmental Management: Integrated Coastal Management Act (No. 24 of 2008, Reg 2012:635), however using existing SQG does not provide reliable results due to regional geochemical differences. The WRC Phase I Report for developing SQG for South Africa (Gordon & Muller, 2010) lists four tasks to establish SQG; one is to identify NBC. Past investigations of river sediment contamination highlights the difficulty in quantifying NBC in the local environment (Loring & Rantala, 1992) as very few areas remain 'pristine' for gathering representative background samples. It is equally difficult to differentiate natural and anthropogenic concentrations in river sediments due to the large scale drainage area covered by the river system and numerous potential source inputs.

The Black River and adjoining tributaries is a prime example of a river system suffering from unsustainable development, and discharges from informal settlements alongside poorly functioning waste control magnifies the difficulties of regulating river pollution in Cape Town (Haskins, 2012). Efforts towards the recovery of the Black River have recently been undertaken and the City of Cape Town's programme to improve the quality of the water discharged from the Athlone wastewater treatment works (WWTW) largely contributed to this improvement (City of Cape Town, 2013). However, there is still inadequate knowledge of sediment pollution in the Black River, along with many other urban rivers (Okonkwo et al., 2005).

An investigation has previously been conducted on heavy metal partitioning in sediments of the Black River (Haniff, 2002). The main aim of this investigation was to understand the forms in which heavy metals were present of which directly relates to the toxicity of the element. The fractions were then combined to provide total elemental concentrations which were used to estimate the contamination status of the Black River sediments using the consensus based approach (Gordon & Muller, 2010), whereby assuming that total concentration of an analyte is the critical factor in its hazardousness. It was revealed that total concentrations of arsenic, selenium, cadmium, chromium, copper, lead, mercury, molybdenum, nickel and zinc exceeded maximum permissible levels of the most relevant guidelines at the time (SABS, 1999).

Investigating contamination in urban rivers such as the Black River can aid meeting targets of Water Quality Regulations of 2006 (Legal Notice No. 121) and assist in the production of South African SQG as described in the WRC Phase I Report for Developing SQG (Gordon & Muller, 2010). Data produced from investigations can also be used in the formation of efficient, site specific remediation strategies.

Current remediation strategies and flood risk mitigation techniques occurring in the Black River include dredging sediments and removing the destructive *Eichhornia crassipes* (water hyacinth) which is an invasive species that depletes the river of oxygen (Newete et al., 2014). Both extraction methods involve heavy machinery and it is likely they are causing adverse environmental effects as dredging leads to the re-suspension of sediments and remobilization of heavy metals (Department of Environmental Affairs, 2011). Another critical factor in the removal of water hyacinth is that the plant is known to be highly efficient in up-taking heavy metals via root cells (Buta et al., 2011). It is therefore of interest to understand its current role in heavy metal up-take and storage in the Black River as this ability could be utilized further in a strategized remediation plan which could indirectly reduce the quantity of heavy metals settling in the river sediment.

This study aims to identify the contamination status of the Black River and critically assess the methods available for quantifying NBC and as a result, identify suitable remediation strategies and contribute to the research required to form SQG for South Africa. Section 2 of this thesis presents the aims and objectives of this study; Section 3 discusses the current setting of the Black River, Section 4 evaluates existing methods available for quantifying NBC and forming SQG; Section 5 presents existing data useful to the objectives of this study and Sections 6, 7, 8 and 9 present the methodology, results, discussion, methodology limitations and conclusions respectively.

# 2. AIMS AND OBJECTIVES

## 2.1. Aim

The aim of this study was to identify the presence and extent of contamination within channel bed deposits of the Black River.

## 2.2. Objectives

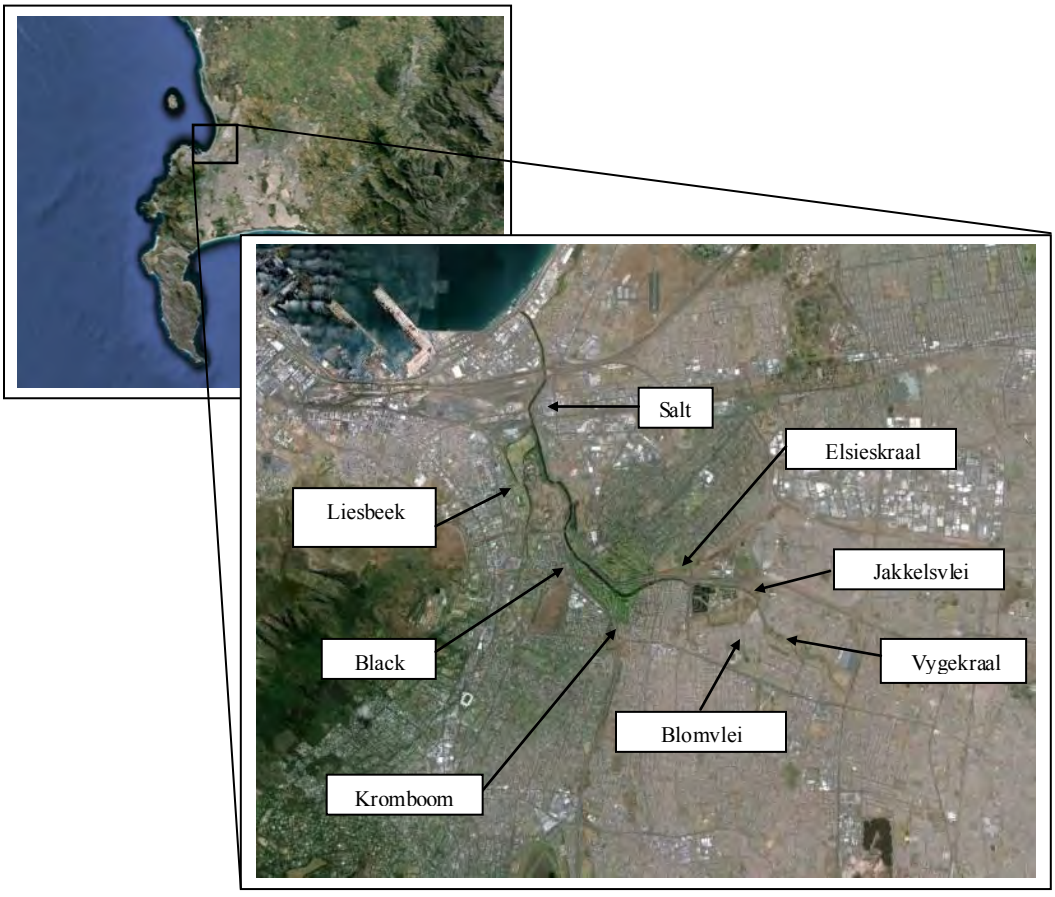
The main objectives of this investigation were as follows;

- From existing sediment and water quality data, select a transect along the Black River in which to investigate heavy metal concentrations in the sediment;
- Analyse sediment samples for heavy metal concentrations;
- Quantify normal background concentration in the Black River;
- Describe and explain acceptable methods of producing normal background concentration to account for the complexity of an urban river's natural sediment input system;
- Provide a baseline data set of sediment toxicity in the Black River; and
- Investigate the efficiency of *Eichhornia crassipes* (water hyacinth) as a phyto-remediator in the Black River.

# 3. CURRENT SETTING

## 3.1. The Black River

The Black River is located within Cape Town's Salt River Catchment area (Figure 1). A tributary of the river arises in Arderne Gardens in Claremont, and then flows underground before being canalized through the suburbs of Claremont and Rondebosch. The river then becomes un-canalized until it forms the Salt River in Maitland. Other major tributaries are the Vygekraal River, which runs through areas that include low cost housing suburbs of Athlone and informal settlements in Vygekraal, and the Elsieskraal River which runs through the industrial area of Epping and suburban areas of Thornton and Pinelands. These rivers join the Black River which flows past open public spaces and the M5 regional highway. The Liesbeek River drains water from Table Mountain and connects with the trunk of the Black River, flowing beneath a busy convergence of railway lines and roads, past industrial areas in the City Bowl and finally joining the ocean at Table Bay.




(Google Earth, 2015)

**Figure 1**. Location of the Black River and main tributaries

### 3.2. Geology

Sediment is a solid matrix of varying material size that has at some point been transported and deposited in a new location due to erosion. It comprises of varying amounts of organic matter and minerals (British Geological Survey, 2003).

The bedrock of the Cape Flats is Malmesbury Group which consists of conglomerates originating from the Berg Formation, and this is characterized by layers of dark grey, fine-grained greywacke and sandstone and is rich in NaCl (Ulanksy, 2000). The bedrock of the river catchment is expected to be overlain by superficial deposits in numerous areas. These deposits are classified as Aeolian, Marine and Fluvial, which are most likely to have contributed to the high sand content in the Black River (Adelana et al., 2010). There is expected to be a high abundance of quartz and carbonates which are relatively poor in metal concentrations and are more or less inert (Windom et al., 1989).

### 3.3. Meteorological data

The Black River catchment receives approximately 650 mm of rainfall a year (World Weather Online, 2015) with precipitation fluctuating according to the season. The water depth reflects these changes and during the dry summer months parts of the river bed are exposed to both hypoxic and anoxic phases (City of Cape Town, 2005). The flow is largely dependent on season and the water discharged from the Athlone Wastewater treatment works (WWTW) (Della Donna et al., 2012).

### 3.4. Surrounding land use

The river receives around 73,000,000 $m^3$/year of wastewater discharge from the Athlone WWTW and 12,000,000 $m^3$/year from Borchards Quarry WWTW (City of Cape Town, 2005). The quality of the wastewater discharged from these treatment works has recently improved as is observed by water quality data captured by the City of Cape Town between 2000 and 2014. Most WWTW have a higher success rate in reducing organics in water and are less efficient in the removal of inorganics due to the high costs and limited availability of technologies for removing inorganics (Barakat, 2011). Common heavy metals found in WWTW discharge includes As, Cd, Fe, Hg, and Pb (Rambol, 2013).

High levels of Pb are expected in the river as a result of particulate matter from various industries and roadside dust (Awadh, 2013). Road surface drainage provides a pathway for rain water to wash roadside dust into drainage systems which often discharge directly into rivers. Impermeable surfacing can often act as a barrier to prevent heavy metals entering the natural ground and consequently into groundwater, however due to the nature of the rainfall periods in Cape Town it is likely that impermeable surfacing does not prevent a pathway occurring to the natural environment, but instead allows sediments and heavy metals to accumulate during dry periods before being collectively washed into rivers during heavy rainfall periods in winter, causing a 'flash pollution' effect.

Canalized rivers often contain high sulphur and high organic content (Windom et al., 1989). These variables prevent natural sedimentation occurring and increase heavy metal accumulation due to their ability to adsorb many heavy metals (Stephens et al., 2001).

### 3.5. Management of the Black River

Historically, the Black River has seen significant alteration with the use of canalization, reworking and lining with cement in many areas, resulting in a river channel very different to a natural one. Along with canalization, the river is expected to have seen significant dumping and infilling. The river is non-tidal due to the extensive changes that have occurred, and backflow from the sea is significantly prevented beneath the bridge of the N1, some 1km inland and upstream of the Salt River. There is little sediment within the canal of the Salt River (Haniff, 2002) and so the effect of the salt wedge on sediment is not known.

The sediments of the lower stretch of the river are intermittently cleared by a dragline clearing operation undertaken by the City of Cape Town. Records state that dredging has occurred since 1983 at least (De Clerk, 2009), however the details of these operations are vague. Deposits have been stored on the banks of the river before being removed to a waste disposal site, during which time mobile heavy metals may have re-entered the river. It is likely that heavy machinery has aerated the sediments and remobilized heavy metals into the water column, and so this activity may not be removing heavy metals but repositioning them further downstream (Stephens et al., 2013).

### *3.5.1. Water hyacinth*

There is an on-going effort to rid the Black River of *Eichhornia crassipes* (water hyacinth) which is an invasive species that depletes the river of oxygen (City of Cape Town, 2005). Set aside its destructive nature, water hyacinth is a hyper-accumulator through the extraction and accumulation of heavy metals (Zhang et al, 2004). Studies suggest the plant possesses the ability to up-take and store Cd, Cu, Ni, Pb and Zn, and has a very high affiliation to Hg (Hasan et al., 2007; Buta et al., 2011).

Due to the Black River hosting invasive water hyacinth it is of interest to investigate the ability of the plant to up-take potential contaminants as it could play a significant role in sediment remediation with the use of sterile strains to control the destructive nature of the species (Kadlec & Wallace, 2009). Once grown, the water hyacinth would be harvested/ removed from the river (along with the up-taken heavy metals), and deposited of accordingly. The main concern from phyto-remediation in most instances is the increased probability of bio-accumulation within the food chain whilst in the river system. Water hyacinth can however limit this impact due to the majority of the up-taken heavy metals remaining in the root system, resulting in few dependant feeders. Another attribute of the water hyacinth is that once up-taken into the root Cr (VI) is reduced to the less toxic form Cr (III) (Lytle et al, 1998).

## 3.6. Conclusions of current setting research

Based on available data of the historic and current setting, the Black River is expected to contain an inclusive range of heavy metals sourcing from industrial activity, roadside dust, raw sewage and water treatment work deposits. It is expected that As, Cd, Cr, Cu, Hg, Ni, Pb and Zn are of high concern in the Black River due to their persistence in aquatic environments and their associated risk levels.

Without disturbance, the less mobile and more persistent pollutants released into the Black River would have likely settled out of the water column close to the source due to the relatively slow and constant speed of the water, thus creating contamination hotspots. However, sporadic sediment disturbances and fluctuating environmental conditions suggest the natural settlement of sediments has been inhibited so currently the Black River sediment can be perceived as point source of pollution.

Given the dredging and canalization of the Black River it is not known whether any ambient or historic heavy metals are still present at depth in the sediment profile, nor can it be concluded whether historic pollutants have been homogenized with new sediments.

# 4. BACKGROUND CONCENTRATION AND SEDIMENT QUALITY GUIDELINES

## 4.1. Contamination

There are many variants to the meaning of terms such as ‘contamination, contaminant, and pollution’. However, contamination generally refers to ‘the presence of an unwanted constituent in a place or substance’, whilst a contaminant is ‘the form or type of said constituent that makes a place or substance impure’ (Oxford Dictionary, 2015). Pollution tends to be used to describe the introduction of contaminants into the natural environment, which is an event that causes adverse effects (Oxford Dictionary, 2015). Heavy metals are therefore referred to as analytes in this report, and only referred to as contaminants once identified as being present in significant concentrations. (As and Sb are two of the focus elements and are in fact metalloids however they are included in the group referenced to as heavy metals). There is no definition of contaminated sediment in South African legislation. The US Water Resources Development Act 1992 Section 501(b)(4) defines contaminated sediment as ‘aquatic sediment which contains chemical substances in excess of appropriate geochemical, toxicological or sediment quality criteria or measures’. As stated in the National Action List for the Screening of Dredged Sediment Proposed for Marine Disposal (Department of Environmental Affairs, 2011), this definition establishes two critical issues, that is whether chemicals are present in ‘higher than normal concentrations’ and whether these substances pose a risk to the health of an ecosystem. These two circumstances do not always occur simultaneously which is why both NBC for establishing enrichment and SQG for establishing toxicity are crucial tools in sediment investigations.

‘Normal background concentration’, ‘ambient background contamination’ and ‘estimated background values’ are all terms which generally refer to the concentration at which chemical substances are naturally present in the environment, however there are variations within the meanings, for example ambient background contamination refers to pristine environment concentrations plus minor anthropogenic inputs where no source can be identified, such as historic industrial activities or minor amounts of particulate matter from atmospheric pollution.

Normal background concentration as defined by the British Geological Survey (Ander, 2013) is the amount of naturally occurring chemical substance which is derived or has originated from natural processes in the environment as close as possible to pristine conditions. Identifying NBC holds higher value as the data is more useful on a wider scale than ambient background contamination.

Anthropogenic activities release heavy metals into the environment. Very fine particles in sediment provide a large surface area that can host heavy metals by adsorption, ultimately controlling their movement and distribution through the environment. These heavy metals pose a higher risk to the environment than NBC, as changes in environmental conditions can result in the release of heavy metals from particles and change its bio-availability (Li et al., 2013). Quantifying NBC is required to evaluate the impact urban development has on the environment however identifying the difference between NBC and anthropogenic contribution of heavy metals is a complex task, particularly in river sediment investigations as there the numerous variables altering the sediment (Chapman, 2007). Obtaining NBC is also one of the initial steps towards forming SQG for classifying a site's toxicity status as stated in the WRC Phase I Report for creating SQG (Gordon & Muller, 2010).

### 4.2. Sediment Quality Guidelines

Sediment is important to ecosystems in both the marine and freshwater environment as it is a socio-economic, environmental and geomorphological resource (European Sediment Research Network, n.d.). Often, one of the main components of environmental Action Lists of many countries is to create SQG in the effort to improve degraded sediments and are intended to be protective of biological resources and predictive of adverse effects (Wenning & Ingersoll, 2002: Department of Environmental Affairs, 2011). Numerous processes that influence the bioavailability of heavy metals in sediment often result in a delineated relationship of adverse biological effects, and so as it stands one SQG cannot be used globally (Wenning & Ingersoll, 2002).

Similar to terminology of background concentration, there are also various terminologies for SQG such as sediment action levels, sediment quality targets, sediment quality benchmarks etc, but ultimately most refer to the same system of numeric chemical concentrations that inform of the risk to biological resources (Department of Environmental Affairs, 2011). Due to the complexities effecting sediment systems, no existing SQG can precisely predict toxicity and can only provide an indication (Department of Environmental Affairs, 2011). All scientifically defensible and internationally applicable research of sediment contamination is useful for collaborating knowledge and advancing methods of best practices for improving SQG (Kwok et al., 2015).

Evaluating sediments using SQG from other regions provides a poor interpretation due to regional variations. In order to achieve a more informed and accurate understanding of risk, regional SQG should be formed (Wenning & Ingersoll, 2002), as what could be an abnormal concentration of an element in one region could be the equivalent of the natural abundance in another. Existing SQG, for example Consensus Based Sediment Quality Guidelines (CBSQG) (MacDonald et al., 2000) usually come in the form of two or three values for each element in order to provide a guide of whether the ecosystem is at low, medium or high risk from contaminated sediments; in the case of CBSQG are written as Effect Level (PEL), Midway Effect Level (MEL) and Threshold Effect Level (TEL). Such values are established by identifying the probability at which adverse affects occur on benthic dwelling organisms. The consensus based approach to developing SQG uses a synthesis of information to identify casual effects as opposed to correlative effects, which also takes into account the assortment of contaminants for predicting sediment toxicity (Gordon & Muller, 2010).

A list of Maximum Permissible Metal and Inorganic Content in Soil for South Africa can be found in The South African Bureau of Standards (1999). This is however specifically for soil. South Africa does not have its own set of sediment quality guidelines, and those created for United States and Canada are most commonly used in place. The National Environmental Management: Integrated Coastal Management Act (Reg 2012:635) states that to form SQG specifically for South Africa, NBC need to be established.

### 4.3. Global Average Values

The bedrock of the Black River basin is mostly Malmesbury Shale. Average Shale Values (ASV) (Turekian and Wedepohl, 1969) and SCO-1 (USGS, 2000) are data sets of major and trace element concentrations expected to be present in continental shale. They were formed by analyzing shale sediments collected from pristine environments and have been used as NBC in previous contamination investigations to estimate sediment enrichment (Greenfield et al., 2007: Ong et al., 2013: El-Sayed et al., 2015).

The grey area within contaminated land regulations in many countries allows regulatory agencies and consultancies to determine a site's pollution status based on the screening of global average values, mainly because of the unrealistic expenses involved in obtaining site specific values. Screening against global averages can result in statistically poor estimations of anthropogenic and natural source input concentrations, and does not take into account toxicity risk. Due to regional geochemical variations it is poor practice to solely rely on global values for quantifying anthropogenic heavy metal input (Amorosi et al., 2014) however screening results with global average values is useful as a preliminary indicator of enrichment and an asset when costs are limited for investigations. There is increasing acceptance that global average values or existing SQG are used as a reference instead of obtaining site specific NBC i.e. investigating concentrations in sediments from pristine environments (Borja & Collins, 2003: Ander et al., 2013: Sakan et al., 2015). A circumstance where global averages are a necessity is when there is little possibility of gathering samples representative of NBC.

### 4.4. Methods of establishing normal background concentration

There are generally three methods used for establishing NBC for investigating contamination which are discussed in literature. These are;

1. Indirect - (Statistical). The statistical frequency method refers to statistical processing, where anomalies in data sets of geochemical results are eliminated using graphical and computational techniques, i.e. with 1 +/- 2 standard deviation (Gałuszka & Migaszewski, 2011).

Another statistical approach to obtaining NBC is spatial analysis, where geochemical maps are used to visually delineate geochemical anomalies which usually results in a clear and robust evaluation. Although this method is relatively easy to conduct it does not take into account soil or geological properties and therefore cannot be used sufficiently to represent spatial distribution of NBC for areas where no existing data are available.

2. Direct - (geochemical). This method uses average results of samples which represent pristine areas (Horckmans et al., 2005), such as deep river sediments or deep soil horizons collected from the study area. These results portray non-subjected data of the study area as the matrix has not undergone geochemical processing. The reliability of this method is questionable as there is no set boundary between pristine and not-pristine environments, in which case the NBC should be used to form a range and not an exact value. This method is costly and requires expert knowledge during the interpretation stage (Matschullat et al., 2000), particularly if isotopes are used to track the source.
3. Integrated - this involves a combination of the two methods, for example collecting samples in the pristine environment and also using ASV. This reduces the cost of the direct approach and makes use of existing data in a more objective manner by taking local geological variations into account (Gałuszka & Migaszewski, 2011).

### *4.4.1. Alternatives and viable recommendations- Integrated approach*

Two recent studies on contaminated sediments present new approaches to discern and compare anthropogenic and NBC. Firstly, instead of identifying contaminant limits, Ander et al., (2013) identified areas of significantly elevated concentrations as contaminant domains and provided an evaluation using upper threshold values. The upper threshold is described as NBC which was calculated using the upper 95% confidence limit of the 95$^{th}$ percentile for the soil analyses of each identified domain. Although useful for comparing samples collected within a given area, this method can provide data of limited reliability if too fewer samples are collected, and the uncertainty is in the percentile values of the results which determine the NBC. This method is highly suiting for well-funded investigations and also a viable method when no data on background concentration exists.

Amorosi et al. (2014) were able to predict the natural spatial distribution of Cr, Ni, Cu, Pb and Zn as a function of three factors; source-rock composition, grain size and the degree of soil weathering. The study was conducted in the urbanized area of the Southern PO Plain in Italy, and the results were presented in the form of a pedogeochemical map. The 95$^{th}$ percentile method (Ander et al., 2013) was also used in this study. The foundation of this research required a significant amount of existing data for the area (lithological and geological) and demonstrates that the statistical approach is only useful when reliable data are available. Conversely, this particular statistical method does allow for gaps of analytical data to be modeled by using the interpretative pedogeochemical map.

In order to produce versatile data that can be used in other regions to help form SQG, Gałuszka & Migaszewski (2012) suggest just one method should be adopted and used for establishing NBC. Similar to the perplexity caused by unclear terminology in this research field as described in sections 4.1 and 4.2, the numerous practices and methods in use for establishing NBC result in little collaborative advancements in research of river sediment. The absence of quality standards for the formation of SQG has caused confusion in remediation strategies and environmental law disputes (Carlon, 2007). In this sense adopting a universal standard method would be useful for clarification in such circumstance. However, limiting investigations to using a singular, globalised method to create NBC would be restricting the use of some resources which may be available for particular investigations, as each method brings its own benefits to the research field and makes use of costs and resources available at the time of the study.

Tuchman (2012) suggests a bifurcated approach should be adopted for contaminated sediment investigations, whereby the method comprises of collecting core samples for site specific research, and investigating water dynamics at the same time to evaluate general behaviour and improve our understanding of heavy metal distribution in sediment. Drawbacks of this method include having more than one domain to investigate i.e. sediment, water and environmental variables which would result in a large expense of the research.

### *4.4.2. Alternatives and viable recommendations; Normal background concentrations*

Gordon & Muller (2010) list three factors in the development of SQG for South Africa. These are biological testing, establishing NBC and making use of existing SQG. Existing SQG do not take regional/ geological variations into account, and NBC alone cannot be used to form SQG for the main reason that it does not take bioavailability into consideration. Although the WRC favors biological testing assessments for the formation of SQG as it provides high certainty in the guideline values, resources available in South Africa may limit this option. Advancing methods of establishing NBC and forming a large data base of NBC for different regions would be a robust advancement in the research field. The WRC report also exhibits the usefulness of aligning SQG with Water Quality Guidelines and therefore stresses the importance of contamination assessments which have a bifurcated end use for data (i.e. data can be used in future contamination investigations as well as being used in evaluating toxicity of the investigation site). A drawback of using NBC as a screening method is that the results suggest that sediment concentrations which are not higher than NBC are not hazardous, which is not always the case: Likewise an exeedence of NBC does not necessarily mean there is a biological risk (Batley & Maher, 2001: Gordon & Muller, 2010). A combination of all three tasks described in the WRC report is the most effective method in assessing sediment quality and so NBC plays a vital role in the production of SQG for South Africa.

Another approach to investigating the contamination status of a site would be to conduct a multiple phase investigation, which would comprise of a preliminary investigation of enrichment of a site based on NBC exceedence. An evaluation at this stage could be followed by a reassessment at a conservative level depending on the outcome of the initial screening and so the biological effects basis would only be required if sediments exceed NBC. A phased methodology such as this would allow for an informed decision to be made for an efficient remediation strategy whilst providing universally applicable data sets to contribute to a standardized national database. Providing such data sets is one of the recommended outcomes in International Conference on Deriving Environmental Quality Standards for the Protection of Aquatic Ecosystems (Kwok et al., 2015).

### *4.4.3. Alternatives and viable recommendations – Coarse grain fraction of sediment*

Kalendar (2013) and Cabral Pinto (2014) suggest that it is reliable to analyse unaltered rocks in the catchment to establish NBC for sediments. When using any approach to establish NBC for river sediment a number of parameters must be assumed. One such assumption within the direct approach is that all natural sediment in the investigated river is derived from the same pristine environment, whereby assuming each grain size fraction of the sediment derives from the same mineral. Another assumption is that sedimentation has provided an even distribution of grain sizes throughout the river bed. Given that the larger particle fraction of sediment is mostly inert compared to mud (and assuming it derived from the same source as the other fractions of the sediment) it could be used to establish NBC provided that any adhered heavy metals on the particles are removed. This concept is similar to that suggested by Kalendar (2013) and Cabral Pinto (2014) above, and aims to provide NBC which take into account the complete geological composition of the river basin. An argument against this proposed method is the large grained sand is assumed to not have undergone lithological, mineral, basic or ultra-basic changes whilst transporting between source and riverbed; such processes can undoubtedly affect the geochemistry of the grains (but are often overlooked in direct approaches of forming NBC anyhow). The simplest strategy to overcome this is by selecting the larger grains as opposed to fine/medium sand, as the smaller grained fractions are likely to have undergone further geochemical processing. It is also a large assumption that the sand derives from the same source as the mud fraction in the same proportions, therefore a starting point of such a method to form NBC would be to compare the chemical compositions of the different grain size fractions in the sediment.

## 4.5. Pollution Indexes

Once NBC are established there are a number of statistical methods available to quantify the anthropogenic input of heavy metal concentrations, such as the Pollution Load Index (Tomlinson et al., 1980), the Enrichment Factor (Sinex et al., 1981) and the Geo-accumulation Index (Muller, 1969). The Pollution Load Index (PLI) represents the number of times by which contaminant concentrations in the sediment exceeds NBC; and provides a singular result for overall pollution in a particular site or sample (Rabee, 2011).

The Enrichment Factor (EF) uses a reference element unlikely to be a pollutant i.e. is not usually an element released into the environment by anthropogenic input and compares the relative concentration with the other heavy metals (Klos et al., 2011). Aluminium and iron are most often used as normalizing factors in the EF, as their elemental concentrations are rarely disturbed by anthropogenic input. Iron is often deemed more favourable as its natural concentration in sediment is relatively uniform, it has a strong affiliation with fine solid surfaces and the geochemical properties of iron are similar to those of many trace metals (Naji & Ismail, 2011). The EF method of quantifying enrichment relies on the fact that the normalizing element is not affected by anthropogenic input. Karbassi et al., (2008) suggests the EF fails to indicate the intensity of pollution. This is true to some extent however the EF is used as an indicator of pollution i.e. the highest EF classification of an enrichment factor is greater than 40. If an analyte is present in a concentration higher than an EF factor of 40, it suggests further investigation would be required in any circumstance, and so the EF is effective in its use as an indicator.

The Geo-Accumulation Index (I-Geo) is used to determine the extent of metal accumulation in each sample and for each element with the use of NBC. The method is similar to that of the EF however a normalizing element is not used. All three methods use similar techniques however the EF and I-Geo are powerful as these methods provide a description of enrichment per element within a particular sample, whereas the PLI provides a status evaluation for all elements combined within a sample. Each method is only effective when used in conjunction with reliable NBC. Using all three allows for verification and to evaluate the suitability of the element chosen as a normalizing factor in the EF.

### 4.6. Summary

Investigating reliable and cost efficient methods to identify NBC would be advanced if ideas, terminology and results were collaborated on a global scale (Kwok et al., 2015). However as suggested in some literature, forming and adopting just one method to create NBC and SQG (Gałuszka & Migaszewski, 2012) i.e. in the form of an accredited standard test method, could ultimately restrict the strength of an NBC data set as every contaminated land investigation is unique.

Direct, indirect and integrated methods should therefore continue to be practiced and selected based on the outcome required of the investigation, with the aim to create collaborative data for use in the formation of SQG. In the case of the Black River, direct methods are of most value as the system has had many alterations and dredging has frequently occurred. Mulitple phased investigations would improve results and methods and would ultimately be more economical.

Continuing to rely on NBC data formed for other countries is not preferred due to the complexities affecting sedimentation and sediment chemistry in the Black River. It has been established in this section that use of global averages or existing NBC is useful as an indication of enrichment, but has limited reliability and so integrated or direct approaches are favorable for producing reliable NBC to evaluate sediment contamination. Pristine environments are difficult to identify for collecting samples for direct methods of forming NBC as there are no obvious boundaries as to what has or hasn't been impacted by anthropogenic activities. Using samples from pristine environments relies heavily on the assumption that the natural sediment in rivers derives from the same geological source on which the sample has been collected. Cleaned and milled coarse grain fractions of sediment collected from the investigation site could be used to identify NBC which takes into account the numerous and unique geological inputs in the river. Similar to many direct approaches, the effectiveness of this method depends on the given budget, as the reliability and precision of the NBC improves with the more samples analysed. This direct method also relies heavily on the efficiency of the technique used to remove the particles of any ambient or anthropogenic input and on the assumption that the the sediment grain sizes derive from the same sources.

# 5. EXISTING DATA

## 5.1. Water quality data

The City of Cape Town has monitored the water quality of the Black River at four selected locations along a transect of the Black River, and data from 2012-2014 has been interpreted for this study. Sampling locations of the monitoring points are presented in Figure 2. Data reveals that both dissolved oxygen and temperature fluctuations are seasonally dependant. Dissolved oxygen increases from 0.9 mg/L in the summer to 8 - 9 mg/L in the winter, whilst temperature falls from around 26 °C in the summer to around 11 °C in the winter. The pH increases very slightly from an average of 7.3 at the location of the Athlone WWTW to a pH of 7.4 downstream, but appears to have no seasonal trends.

The data suggests that the water quality observed in organic pollutant concentrations improves downstream. The Athlone WWTW appears to improve the water quality in the vicinity of the discharge point between sampling locations NR03 and NR04. Increased dissolved oxygen in the winter is likely to transform anoxic conditions, alter sulphur concentrations and therefore change heavy metal speciation (Li et al., 2013).


(Google Earth, 2015)

**Figure 2.** Water quality (NR) and sediment (H) sampling points from the City of Cape Town (2000-2014) and Haniff's sampling (2002)

### 5.2. Black River sediment mineralogy

X-Ray Diffraction (XRD) results of sediments taken from the Black River in 2002 are shown in Table 1 in order from upper reach to downstream (Haniff, 2002). Results suggest illite and kaolinite are the most abundant minerals. The origin of both illite and kaolinite is typically shale however kaolinite can also be clay derived from feldspar rocks (Webmineral, 2015). Sample H.05 collected after the confluence of the Liesbeek River is somewhat different to other samples due to the (albeit small) presence of gibbsite.

**Table 1**. XRD of clay separates; Black River sediment

| Sample | Major minerals present | Main collective elemental compositions |
|---|---|---|
| **H.08** | Kaolinite, calcite, lesser illite | $Al_2O_3$, $SiO_2$, $H_2O$, CaO, $CO_2$, $K_2O$, MgO, FeO. |
| **H.06** | Illite, kaolinite | $K_2O$, MgO, $Al_2O_3$, FeO, $SiO_2$, $H_2O$. |
| **H.01** | Illite/ mica-smectite, kaolinite | $K_2O$, MgO, $Al_2O_3$, FeO, $SiO_2$, $H_2O$, $Na_2O$, CaO. |
| **H.02** | Illite/ mica-smectite, kaolinite | $K_2O$, MgO, $Al_2O_3$, FeO, $SiO_2$, $H_2O$, $Na_2O$, CaO, |
| **H.03** | Mainly kaolinite, lesser illite | $Al_2O_3$, $SiO_2$, $H_2O$, $K_2O$, MgO, $Al_2O_3$, FeO. |
| **H.04** | Mainly kaolinite, lesser illite/ mica-smectite | $Al_2O_3$, $SiO_2$, $H_2O$, $K_2O$, MgO, $Al_2O_3$, FeO, $Na_2O$, CaO. |
| **H.07** | Kaolinite, illite/mica-smectite | $Al_2O_3$, $SiO_2$, $H_2O$, $K_2O$, MgO, $Al_2O_3$, FeO, $Na_2O$, CaO. |
| **H.05** | Kaolinite, mica, smectite, gibbsite | $Al_2O_3$, $SiO_2$, $H_2O$, $Na_2O$, CaO. |

(Hannif, 2002)

### 5.3. Normal background concentration

The XRD data suggests the Black River sediments derive from shale. Two previous investigations on pristine sediments and soils of the Malmsebury Shale (Soderberg, 2003: Herselman, 2007) were used with ASV to form NBC for the Black River basin and are provided in Table 2. Obtaining site specific data is preferable than using ASV, however too few values were available from existing data of the region's pristine environment therefore the ASV were also used. The two sets of ASV were those of Turekian and Wedepohl (1961) and Cody Shale reference material from Upper Cretaceous Shales (USGS, 1995).

**Table 2.** Normal background concentrations of focus elements (mg/kg)

| | Al | As | Cd | Cr | Cu | Fe | Ni | Pb | Sb | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **Turekian & Wedepohl (1961)** | 88000 | 13 | 0.3 | 90 | 45 | 47200 | 50 | 20 | 1.5 | 95 |
| **SCO-1 (1995)** | 72300 | 12 | 0.14 | 68 | 29 | 35900 | 27 | 31 | 2.5 | 100 |
| **Soderberg (2003)** | - | - | - | 66 | - | - | - | 16 | - | - |
| **Herselman (2007)** | - | - | 0.1 | 71.9 | 29.5 | - | 38.7 | 21.7 | - | 45.2 |
| **NBC** | **80150** | **12.5** | **0.18** | **74** | **34.5** | **41550** | **38.6** | **22.2** | **2** | **71** |

## 5.4. Heavy metals in Black River sediment

Haniff (2002) conducted an investigation on the chemical partitioning of heavy metals in the sediments of the Black River and Table 3 shows the combined chemical partitioning concentrations for each heavy metal investigated. Samples were collected from locations shown as 'H' in Figure 2. The specific fractions of heavy metals were measured to quantify the bio-availability, therefore risk levels were based on an equilibrium state of variables in the investigation. The sediment tested contained grain sizes of less than 2 mm. The chemical partitioning revealed the organic matter to be the main host for Cu and Pb in the sediments. Haniff suggested there should be concern regarding phyto-toxicity in the Black River due to high concentrations of Cd, Cr, Cu, Hg, Pb and Zn.

Sililo (1997) cautions that it should not be assumed that an anoxic zone entirely attenuates and immobilizes contaminants, and so any concentrations present should be deemed hazardous regardless of its current form, as it has the potential to become bio-available with the offset of changing environmental conditions (which undoubtedly occurs frequently in the Black River).

### *5.4.1. Total heavy metal concentration in 2002*

To understand the contaminative and toxic state of the river in 2002, concentrations of Haniff's chemical partitioning were combined to provide total concentrations of each element. The totals were applied to the CBSQG (MacDonald et al., 2000) as described in Section 4.2 and exceedances are shown in red in Table 3. Threshold Effect Levels (TEL) were exceed on a number of occasions which suggests high probability of the analytes having a toxicological effect. It is evident that in 2002 the highest toxicological concern arose from As, Cd, Cr, Cu, Pb and Zn concentrations.

It was revealed that samples H.03 and H.04 collected close to the Raapenberg Road and next to the Raapenberg Wetland bore the highest toxic risk. There was also a significant increase in two of the analyte concentrations, and a minor increase in some, between samples H.05 and H.01, which were located before and after Athlone WWTW. Lead was present in high concentrations in most of the samples collected. The values were not indicators of worst case toxicity risk as the sediment used was < 2 mm, whereas most contamination is found within the (usually organic rich) <0.064 mm range (Zhang et al., 2012), and could explain the increase between H.02 and H.03 as the location of H.03 was organic rich and beneath slow moving water of the river.

**Table 3.** Total combined chemical partitions of bulk sediment from Haniff's 2002 results (mg/kg)

| | As | Ca | Cd | Cr | Cu | Fe | Hg | Ni | Pb | Si | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **H.08** | 1.3 | 4358 | 0.23 | 9.2 | 15.5 | 1095 | 0.046 | 2.3 | **63.1** | 398.6 | 109.4 |
| **H.06** | 0.5 | 1851 | 0.06 | 3.3 | 4.2 | 202 | 0.244 | 0.5 | 12.8 | 116.7 | 46.8 |
| **H.01** | 3.4 | 11474 | 0.33 | 16.6 | 30.9 | 1161 | 1.075 | 6.1 | **106** | 424.7 | **217.3** |
| **H.02** | 1.4 | 3571 | 0.05 | 6.2 | 5.6 | 536 | 0.786 | 1.9 | 11.6 | 190.1 | 59.9 |
| **H.03** | **10.5** | 12609 | **1.26** | **60.8** | **95** | 3765 | 0.878 | **31.4** | **275.9** | 1199 | **618.2** |
| **H.04** | **9.8** | 4531 | **1.04** | **70.5** | **58.3** | 5210 | 0.447 | 20 | **180** | 1502.8 | **480.5** |
| **H.05** | **15.7** | 1762 | 0.58 | **54** | **72.1** | 4200 | 0.354 | 12.8 | **381.4** | 1507.8 | **372.6** |
| **H.07** | **12.9** | 1330 | 0.47 | 34.9 | **34.6** | 2998 | 0.154 | 10.7 | **91.6** | 741.7 | **190.2** |

**Figures in red are exceedances of CBSQG*

### 5.5. Heavy metal behaviour in river sediments

Although no two contaminated sites are the same, conclusions from previous studies were used to understand heavy metal behaviour. Some of the more significant influential variables which effect heavy metal presence are described in this section. Knowledge of geochemical cycling of heavy metals can be used to ascertain the likely variation in concentrations based on the conditions of the river at the time of sampling. Bio-availability has been overlooked in the consensus based approach as each form of an analyte has the potential to become bio-available with a change in conditions. Urban rivers are complex systems with continuous physicochemical changes occurring from shifting environmental conditions and the redistribution of sediments. Previous studies suggest that overall mobility reduces in order from Cd, Pb, Cu, Ni to Cr, which would result in most Cr remaining in sediment and Cd mostly residing in dissolved state (Filgueiras, 2004).

### *5.5.1. Grain size*

Most sediment contamination investigations conclude that coarse grain fractions of sediment nearly always contain less heavy metal concentrations than mud fractions (Rubio et al., 2000: Haiyan et al., 2015). A study conducted on heavy metal contamination in a river and estuary in northwest Spain (Filgueiras, 2004) concluded that the average concentration of Cu and Zn in the mud fraction was seven times higher than the average concentration in sand. Concentrations of Pb and Cr were four times higher in the mud fraction than sand and Ni and As concentrations were double in the mud fraction than sand (Rubio et al 2000). This predictability between grain sizes concentrations could be used to form conclusions on the ability of sand to buffer the more polluted mud fraction.

### *5.5.2. pH and oxygen*

Although there are many factors which control heavy metal mobility, pH is one of the more influential variables. Under oxidized conditions Cr is most mobile, particularly with high $H_2S$ levels, whereas Fe and Mn are most mobile under reduced conditions in which dissolved oxygen and $H_2S$ are absent (Rambol, 2013). An oxidized condition averts the release of Sulphur which in turn prevents the reduction of metals and so they remain mobile in the environment. Anoxic conditions often contain the highest concentrations of immobilized heavy metals (Jain & Ram, 2009).

### *5.5.3. Free ions*

Samples collected from close to the river mouth in the same study described in 5.5.1 (Rubio et al, 2000) showed less heavy metal concentrations than further upstream. The possible reason for this is naturally higher P, $K^+$ and $Na^+$ levels within saline water will inhibit charged sites on clay particles, subsequently remobilizing the heavy metals which were previously hosting the charged sites on the clay surface (Jain & Ram, 2009). A study conducted on Table Mountain Group soils revealed high abundance of $Na^+$ and $K^+$ (Ulanksy, 2000). With the Liesbeek draining land on the Table Mountain Group and converging with the Black River close to the river mouth, it is possible that inhibiting ions such as $Na^+$ and $K^+$ are highest from this convergence onwards and could have the same inhibiting effect on charged clay surfaces; remobilizing heavy metals (Flyhammer & Håkansson, 1999).

Although mud can hold metal ions with higher efficiency than larger grained sediment, it is important to note that river sediments are commonly around 90 % sand and 10 % mud and so it is only a minor fraction of the sediment which can hold significant quantities of heavy metals.

### *5.5.4. Organic content*

Organic matter is able to bind heavy metals and has a strong affiliation with heavy metal concentration in sediments (Sklodowski, 2006). With exceptionally high input of organic wastes from multiple sources it is likely that heavy metals in the Black River bind with organic matter in considerable quantities. The most significant inputs of organic matter in urban rivers are likely to be industrial and storm water drainage and to a lesser extent wastewater from informal settlements. Like most influential variables, each focus element behaves and binds differently with organic matter, often dependant on the form in which the element is present. Likewise the presence of organic matter can influence the form in which a heavy metal is present. Once bound, heavy metals are likely to settle out of the water column along with the organic matter into the river sediment.

### *5.5.5. Toxic elements, likely anthropogenic sources and typical behaviour*

As the sediments of the Black River are frequently disturbed and due to the numerous possibilities of sources and pathways, it is unlikely that point-sources of pollution in the Black River can be directly linked to contamination. However, understanding element behaviour in different conditions, identifying typical sources and its relative toxicity can assist in the identification of suitable remediation strategies and in forming SQG. Commonly investigated elements in contamination studies are chosen based on their known toxicity risks and persistence in the environment, most of which are metals or metalloids. Those which have been chosen as analytes for this investigation have been summarized below.

Antimony is relatively soluble in water. It has been reported as the most enriched trace element in some aerosols (Shotyk et al., 1996; Krachler et al., 2005) and is also a waste product/released from mining and smelting and mineralized areas (Fu et al., 2010).

Antimony is not readily mobilized in the environment, and is expected to have low bioavailability in soils, plants and animals surrounding such sources according to a study conducted on the surrounding ecosystem of a smelter in England (Ainsworth et al., 1990). Arsenic is unique as it is sensitive to mobilization in relatively neutral pH conditions and under both oxidizing and reducing conditions. It is a by-product of smelting and mining processes and has a relatively high toxicity (Adal, 2015).

Cadmium is present in most mobile fractions within a river environment but is often bound to suspended matter, and becomes mobile when it comes into contact with saline water (Occupational Safety and Health Administration, 2015) however the main limiting factor of its mobility is pH. Cadmium is highly toxic (Adal, 2015) and is a by-product of tyre fillers, insecticides and metal processing. Chromium is often hosted by the organic and residual fractions (Haniff, 2002) and has low potential for mobilization. Its speciation significantly affects its toxicity and is potentially very toxic. Chromium is often released into the environment as a result of engine wear. Copper holds a positive correlation with organic carbon and soluble organics. Its toxicity is moderate to high (Adal, 2015) and is most commonly released into the environment as a result of vehicle engine and break lining deterioration. Lead becomes mobilized in decreased pH conditions and has been observed to have a low association with organic carbon (Naji & Ismail, 2011). It has a high toxicity rating (Adal, 2015) and is commonly released into the environment from petrol, tyre wear, oil and grease. The toxicity of Hg depends on the form in which it is present. It is often released into the environment from anthropogenic activities such as alkali and metal processing, incineration of coal and mining of Au and Hg. Mercury is insoluble in water (Adal, 2015). Nickel demonstrates little reactivity with oxygen and water. It has affinity for adsorption to clay and Mn oxides and is relatively low in toxicity (Adal, 2015). Zinc is soluble in most water conditions and does not become mobile easily when a change in temperature or pH occurs in the environment. Zinc can be released into the environment by tyre wear, oil and waste combustions and is also commonly found in wastewater discharge. It is of a low to moderate concern in terms of toxicity (Adal, 2015).

### 5.6. Conclusions of existing data

It appears the Black River sediments in 2002 were moderately polluted based on CBSQG exceedances, and that the quality of sediment decreased downstream of the Athlone WWTW. However, it is not known whether the WWTW was the main source of heavy metal concentrations due to the number of other inputs which potentially contributed to sediment contamination.

Based on element toxicity ratings from the Occupational Safety and Health Administration (2015) and concentrations recorded in 2002, elements of highest concern in the Black River are As, Cr, Pb and Zn. The reliability of the data is limited due to the number of unknowns of the methodology used in 2002 (i.e. measuring the fractions of an element individually by partitioning then adding the total fractions together to identify total concentration would ultimately create a wider margin of error) and due the conditions at the time of sampling.

The City of Cape Town's water monitoring data of the Black River suggests that nitrate levels have decreased and oxygen levels have increased, and ultimately water quality has improved in recent years. However, continuous monitoring has not been conducted on heavy metal concentrations in the water, and effects of clear up operations are reflected quicker in river water than in sediments.

# 6. METHODOLOGY

## 6.1. Preliminary investigation

The study began in September 2014 with an investigation of factors affecting the composition and distribution of sediments in the Black River. This included studying historic and current land uses, previous clearing operations and summarizing the micro-climate of the catchment. Common analytes investigated in contamination studies along with their typical behaviour in particular conditions were also researched.

Literature was reviewed to draw together results of previous Black River contamination investigations. Methods of establishing NBC was also evaluated and a new method was proposed which was based on requirements described in literature for producing NBC and SQG.

## 6.2. Sampling

Findings of the site investigation along with a standard method shaped the methodology chosen for the fieldwork. The American Society for Testing and Materials (ASTM) E1391 Standard Guide for Collection, Storage, Characterization, and Manipulation of Sediment for Toxicological Testing Method (2002) was followed in order to meet international standards of sediment sample collecting and to restrict the margin of error.

Sediment samples were collected at 27 points from the centre of the river bed at regular intervals along the selected stretch of the Black River and from tributaries as shown in Figure 3 (GS). Areas where the centre of the river was not accessible, a sample would be collected from the closest possible locality. Water hyacinth material which had recently been cut in preparation for removal and left in-situ was collected from four locations (WH) in close proximity to Athlone WWTW shown in Figure 4. The plant material was placed into bags and transported to the laboratory. As fieldwork was conducted doing the summer months, the river was shallow enough to wade between locations and equipment was kept on a canoe that was pulled along whilst wading.

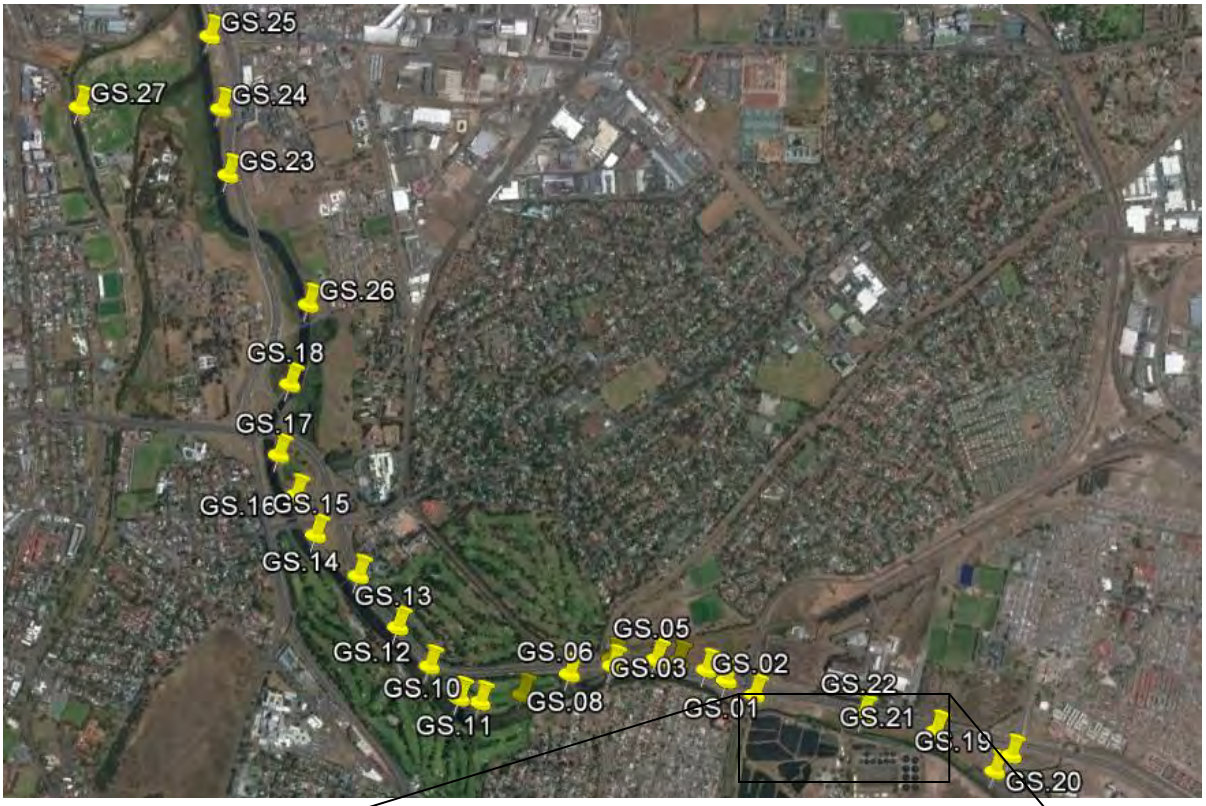



**Figure 3.** Sediment sampling locations


(Google Earth, 2015)

**Figure 4.** Locations of water hyacinth extraction

Sediment samples were extracted using a 70 mm diameter cylinder PVC pipe (acting as a corer to reduce disturbance) which was pushed by hand into the sediment at a slow, steady rate. The top of the pipe was covered to create suction before being pulled from the river. At least 500 g of sediment was collected from each site and each extraction reached 150 - 200 mm in depth from the sediment surface. If this method had to be compromised at particular sites then deviations were noted in the sediment log (Appendix I).

The sediment was placed into a tray directly from the pipe and laid out in profile where ever possible. A photograph was taken of each sample, the GPS coordinates were noted and descriptions (colour, biota, debris, odour, changes in depth, oily sheens, texture, consistency etc) were recorded with any other relevant details of the site including time, date, sample number, site identification and the water depth. The presence of redox potential discontinuity layers were also noted (a visual indication of black sediment is adequate for documenting anoxia according to ASTM 1391). All sample notes and information are presented in Appendix I. The sediment samples were transferred into an air-tight sealable bag and labelled. They were then stored in cooler boxes and on return to the laboratory were kept in a refrigerator until processed.

### 6.3. Sample preparation and processing

Small amounts of homogenized sediment of <2 mm grain size were selected from GS.22, GS.27, GS.10, GS.15, GS.23 and GS.24 and were dried and milled (these samples represent locations H.06, H.01, H.02, H.03, H.04 and H.07 of Haniff's 2002 investigation). All samples were milled to a size between 50 microns and 100 microns using a Seibtechnik swing mill. The milled samples were pressed into pellets of 9 g sample: 1 g Sasol Wax using a PE-EL hydraulic press*. The remaining sediment samples were dried at 40 °C for two days (or until fully dried) and weights were monitored and until a steady weight was maintained of each to ensure the sample was dry. Dry mass was recorded. The dry samples were divided into grain size of gravel, sands, mud by use of a sieve stack. Sieve sizes were based on Wentworth (1922) grain size classification system as shown in Table 4.

**Table 4**. Grain size classification

| Grain classification | Sieve space (mm) |
|---|---|
| Gravel | 2 - 64 |
| Very coarse sand | 1 – 2 |
| Coarse sand | 0.5 – 1 |
| Medium sand | 0.25 – 0.5 |
| Fine sand | 0.125 – 0.25 |
| Very fine sand | 0.0625 – 0.125 |
| Mud | < 0.0625 |

(Wentworth, 1922)

**Weights were recorded using a digital balance. All weights specified in methods (i.e. for the formation of a fusion disc) were all within 0.0005 -/+ g.*

The mud fractions were split; with half pressed into pellets of 9 g sample: 1 g Sasol Wax using a PE-EL hydraulic press, and the other half heated at 1000 °C for five hours to very loosely estimate organic matter content by loss on ignition. This was calculated using the equation provided in method ASTM D2974 (2000); Organic matter (wt%) = 100.0 – ((A x 100) / B), where (A) is weight of ash sample (g) and (B) is dried weight of sample (g). After weighing, the mud fractions were then roasted at 1000 °C for five hours to removal volatiles and all organic content. The roasted samples were then fused into fusion discs using 0.7 g roasted sample and 7 g 66:33 lithium borate flux in a Claisse M4 Fluxer.

The coarse grain fraction of the randomly selected samples GS.11 and GS.15 were viewed using a digital microscope, and micrographs are displayed in Appendix II. The coarse grain fraction of samples GS.21, GS.22, GS.02, GS.01, GS.04, GS.11, GS.15, GS.13, GS.23 and GS.25 were washed in 5% acetic acid, rinsed thoroughly using de-ionized water, dried and then milled.

A calibration curve for major and trace elements on the XRF was created using African Mineral Standards (AMIS) certified reference material (CRM) for major and trace elements listed in Table 5 and pellets were measured using this program. The fusion discs were run on a general majors program.

**Table 5.** Major and trace elements calibrated in the XRF major and traces program

| **Majors** | | | **Traces** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | MnO | MgO | As | Cl | Hf | Nb | Sb | Sr | U | Zn |
| CaO | $Na_2O$ | $TiO_2$ | Ba | Co | Hg | Nd | Sc | Ta | V | Zr |
| $Cr_2O_3$ | $P_2O_5$ | | Bi | Cu | La | Ni | Se | Te | W | |
| $Fe_2O_3$ | $SiO_2$ | | Cd | Ga | Lu | Pb | Sm | Th | Y | |
| $K_2O$ | $SO_3$ | | Ce | Ge | Mo | Rb | Sn | Tl | Yb | |

Finally four samples of 500 g of dried water hyacinth were roasted at 1000 °C for 5 hours. The resulting material was then crushed and run on 'Omnian' program on the XRF with use of a cup and film. Any elements present in the material identified using the generic Omnian program are provide in estimated wt %. This program is a standard suite already provided on the XRF software.

Based on the material (solid, liquid) and on the preparation method (pressed pellet or cup and film), the Omnian program provides a rough estimate of weight percentage of elements detected within the sample. The concentrations are provided with relatively low accuracy.

## 6.4. Data analysis

Values of the major elements Al, Cr and Fe are provided by XRF in wt % in oxidized forms of $Al_2O_3$, $Cr_2O_3$ and $Fe_2O_3$ respectively. The XRF results for the oxidized forms were divided by 10,000 for wt % to ppm values, and then divided by the stoichiometric oxide conversion factor 1.4615 for $Cr_2O_3$ to Cr,1.4297, 1.4297 for $Fe_2O_3$ to Fe and 1.8895 for $Al_2O_3$ to Al in order to compare the results against reference values which provide values in ppm.

### *6.4.1. Toxicity*

Total heavy metals recorded in the 2002 study and the mud results for the selected heavy metals of As, Cd, Cr, Cu, Ni, Pb and Zn were analysed using existing CBSQG (2000) Threshold Effect Levels (TEL) that if the element exceeds in concentration has a chance of causing harm to benthic dwelling organisms. If the concentrations exceed the Probable Effect Level (PEL) there is a high chance of toxic effect to benthic dwelling organisms. Although larger sized particles act as a buffer for heavy metal concentrations in sediment, the results for the mud are used without taking into account grain size distribution due to the importance of predicting worst case scenario of the toxicological risk to receptors. Concentrations are shown in Table 6. Results of Haniff's investigation were interpreted using the CBSQG to observe any changes that occurred between 2002 and 2015.

**Table 6.** CBSQG values

| Element | TEL | MEL | PEL |
|---|---|---|---|
| **As** | 9.8 | 21.4 | 33 |
| **Cd** | 0.99 | 3 | 5 |
| **Cr** | 43.0 | 76.5 | 110 |
| **Cu** | 32 | 91 | 150 |
| **Pb** | 36 | 83 | 130 |
| **Sb** | 2 | 13.5 | 25 |
| **Ni** | 23 | 36 | 49 |
| **Zn** | 120 | 290 | 460 |

TEL= Toxicity to benthic-dwelling organisms unlikely;
MEL= Chance of toxicity to benthic-dwelling organisms;
PEL= High chance of toxic effect to benthic-dwelling organisms.

| | |
|---|---|
| Below TEL | Level 1 |
| Between TEL and MEL | Level 2 |
| Between MEL and PEL | Level 3 |
| Above PEL | Level 4 |

(MacDonald et al., 2000)

### *6.4.2. Pollution indicators*

The EBV and the XRF results of the cleaned coarse grain fraction of the Black River sediments were applied along with the mud fraction XRF results to the Pollution Load Index (PLI), Enrichment Factor (EF) and Geo-Accumulation Index (I-Geo) to identify the level of enrichment of the selected analytes.

#### *6.4.2.1. Pollution Load Index*

A PLI value of less than 1 suggests the site is unpolluted whereas a PLI value greater than one signifies pollution. The equation for the PLI is as follows;

$$CF = C\ metal / C\ background\ value$$

$$\Rightarrow \quad PLI = n\sqrt{(CF1 \times CF2 \times CF3x \ldots xCFn)}$$

*CF = contamination factor; C metal = metal concentration in Black River mud fractions; C Background value = background value of that metal; n = number of metals.*

#### *6.4.2.2. Enrichment Factor*

The classification system for this index is as follows; EF < 1= background concentration; 1- 2 depletion to minimal enrichment; 2 – 5 moderate enrichment; 5 – 20 significant enrichment; 20 – 40 very high enrichment and > 40 extremely high enrichment. The XRD results in Table 1 section 5.2 show the presence of Fe which verifies the suitability of Fe as a normalizing factor. The element chosen as a normalizing factor needs to be one which is relatively consistent in concentrations in the environment and unlikely to be affected by anthropogenic sources. The EF was calculated using the following equation along with the concentration of Fe as the normalizing element;

$$(Cn_1 / x_1) / (Cn_2 / x_2)$$

*$Cn_1$ = concentration of heavy metal to investigate in selected sample; $Cn_2$ = expected natural input of selected element; $x_1$ = normalizing element (Fe) concentration; $x_2$ = normalizing element (Fe) concentration*

#### *6.4.2.3. Geo-accumulation Index*

The grading system for the I-Geo is as follows; I-geo ≤ 0 (grade 0) = unpolluted; 0< I-geo ≤1 (grade 1) = slightly polluted; 1 < I-geo ≤ 2 (grade 2) = moderately polluted; 2< I-geo ≤3 (grade 3) moderately severely polluted; 3< I-geo ≤4 (grade 4) severely polluted; 4< I-geo ≤5 (grade 5) severely extremely polluted; and I-geo > 5 (grade 6) extremely polluted. A factor of 1.5 is used to consider potential variations of the reference values from lithological differences within the sites. The equation for the I-Geo is as follows;

$$\text{I-Geo} = \log_2 (Cn / 1.5\ Bn)$$

*Cn=measured concentration of heavy metal in the Black River sample; Bn= NBC or coarse grain fraction concentration.*

### *6.4.3. NBC and Coarse grain fraction XRF results*

The XRF results of the coarse grain fractions were compared with NBC using the t-test to identify whether the natural input of inorganic sediment is of expected concentrations based on past studies.

## 6.5. Quality control

Quality control is important at all levels within fieldwork, sample preparation and sample processing. The purpose is to reduce the margin of error, provide data which is accurate and consistent and meet objectives of the project given the limitations of the methodology (United States Department of Agriculture, 2010). It is not possible to control all variables which affect data quality but such exceptions were duly noted.

Contamination between samples is a concern both in the field and laboratory. Measures taken to reduce cross-contamination included cleaning the field equipment thoroughly with water between each collection (water is deemed efficient without detergent as stated in ASTM 1391), and laboratory equipment was cleaned with ethanol before each new sample was processed.

Measures were taken to reduce the possibility of chemical changes occurring within the sediment after it was collected by stabilizing the environmental conditions during transportation to the laboratory. This included placing samples in air tight bags and storing them in cooler boxes. Although speciation is not a concern in this particular investigation, stability of environmental conditions was relevant in order to prevent heavy metals freeing from the particular grain size in which they were present.

Supernatants collected along with the sediment often washed out the finer particles before reaching the sample tray. This hindrance was overcome by creating suction from the top of the tube and covering the base whilst moving the sediment load promptly from the river bed to the tray. The supernatants were placed in the bag for transportation to the lab and were dried in the oven along with the sediments. Another common problem faced during the sampling was that if not enough sediment was collected in the first extraction another sample had to be taken. The second sample would then be taken within 400 mm from the original extraction.

### 6.6. Limitations

There are many variables which can affect the mobility and bioavailability of heavy metals. These include; pH (primary variable), temperature, sedimentation processes, sorption/adsoption, desorption, complexation, redox potential, organic matter content, Fe and Mn oxides, particle size, sulphur/ oxygen content, living organisms (bioturbation), conductivity, solar radiation (Winch, 2015), precipitation, wind patterns, hydraulic systems and mineralogy. These variables make sediment investigations in flowing aquatic systems difficult to assess. It was therefore imperative to identify any assumptions made in the limited conditions whilst analysing results.

This investigation targets the abundance and concentration of elements, and therefore the form in which the element is present is ignored. The complexities within the hydraulic system and sedimentation processes along with the data made available by the XRF prevent these factors being taken into account.

The fieldwork was conducted during the summer months. Based on available water quality data and noticeable trends, it is expected that the water temperature was some 26 °C and the pH was in the relatively neutral region of 7.3 - 7.5 at the time of sampling. No precipitation had occurred in the vicinity in the previous two weeks at least and dissolved oxygen would have been present in the annually low range between 0.6 mg/L and 1.4 mg/L. This suggests the stable environmental conditions at the time were unlikely to have recently initiated large scale redox reactions which would have mobilized or immobilized heavy metals.

Processing of the samples included wet chemistry (for acid rinsing the coarse grain fraction), roasting and weighing. Analysis of the samples was all conducted using XRF. Analytical uncertainties lay within both sample processing and equipment error.

The method used to identify organic matter was loss on ignition, and roasting a sample can only provide a rough indication of organic matter content. As organic matter was not a significant focus point of the investigation, it was the most suiting method given the budget of the project, as loss on ignition (after recording weight from heating at 100 °C to remove volatiles) does remove organic content, whilst oxidizing samples to avoid damaging the fluxer whilst being fused.

Secondary data used for this investigation had limited reliability as the 2002 total elemental concentrations were totals of the individual partitioning results. Each fraction of the elements were measured using different methods during the partitioning process so totals were captured from a different means to XRF. The comparative study therefore provides a generalized indication of the changes that occurred between 2002 and 2015, and is comparing results captured by two different forms of chemical analysis.

Similar to identifying the source of pollution, quantifying toxicity is also a complex task (Gordon and Muller, 2010). Many SQG for rating toxicity are available however variations between environments make it near impossible to form one data set that can be used in any location to rate toxicity.

Assuming the total concentration of an element is the most critical aspect in terms of toxicity allows for the mechanistic approach to be used rate toxicity. The CBSQG were therefore chosen to evaluate the toxicity of the mud fraction and the interpretation is of relatively broad observations.

There were two main limitations of the proposed method to form NBC by coarse grain fraction of sediment. Firstly, sedimentation dynamics could result in the division of larger and smaller particles when settling on the river bed, providing an uneven distribution. Secondly, using the correct pH for the acid rinsing technique to rid the coarse grain fraction of adhered heavy metal concentration requires further investigation; too weak and analytes stay on the surface of the sediments and too strong results in the disturbance of the elements inside the grains.

The plant material extracted for the purpose of the heavy metal investigation had already been cut down as part of the Black River management project and was awaiting removal for disposal. Collecting cut material was relevant in order to portray the plant material that is extracted during the normal practice of clearing the water hyacinth by the City of Cape Town, however the length of time the material had been cut for prior to collection was not known which may have caused affect on the heavy metals if decomposition of the plant material had already began. Analyzing the water hyacinth was to present a very basic indication of its ability to uptake heavy metals in the Black River and provide a foundation for further research. The Omnian results of the water hyacinth material only provide an indication of the plants potential in the remediation of the Black River as it only produces rough wt % values for the elements detected in the material. The resulting data indicated that the water hyacinth plant does contain high quantities of heavy metals but due to the reduced weight and increased density of the homogenized ashed plant material the true efficiency per wt% is not known nor can it be confirmed that the majority of heavy metals remained in the roots. Another limitation of the water hyacinth data is that XRF is not the favoured analytical method for measuring such material. ICP-MS would have been more suiting however the budget for the investigation prevented this from being an option. In order to obtain enough material for XRF analysis a large amount of water hyacinth was ashed and so concentrations appear high however the quantity of dried plant material to make enough ash was 500 g.

# 7. RESULTS

## 7.1. Overview

The sediments were analysed for organic content, particle sizing, and major and trace element concentrations and the ashed water hyacinth material was measured for heavy metal concentrations. The results of the laboratory testing are included in this chapter. Samples are placed in order of their appearance from the up-most point in the river prior to the Athlone WWTW, to the lowest point located in the Salt River, with the exception of the sample collected in the Liesbeek River (GS.27).

## 7.2. Observations of sediment

Sediments appeared loaded with organic material throughout the river. Disturbing the sediment in all locations resulted in increased turbidity due to the release of small particles into the water. The odour of $H_2S$ was noticeable in many areas, but was most pungent after disturbing sediments in the stretch of the river between GS.18 and GS.26. At the locations of GS.19, GS.21 and GS.22, sediments on the surface had a green algal covering. This covering was seen less frequently after the Athlone WWTW.

A digital microscope was used to view the coarse grain and fine grain fractions of the randomly selected samples GS.11 and GS.15. Particles of all sizes were well-rounded, suggesting a lengthy travel from source and the vast majority of the particles were quartz grains. It was common for the particles to have a black or green covering. The finer fraction particles appeared to statically hold small dust particles on the surfaces as shown in Appendix II. It was also noted that a small number of red-orange particles were present amongst the coarse grain fraction which could have been the result of Fe oxidation on the particle surfaces. Hand specimens of GS.05, GS.08 and GS.19 demonstrated that a large portion of gravel-sized grains in the samples were small (and often whole) horn shells (Cerithiidae family; unknown genus).

### 7.3. Organic content

Organic content was estimated for the mud fractions of the Black River sediments and is shown in Figure 5 by wt% loss on ignition at 1000 °C. Full results are provided in Appendix IV.

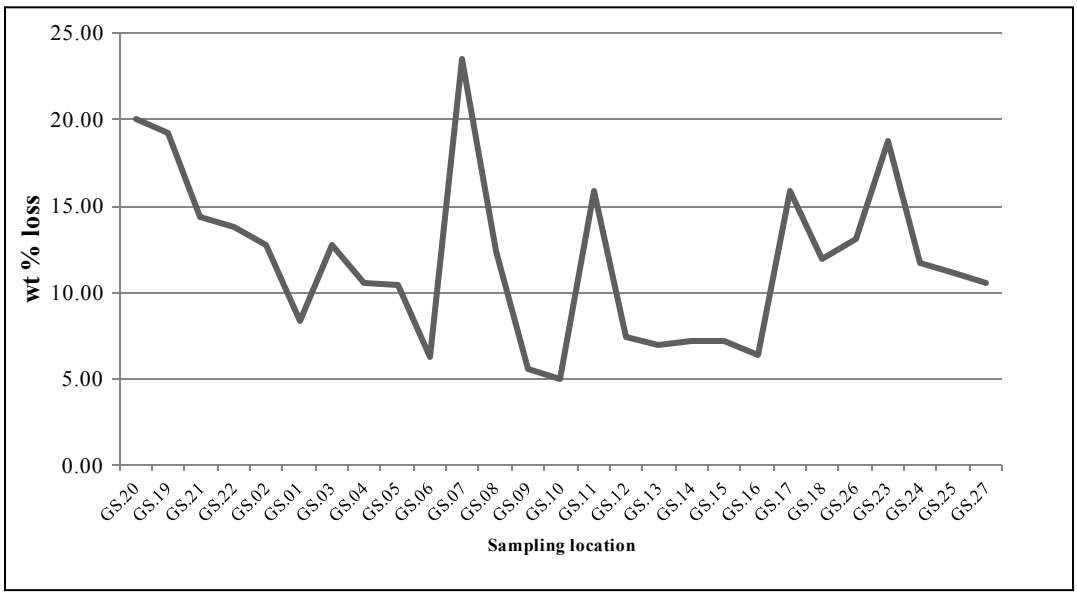



**Figure 5.** Loss on ignition of mud fractions (wt %)

### 7.4. Particle sizing

The percentage weight of each fraction is shown below in Figure 6 and full results are shown in Appendix IV.

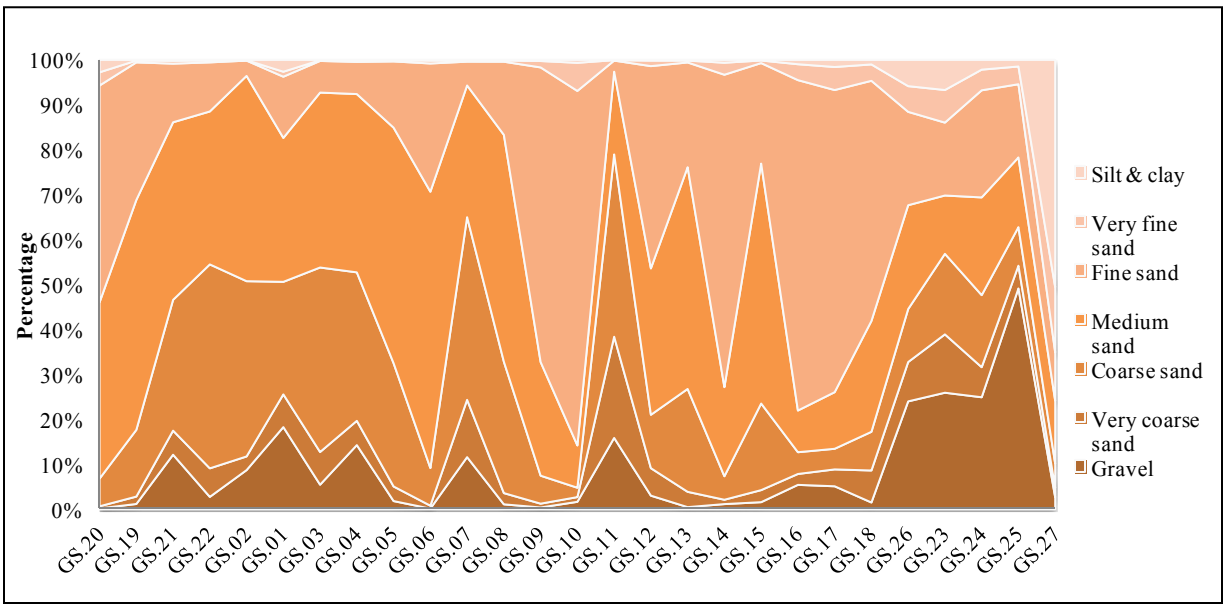



**Figure 6.** Particle size distributions in Black River sediments (wt %)

### 7.5. Coarse grain fraction

Focus elements for the identification of toxicity and elements required for the pollution indexes are provided in Table 7. Full results are provided in Appendix IV.

**Table 7**. Acid rinsed coarse grain fraction XRF results for selected determinands (mg/kg)

| Sample ID | As | Cd | Cr | Cu | Fe | Ni | Pb | Sb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| **GS.21** | 0.0 | 0.0 | 0.0 | 0.0 | 1858 | 3.5 | 15.6 | 0.0 | 41 |
| **GS.22** | 1.7 | 0.0 | 68 | 0.0 | 8184 | 9.9 | 28.8 | 0.3 | 84 |
| **GS.02** | 8.6 | 0.0 | 68 | 0.0 | 22382 | 24.3 | 35.8 | 0.4 | 56 |
| **GS.01** | 0.0 | 0.8 | 0.0 | 0.0 | 2144 | 0.9 | 5.7 | 1.5 | 94 |
| **GS.04** | 0.0 | 0.0 | 0.0 | 0.0 | 8292 | 2.7 | 4.9 | 2.3 | 41 |
| **GS.11** | 6.6 | 0.0 | 68 | 0.0 | 24900 | 31.0 | 44.5 | 0.4 | 115 |
| **GS13** | 0.0 | 0.0 | 0.0 | 0.0 | 10722 | 5.4 | 27.8 | 1.7 | 145 |
| **GS.15** | 4.0 | 0.0 | 0.0 | 0.0 | 8463 | 10.0 | 37.0 | 0.0 | 114 |
| **GS.23** | 0.0 | 0.1 | 0.0 | 0.0 | 2716 | 1.6 | 7.4 | 0.9 | 98 |
| **GS.25** | 1.3 | 0.8 | 137 | 59.5 | 90019 | 74.7 | 183.2 | 1.2 | 236 |
| **Av. coarse** | 2.2 | 0.2 | 34.2 | 6.0 | 17968 | 16.4 | 39.1 | 0.9 | 102 |

*Chromium is present in low concentrations and only detected to the nearest 0.1mg/kg. Due to the conversion factor between $Cr_2O_3$ and Cr, the results appear to be the same value, however this is due to XRF inaccuracy

### 7.6. Mud fraction analyte results

The analytes investigated for toxicity and enrichment were As, Cd, Cr, Cu, Hg, Ni, Sb, Pb and Zn as shown in Table 8. Sample GS.06 and GS.12 were applied to the Omnian program (Appendix III) due to the intensity of the material saturating the XRF on the major and trace program. Samples were arranged in occurrence from the upper reach of the Black River to downstream.

**Table 8.** Toxicity of mud using CBSQG values (MacDonald et al., 2000) in mg/kg

| | As | Cd | Cr | Cu | Ni | Pb | Sb | Zn |
|---|---|---|---|---|---|---|---|---|
| **GS.20** | 30.8 | 8 | 116 | 179 | 42.4 | 269 | 1.8 | 1430 |
| **GS.19** | 29.3 | 2.9 | 229 | 325 | 64.7 | 226 | 0.0 | 2193 |
| **GS.21** | 19.4 | 0.0 | 148 | 196 | 58.7 | 135 | 2.7 | 1286 |
| **GS.22** | 21.3 | 0.9 | 241 | 265 | 51.6 | 149 | 0.0 | 1225 |
| **GS.02** | 8.6 | 0.0 | 77 | 121 | 50.9 | 78 | 0.0 | 496 |
| **GS.01** | 5.9 | 0.0 | 49 | 23 | 24.0 | 41 | 0.0 | 166 |
| **GS.03** | 14.3 | 0.8 | 155 | 508 | 56.1 | 104 | 0.0 | 752 |
| **GS.04** | 15.7 | 1.9 | 77 | 525 | 60.1 | 147 | 1.9 | 1221 |
| **GS.05** | 16.0 | 1.5 | 172 | 377 | 60.1 | 171 | 0.0 | 1013 |
| **GS.07** | 23.4 | 4.9 | 112 | 333 | 36.0 | 177 | 1.5 | 1958 |
| **GS.08** | 12.7 | 2.8 | 124 | 200 | 25.8 | 115 | 1.5 | 1569 |
| **GS.09** | 13.1 | 1.6 | 122 | 54 | 13.0 | 67 | 1.8 | 541 |
| **GS.10** | 5.7 | 0.7 | 104 | 63 | 16.4 | 63 | 3.0 | 626 |
| **GS.11** | 27.8 | 2.6 | 123 | 373 | 54.5 | 305 | 0.0 | 1564 |
| **GS.13** | 14.8 | 3.1 | 88 | 144 | 22.5 | 142 | 1.5 | 671 |
| **GS.14** | 9.5 | 0.9 | 100 | 63 | 23.9 | 72 | 1.8 | 660 |
| **GS.15** | 56.8 | 0.5 | 94 | 65 | 33.8 | 728 | 0.0 | 966 |
| **GS.16** | 11.2 | 0.5 | 70 | 62 | 27.6 | 85 | 0.0 | 780 |
| **GS.17** | 19.7 | 3.5 | 89 | 159 | 46.8 | 159 | 0.0 | 1898 |
| **GS.18** | 16.5 | 1.8 | 111 | 135 | 43.2 | 156 | 2.3 | 1428 |
| **GS.26** | 41.2 | 3.5 | 186 | 172 | 75.1 | 441 | 2.1 | 1442 |
| **GS.23** | 28.3 | 1.2 | 135 | 210 | 60.5 | 226 | 2.8 | 1839 |
| **GS.24** | 22.7 | 1.2 | 105 | 144 | 51.3 | 183 | 0.0 | 1314 |
| **GS.25** | 17.7 | 1.3 | 132 | 123 | 59.2 | 212 | 1.1 | 893 |
| **GS.27** | 20.7 | 0.0 | 60 | 4 | 51.6 | 71 | 1.2 | 124 |

*Unlikely chance of toxic effect to benthic-dwelling organisms*
*Chance of toxic effect to benthic-dwelling organisms*
*High chance of toxic effect to benthic-dwelling organisms*
*Very high chance of toxic effect to benthic-dwelling organisms*

### 7.7. Pollution Indication Results

Results are provided in Table 9, 10 and 11 for PLI, I-Geo and EF respectively. Both NBC and the coarse grain fraction results of the sediments were used as reference values in the indexes. Elements evaluated were As, Cd, Cr, Cu, Ni, Pb, Sb and Zn, as no Hg was determined.

**Table 9.** Pollution Load Index using both NBC and coarse grain fraction results

| | NBC | Coarses |
|---|---|---|
| **GS.20** | 4.1 | 6.4 |
| **GS.19** | 5.3 | 7.4 |
| **GS.21** | 2.8 | 4.5 |
| **GS.22** | 3.1 | 4.9 |
| **GS.02** | 1.7 | 2.5 |
| **GS.01** | 0.8 | 1.2 |
| **GS.03** | 3.2 | 4.5 |
| **GS.04** | 3.7 | 5.7 |
| **GS.05** | 3.4 | 5.3 |
| **GS.07** | 4.3 | 6.6 |
| **GS.08** | 3.1 | 4.8 |
| **GS.09** | 1.9 | 2.9 |
| **GS.10** | 1.7 | 2.6 |
| **GS.11** | 4.3 | 6.6 |
| **GS.13** | 2.7 | 4.1 |
| **GS.14** | 1.9 | 2.9 |
| **GS.15** | 2.6 | 4.1 |
| **GS.16** | 1.8 | 2.6 |
| **GS.17** | 3.8 | 5.2 |
| **GS.18** | 3.3 | 5.1 |
| **GS.26** | 5.4 | 7.3 |
| **GS.23** | 4.2 | 6.5 |
| **GS.24** | 3.0 | 4.7 |
| **GS.25** | 3.0 | 4.6 |
| **GS.27** | 1.0 | 1.5 |

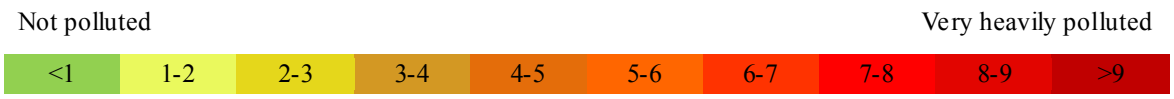


**Table 10.** Geo-Accumulation Index results

| | I-Geo using NBC | | | | | | | | | | I-Geo using Coarse grain | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Al | As | Cd | Cr | Cu | Fe | Ni | Pb | Sb | Zn | Al | As | Cd | Cr | Cu | Fe | Ni | Pb | Sb | Zn |
| GS.20 | -1.7 | 0.7 | 3.6 | 0.1 | 1.8 | -1.1 | -0.4 | 3.0 | -0.7 | 3.7 | 0.5 | 2.2 | 3.1 | 0.4 | 4.3 | -0.4 | 0.8 | 2.2 | 0.5 | 3.2 |
| GS.19 | -2.0 | 0.6 | 3.5 | 1.0 | 2.6 | -0.6 | 0.2 | 2.8 | 0.0 | 4.4 | 0.5 | 2.1 | 3.0 | 1.4 | 5.2 | 0.1 | 1.4 | 1.9 | 0.0 | 3.8 |
| GS.21 | -2.0 | 0.0 | 0.0 | 0.4 | 1.9 | -0.8 | 0.0 | 2.0 | -0.1 | 3.6 | 0.5 | 1.5 | 0.0 | 0.8 | 4.5 | -0.1 | 1.3 | 1.2 | 1.1 | 3.1 |
| GS.22 | -2.0 | 0.2 | 1.8 | 1.1 | 2.4 | -1.1 | -0.2 | 2.2 | -2.4 | 3.5 | 0.5 | 1.7 | 1.4 | 1.5 | 4.9 | -0.4 | 1.1 | 1.3 | -1.2 | 3.0 |
| GS.02 | -2.5 | -1.1 | 0.0 | -0.5 | 1.2 | -1.8 | -0.2 | 1.2 | 0.0 | 2.2 | -0.3 | 0.4 | 0.0 | -0.1 | 3.8 | -1.0 | 1.0 | 0.4 | 0.0 | 1.7 |
| GS.01 | -1.3 | -1.7 | 0.0 | -1.2 | -1.1 | -1.9 | -1.3 | 0.3 | -2.9 | 0.6 | 0.9 | -0.2 | 0.0 | -0.8 | 1.4 | -1.1 | 0.0 | -0.5 | -1.7 | 0.1 |
| GS.03 | -2.4 | -0.4 | 1.6 | 0.5 | 3.3 | -1.3 | 0.0 | 1.6 | 0.0 | 2.8 | -0.2 | 1.1 | 1.1 | 0.9 | 5.8 | -0.6 | 1.2 | 0.8 | 0.0 | 2.3 |
| GS.04 | -2.1 | -0.3 | 2.8 | -0.5 | 3.3 | -1.0 | 0.1 | 2.1 | -0.7 | 3.5 | 0.1 | 1.2 | 2.3 | -0.1 | 5.9 | -0.2 | 1.3 | 1.3 | 0.6 | 3.0 |
| GS.05 | -2.0 | -0.2 | 2.5 | 0.6 | 2.9 | -0.4 | 0.1 | 2.4 | -1.9 | 3.2 | 0.2 | 1.3 | 2.1 | 1.0 | 5.4 | 0.4 | 1.3 | 1.5 | -0.7 | 2.7 |
| GS.07 | -2.2 | 0.3 | 4.2 | 0.0 | 2.7 | -1.0 | -0.7 | 2.4 | -1.0 | 4.2 | 0.0 | 1.8 | 3.7 | 0.4 | 5.2 | -0.3 | 0.5 | 1.6 | 0.2 | 3.7 |
| GS.08 | -2.6 | -0.6 | 3.4 | 0.2 | 1.9 | -1.7 | -1.2 | 1.8 | -1.0 | 3.9 | -0.4 | 0.9 | 2.9 | 0.5 | 4.5 | -0.9 | 0.1 | 1.0 | 0.2 | 3.3 |
| GS.09 | -3.2 | -0.5 | 2.6 | 0.1 | 0.1 | -2.0 | -2.2 | 1.0 | -0.8 | 2.3 | -1.0 | 1.0 | 2.2 | 0.5 | 2.6 | -1.2 | -0.9 | 0.2 | 0.4 | 1.8 |
| GS.10 | -2.9 | -1.7 | 1.4 | -0.1 | 0.3 | -2.2 | -1.8 | 0.9 | 0.0 | 2.5 | -0.7 | -0.2 | 1.0 | 0.3 | 2.8 | -1.5 | -0.6 | 0.1 | 1.2 | 2.0 |
| GS.11 | -1.9 | 0.6 | 3.3 | 0.1 | 2.9 | -0.5 | -0.1 | 3.2 | -1.7 | 3.9 | 0.3 | 2.1 | 2.8 | 0.5 | 5.4 | 0.3 | 1.1 | 2.4 | -0.5 | 3.3 |
| GS.13 | -2.7 | -0.3 | 3.5 | -0.3 | 1.5 | -1.8 | -1.4 | 2.1 | -1.1 | 2.6 | -0.6 | 1.1 | 3.1 | 0.0 | 4.0 | -1.0 | -0.1 | 1.3 | 0.1 | 2.1 |
| GS.14 | -2.7 | -1.0 | 1.8 | -0.1 | 0.3 | -2.2 | -1.3 | 1.1 | -0.7 | 2.6 | -0.5 | 0.5 | 1.3 | 0.2 | 2.8 | -1.5 | 0.0 | 0.3 | 0.5 | 2.1 |
| GS.15 | -2.4 | 1.6 | 0.9 | -0.2 | 0.3 | -1.4 | -0.8 | 4.5 | -3.0 | 3.2 | -0.2 | 3.1 | 0.5 | 0.1 | 2.9 | -0.7 | 0.5 | 3.6 | -1.8 | 2.6 |
| GS.16 | -2.5 | -0.7 | 1.0 | -0.7 | 0.3 | -2.0 | -1.1 | 1.4 | 0.0 | 2.9 | -0.3 | 0.8 | 0.5 | -0.3 | 2.8 | -1.2 | 0.2 | 0.5 | 0.0 | 2.3 |
| GS.17 | -1.9 | 0.1 | 3.7 | -0.3 | 1.6 | -1.4 | -0.3 | 2.3 | 0.0 | 4.1 | 0.3 | 1.6 | 3.3 | 0.1 | 4.2 | -0.7 | 0.9 | 1.4 | 0.0 | 3.6 |
| GS.18 | -2.1 | -0.2 | 2.8 | 0.0 | 1.4 | -1.5 | -0.4 | 2.2 | -0.4 | 3.7 | 0.1 | 1.3 | 2.3 | 0.4 | 3.9 | -0.8 | 0.8 | 1.4 | 0.8 | 3.2 |
| GS.26 | -0.8 | 1.2 | 3.7 | 0.7 | 1.7 | -0.6 | 0.4 | 3.7 | -0.5 | 3.8 | 1.3 | 2.7 | 3.3 | 1.1 | 4.3 | 0.2 | 1.6 | 2.9 | 0.7 | 3.2 |
| GS.23 | -1.1 | 0.6 | 2.1 | 0.3 | 2.0 | -0.8 | 0.1 | 2.8 | -0.1 | 4.1 | 1.1 | 2.1 | 1.7 | 0.7 | 4.6 | -0.1 | 1.3 | 2.0 | 1.1 | 3.6 |
| GS.24 | -1.6 | 0.3 | 2.2 | -0.1 | 1.5 | -1.0 | -0.2 | 2.5 | -1.6 | 3.6 | 0.6 | 1.8 | 1.7 | 0.3 | 4.0 | -0.2 | 1.1 | 1.6 | -0.4 | 3.1 |
| GS.25 | -1.0 | -0.1 | 2.2 | 0.2 | 1.2 | -0.6 | 0.0 | 2.7 | -1.4 | 3.1 | 1.2 | 1.4 | 1.8 | 0.6 | 3.8 | 0.1 | 1.3 | 1.9 | -0.2 | 2.5 |
| GS.27 | -0.2 | 0.1 | 0.0 | -0.9 | -3.6 | -0.4 | -0.2 | 1.1 | -1.4 | 0.2 | 2.0 | 1.6 | 0.0 | -0.5 | -1.0 | 0.4 | 1.1 | 0.3 | -0.2 | -0.3 |

I-geo grade classification:

| |
|---|
| I-geo ≤ 0 (grade 0), unpolluted; |
| 0< I-geo ≤1(grade 1), slightly polluted; |
| 1 < I-geo ≤ 2 (grade 2), moderately polluted; |
| 2< I-geo ≤3 (grade 3), moderately severely polluted; |
| 3<I-geo ≤4 (grade 4), severely polluted; |
| 4< I-geo ≤5 (grade 5), severely extremely polluted; |
| I-geo > 5 (grade 6), extremely polluted (17). |

**Table 11.** Enrichment Factor results using Fe

| | EF using NBC | | | | | | | | EF using Coarse grain | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | As | Cd | Cr | Cu | Ni | Pb | Sb | Zn | As | Cd | Cr | Cu | Ni | Pb | Sb | Zn |
| **GS.20** | 3.6 | 26.1 | 2.3 | 7.5 | 1.6 | 17.6 | 1.3 | 29.1 | 5.9 | 11.4 | 1.7 | 26.0 | 2.2 | 5.9 | 1.8 | 12.0 |
| **GS.19** | 2.4 | 17.1 | 3.2 | 9.8 | 1.7 | 10.6 | 0.0 | 31.9 | 4.1 | 7.5 | 2.5 | 33.7 | 2.4 | 3.6 | 0.0 | 13.2 |
| **GS.21** | 1.9 | 0.0 | 2.4 | 6.8 | 1.8 | 7.3 | 1.6 | 21.6 | 3.1 | 0.0 | 1.8 | 23.5 | 2.5 | 2.5 | 2.2 | 8.9 |
| **GS.22** | 2.5 | 7.9 | 4.8 | 11.3 | 2.0 | 9.9 | 0.4 | 25.3 | 4.2 | 3.4 | 3.7 | 39.0 | 2.8 | 3.3 | 0.6 | 10.5 |
| **GS.02** | 1.6 | 0.0 | 2.4 | 7.9 | 3.0 | 8.0 | 0.0 | 15.7 | 2.6 | 0.0 | 1.8 | 27.4 | 4.2 | 2.7 | 0.0 | 6.5 |
| **GS.01** | 1.1 | 0.0 | 1.6 | 1.7 | 1.5 | 4.4 | 0.5 | 5.6 | 1.9 | 0.0 | 1.2 | 5.7 | 2.1 | 1.5 | 0.6 | 2.3 |
| **GS.03** | 1.9 | 7.4 | 3.5 | 24.6 | 2.4 | 7.8 | 0.0 | 17.6 | 3.2 | 3.3 | 2.7 | 85.0 | 3.4 | 2.6 | 0.0 | 7.3 |
| **GS.04** | 1.6 | 13.3 | 1.3 | 19.7 | 2.0 | 8.6 | 1.2 | 22.1 | 2.7 | 5.8 | 1.0 | 67.8 | 2.8 | 2.9 | 1.7 | 9.1 |
| **GS.05** | 1.1 | 7.3 | 2.0 | 9.3 | 1.3 | 6.6 | 0.3 | 12.1 | 1.8 | 3.2 | 1.5 | 32.3 | 1.9 | 2.2 | 0.5 | 5.0 |
| **GS.07** | 2.6 | 36.9 | 2.1 | 13.2 | 1.3 | 10.9 | 1.0 | 37.6 | 4.3 | 16.2 | 1.6 | 45.6 | 1.8 | 3.7 | 1.4 | 15.5 |
| **GS.08** | 2.2 | 33.0 | 3.6 | 12.4 | 1.4 | 11.2 | 1.6 | 47.2 | 3.6 | 14.5 | 2.8 | 42.8 | 2.0 | 3.8 | 2.1 | 19.5 |
| **GS.09** | 2.7 | 23.6 | 4.3 | 4.1 | 0.9 | 7.9 | 2.3 | 19.7 | 4.5 | 10.3 | 3.3 | 14.0 | 1.2 | 2.7 | 3.2 | 8.2 |
| **GS.10** | 1.4 | 12.4 | 4.4 | 5.7 | 1.3 | 8.9 | 4.7 | 27.6 | 2.4 | 5.4 | 3.4 | 19.7 | 1.9 | 3.0 | 6.4 | 11.4 |
| **GS.11** | 2.0 | 13.3 | 1.5 | 10.0 | 1.3 | 12.7 | 0.4 | 20.2 | 3.4 | 5.8 | 1.2 | 34.4 | 1.8 | 4.3 | 0.6 | 8.3 |
| **GS.13** | 2.7 | 40.0 | 2.8 | 9.7 | 1.4 | 14.8 | 1.7 | 21.8 | 4.6 | 17.5 | 2.1 | 33.5 | 1.9 | 5.0 | 2.3 | 9.0 |
| **GS.14** | 2.3 | 15.8 | 4.2 | 5.6 | 1.9 | 10.1 | 2.8 | 28.6 | 3.9 | 6.9 | 3.2 | 19.3 | 2.7 | 3.4 | 3.8 | 11.8 |
| **GS.15** | 8.0 | 5.0 | 2.2 | 3.3 | 1.5 | 57.9 | 0.3 | 23.9 | 13.4 | 2.2 | 1.7 | 11.5 | 2.2 | 19.5 | 0.4 | 9.9 |
| **GS.16** | 2.4 | 7.8 | 2.5 | 4.8 | 1.9 | 10.2 | 0.0 | 29.0 | 4.0 | 3.4 | 1.9 | 16.4 | 2.6 | 3.4 | 0.0 | 12.0 |
| **GS.17** | 2.9 | 35.4 | 2.2 | 8.4 | 2.2 | 13.0 | 0.0 | 48.3 | 4.8 | 15.5 | 1.7 | 29.0 | 3.1 | 4.4 | 0.0 | 20.0 |
| **GS.18** | 2.5 | 19.6 | 2.9 | 7.5 | 2.1 | 13.5 | 2.2 | 38.3 | 4.2 | 8.6 | 2.2 | 25.9 | 3.0 | 4.5 | 3.0 | 15.8 |
| **GS.26** | 3.4 | 19.7 | 2.5 | 5.0 | 2.0 | 20.1 | 1.1 | 20.4 | 5.7 | 8.6 | 2.0 | 17.3 | 2.7 | 6.8 | 1.5 | 8.4 |
| **GS.23** | 2.7 | 7.7 | 2.2 | 7.2 | 1.8 | 12.0 | 1.7 | 30.4 | 4.5 | 3.4 | 1.7 | 24.8 | 2.6 | 4.1 | 2.3 | 12.5 |
| **GS.24** | 2.4 | 8.9 | 1.8 | 5.4 | 1.7 | 10.7 | 0.6 | 23.9 | 3.9 | 3.9 | 1.4 | 18.7 | 2.4 | 3.6 | 0.9 | 9.9 |
| **GS.25** | 1.5 | 7.4 | 1.9 | 3.7 | 1.6 | 10.0 | 0.6 | 13.0 | 2.5 | 3.2 | 1.4 | 12.8 | 2.2 | 3.4 | 0.8 | 5.4 |
| **GS.27** | 1.4 | 0.0 | 0.7 | 0.1 | 1.2 | 2.8 | 0.5 | 1.5 | 2.4 | 0.0 | 0.5 | 0.4 | 1.6 | 0.9 | 0.7 | 0.6 |

EF<2= Deficiently to minimal enrichment

2≤EF<5= Moderate enrichment

5≤EF<20= Significant enrichment

20≤EF<40= Very high enrichment

EF≥ 40= Extremely high enrichment

## 7.8 Water hyacinth heavy metal concentrations

Analyte concentrations of ashed water hyacinth are shown in Table 12. The weight of dried material prior to ashing was 500 g.

**Table 12.** Water hyacinth heavy metal concentrations in mg/kg

| Sample ID | As | Cd | Cr | Cu | Hg | Ni | Pb | Sb | Zn |
|---|---|---|---|---|---|---|---|---|---|
| **WH.01** | 41.2 | 8.7 | 10.2 | 52.2 | 0.01 | 1558 | 109 | 29 | 122 |
| **WH.02** | 0.3 | 6.0 | 1.5 | 18.1 | 0.02 | 6 | 46 | 0.0 | 40 |
| **WH.03** | 4.5 | 8.1 | 11.7 | 24.6 | 0.01 | 11 | 20 | 9.5 | 46 |
| **WH.04** | 122.7 | 12.4 | 73.1 | 142.0 | 0.00 | 657 | 821 | 192 | 123 |
| **Average in plant** | 42.2 | 8.7 | 24.1 | 59.2 | 0.01 | 558 | 249 | 57.6 | 83 |
| **Average sediment** | 20.3 | 0.5 | 194 | 230 | 0.00 | 55.12 | 141.7 | 1.65 | 1255 |
| **BAF*** | **2.1** | **18.3** | 0.2 | 0.3 | **>1** | **10.1** | **1.6** | **35.2** | 0.1 |

**BAF= Bio-Accumulation Factor*

# 8. OBSERVATIONS & DISCUSSION

## 8.1.Toxicity of mud fraction

Based on exceedances of CBSQG the most toxic sample was GS.26 with values of As 41.9 mg/kg, Cd 3.5 mg/kg, Cr 185.7 mg/kg, Cu 171.7 mg/kg, Ni 75.1 mg/kg, Pb 441 mg/kg and Zn 1443 mg/kg. Sample GS.26 was collected from anoxic conditions beneath the Ripenburg Bridge. Sample GS.23 was collected within close proximity to GS.26 and showed similar heavy metal concentrations. Other hotspots were all located slightly downstream of a river convergence or within 50 m of one, represented by the samples GS.20, GS.19, GS.07 and GS.11 which were collected from convergences of Vygekraal, Jakkelsvlei, Elieskraal and Kromboom rivers respectively. Exceedances in all samples were most common for Cr, Cu, Pb, Ni and Zn. Antimony was present in low concentrations (1.2 mg/kg +/- 0.94) whilst Hg remained undetectable by XRF in all sediment samples (<0.02 mg/kg). Given the main locations of pollution and types of heavy metals present it is likely the largest sources are roadside dust (particularly for Pb) and wastewater from industry and informal settlement (particularly for Ni, Cr and Zn). The most enriched elements in the Black River are not necessarily the result of higher anthropogenic input but could be the result of the elements chemical properties. As stated in Section 5.5.5 Cr, Ni, Pb and Zn are some of the more immobile elements investigated, all of which have high affinity to clay and organic matter and are all relatively unreactive.

The least toxic sediment sample (GS.01) was collected 160 m downstream of the Athlone WWTW, with one sample collected between the two (GS.02) also showing relatively low toxicity for that which is expected, suggesting the Athlone WWTW significantly improves sediment quality in the Black River. However due to adjoining rivers downstream, the sediment quality improvement is short lived. There were three other areas which appeared to be less toxic in comparison with the remainder of the Black River, and these locations were GS.10 (prior to the Kroomboom River convergence) and GS.13-16 (located next to the golf course). Sample GS.27 was taken from the Liesbeek River and appeared less toxic than other samples, most likely as the Lisebeek River acquires less residential and industrial wastewater.

Samples GS.06 and GS.12 saturated the XRF detector on the major and trace program perhaps due to a particular element present in high quantities. Omnian program (a basic indicator of element presence shown in wt%) suggest the main elements present in sample GS.06 were $SiO_2$ (70 wt%), $P_2O_5$ (5.1 wt%) and Zr (5.8 wt%), and those in sample GS.12 were $SiO_2$ (73.9 wt%), $P_2O_5$ (2.5 wt%) and Zr (2.5 wt%).

It appears from exceedances of CBSQG that the river is most toxic from Cr, Cu and Pb. Heavy metals Ni and Pb are also present in high concentrations however these elements are less of a toxicity risk to receptors. The magnitude of severity caused by exceedances of the PEL cannot be determined using the CBSQG.

### 8.2. Comparison between data from 2002 and 2012

The homogenized and milled mud and sand samples of GS.22, GS.27, GS.10, GS.15, GS.23 and GS.24 and the corresponding samples of Haniff's investigation in 2002 are presented in Table 13 to identify changes which have occurred in the Black River in 13 years. Location D close to the Ripenberg Bridge was concluded to be the most toxic area in 2002, and remains a relatively highly toxic area. Sampling locations are shown in Figure 3.

**Table 13.** Comparison of element concentrations in 2002 and 2015 (mg/kg)

| | Location A | | Location B | | Location C | | Location D | | Location E | | Location F | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **2002** | **2015** | **2002** | **2015** | **2002** | **2015** | **2002** | **2015** | **2002** | **2015** | **2002** | **2015** |
| **As** | 0.5 | 4.0 | 3.4 | 4.2 | 1.4 | 2.5 | 10.5 | 7.2 | 9.8 | 4.6 | 12.9 | 4.1 |
| **Cd** | 0.1 | 0.2 | 0.3 | 0.6 | 0.1 | 0.2 | 1.3 | 0.2 | 1.0 | 0.3 | 0.5 | 0.3 |
| **Cr** | 3.3 | 53.0 | 16.6 | 41.3 | 6.2 | 40.5 | 60.8 | 39.6 | 70.5 | 43.4 | 34.9 | 40.7 |
| **Cu** | 4.2 | 29.5 | 30.9 | 35.7 | 5.6 | 11.1 | 95.0 | 11.3 | 58.3 | 24.6 | 34.6 | 18.5 |
| **Hg** | 0.2 | 0.0 | 1.1 | 0.0 | 0.8 | 0.0 | 0.9 | 0.0 | 0.4 | 0.0 | 0.2 | 0.0 |
| **Ni** | 0.5 | 19.6 | 6.1 | 18.2 | 1.9 | 16.4 | 31.4 | 18.0 | 20.0 | 20.4 | 10.7 | 19.6 |
| **Pb** | 13 | 49 | 106 | 52 | 12 | 239 | 276 | 102 | 180 | 56 | 92 | 52 |
| **Zn** | 47 | 205 | 217 | 271 | 60 | 150 | 618 | 181 | 481 | 261 | 190 | 213 |

Location A= H.06 and GS.22 (before Athlone WWTW)
Location B= H.01 and GS.07 (Esliekraal convergence)
Location C= H.02 and GS.10 (Kroomboom convergence)
Location D= H.03 and GS.15 (Ripenberg Bridge)
Location E= H.04 and GS.23 (Close to Raapenberg wetland)
Location F= H.07 and GS.24 (Before Liesbeek Convergence)

Results from Haniff's study in 2002 reveal that samples collected downstream of the Athlone WWTW were higher in heavy metal concentrations than those collected upstream; with concentrations increasing between H.06 and H.01 (Locations A and B) for each focus element, and mostly significantly Ni, Pb, Cu and As. The results of the recent study suggest the Athlone WWTW now improves sediment quality based on heavy metal concentrations reduction between GS.22 and GS.02. It is expected however this improvement is short lived due to other river inputs. In 2002, Hg concentrations were present in ranges between 1.1 and 1.5 mg/kg however no Hg was detected in the samples by XRF in 2015 (which is capable of detecting Hg concentrations as low as 0.02 mg/kg). The comparison suggests heavy metal concentrations throughout the selected stretch of the Black River have generally increased since 2002, except for Cd in Location D which decreased by three-fold. Interpretations as a result of comparing 2002 and 2015 data are limited to general observations due to the different methods used in capturing the total concentrations (chemical partitioning and XRF).

### 8.3. Organic content

Based on loss on ignition results, there appears to be a slight decrease in organic matter downstream all bar the four visible exceptions GS.07, GS.11, GS.17 and GS.23; all of which except for GS.17 were located immediately after (or slightly upstream of) inputs to the Black River as shown in Figure 3. Sample GS.17 was collected from a slow moving relatively deep section of the river with dense vegetation either side on the river bank, and is expected that more organic content is present at this location from dead plant matter as opposed to effluent from anthropogenic sources. Sample GS.07 is expected to have higher organic content (based on the fact the sample lost most weight from roasting), and was collected slightly upstream of the Elieskraal River. Based on loss on ignition results, sample GS.10 was expected to have held the lowest organic content and was one of the least toxic samples, and GS.26 (albeit containing the highest toxicity) held low organic content. These results disagree with Naji & Ismail's suggestion (2011) that organic content holds more influence over heavy metal distribution than grain size, however there was a correlation between organic content and toxicity due to affinity between heavy metals and organics (Sklodowski et al., 2006).

Sample GS.07 located at the convergence of Elsieskraal River appeared to contain the highest wt % of organic matter, with the next highest portions found in samples GS.20, GS.19 and GS.23. There is no linear pattern of organic content along the river profile and instead appears to be influenced by river inputs shown by the sharp peaks for GS.20 (Blomvlei) and GS.11 (Kromboom).

### 8.4. Particle sizing

It can be seen the largest portion of the sediment in the selected section of the Black River is of fine and very fine sand. The mud fraction of the sediment of the Black River is small (i.e. 2.92 +/- 1.7 %); therefore the larger grain particles act as a buffer in the sediments and so the toxicity levels which are based on the mud fraction are worst case scenarios. Sample GS.27 contained some 50 % mud and was collected after the convergence of the Liesbeek River. Samples GS.20, GS.01, GS.10, GS.14 and GS.23 also contained higher mud content, and so these samples are of interest due to the affinity of heavy metals to mud particles.

Comparing results of the grain size distribution and organic content reveals an unexpected association as is usually the case that mud is associated with organic content however some samples which consist of larger grain sizes are comparable with high organic content as demonstrated by GS.07, GS.11 and GS.23 in Figures 5 and 6.

### 8.5. Coarse grain fraction

There is a significant difference between the geochemistry of the coarse grain fractions of the Liesbeek River and the Black River, with the Liesbeek tending to have higher heavy metal concentrations which are statistically more similar to ASV, albeit it theoretically deriving from sandstone not shale. The samples collected after the convergence of the Liesbeek therefore showed little enrichment yet high toxicity when applied to the PLI and I-Geo.

The XRF results shown in Table 7 suggest toxicity from NBC is relatively low in the coarse fraction and all appear to have lower concentrations than EBV, except for the concentrations measured in GS.25 which show relatively different concentrations in comparison with the other samples. This difference is most likely a result of the sandstone origin of the Liesbeek River which converges with the Black River upstream of GS.25.

Iron concentrations in the Black River sediments were measured for use as a normalizing factor in the EF. Concentrations of Fe fluctuate throughout the coarse grain samples, which possibly reflect the deposition processes changing along the course of the river. Iron should however be adequate to act as a normalizing factor for the EF as it is unlikely that it has been enriched in the river from anthropogenic activities. Concentrations of Fe are not consistent between the coarse grain fractions and the mud fractions, but Fe is still the best option as a normalizing element in comparison with Al, due to the larger fluctuations of Al concentrations throughout the samples.

### 8.6. Normal background concentration and coarse grain fraction comparison

These results were applied with NBC to the t-test to establish whether there was a statistical similarity for major and trace elements. It was concluded that Si, Fe, Ca, P, Cr, Cd, Co, Ge, Hf, Nd, Ni, PB, Sc, Se, Sn, Th, Tl, Zn and Zr concentrations in the coarse fraction of the sediments are similar to NBC with 95% certainty. However, the results of GS.25 were significantly different to the other four coarse fractions measured. The reliability of using either set of standards in quantifying pollution remains dubious due to the drastic effect of dredging and canalization, and leaves to question whether the majority of normal background concentration in the Black River is even derived from the bedrock of the river catchement. The use of coarse grain fraction results as background concentration could be more reliable than NBC in some cases, as studies suggest a higher level of reliability when element concentrations of virgin soils and sediments of the site are used to estimate background values of contaminants (Gałuszka & Migaszewski, 2011: Sakan et al, 2015: Amorosi et al., 2014). However in the instance of the Black River, too many variables and changes to the sediment make the assumption that the sediment is derived from the same source to be an unreasonable one.

### 8.7. Pollution indicators

Applying the NBC to the PLI revealed that the highest enrichment was in GS.26 (5.4), followed by GS.19 (5.3), GS.07 (4.3), GS.11 (4.3) and GS.23 (4.2). The PLI results using the coarse grain fraction highlighted the same 5 samples but at higher risk levels; GS.19 (7.4), GS.26 (7.3), GS.07 (6.6), GS.11 (6.6) and GS.23 (6.5).

Using the NBC as reference, the I-Geo results showed most elements were within the I-Geo classifications of not polluted to moderate pollution (<3 I-Geo), with most enrichment in Zn, Pb, Cu and Cd. Using the coarse fraction results as reference in the I-Geo also revealed the same elements to be a cause for concern (but at higher risk similar to PLI) with average classification as moderately to severely polluted (1<I-Geo<4). Applying the coarse fraction to the I-Geo also revealed As to be a concern (moderately to severely polluted) in the mud fraction, which was deemed otherwise an unpolluted element by the NBC. The I-Geo results confirmed that the most effective normalizing element for use in EF was Fe as concentrations remained relatively consistent and not enriched with reference to both the NBC and the coarse fraction, whereas Al fluctuated and showed enrichment using the coarse fraction results. The NBC used in the EF reveal Zn to be extremely enriched, followed by Cd, Pb and Cu which were all significantly enriched based on the EF grading system. Applying the coarse fraction results with the mud results to the EF using Fe as the normalizing element revealed Cu to be significantly enriched, followed by Zn, Cd, Pb and As.

The application of NBC to the PLI, I-Geo and EF suggested low enrichment in the mud fraction whereas applying the coarse grain results revealed much higher levels of pollution enrichment in the Black River mud fraction. Patterns were similar within the indexes used, suggesting similarity between the coarse fraction and the NBC however the EF using Fe provided different results. The EF is useful in identifying enrichment, but its effectiveness is highly dependent on the normalizing factor used and in this instance the concentrations of Fe vary dramatically between the NBC and coarse grain fraction results and the average Fe concentrations held a high standard deviation.

The data in Table 9 in section 7.7 is displayed with colour which is based on the pollution classification level. This helps visualize the comparisons between the NBC and the coarse grain fraction results in the PLI. The NBC show a sample's PLI to be usually one class more polluted than what the coarse grain fraction suggests. Applying NBC to the I-Geo with the mud fraction XRF results suggests Cd, Pb and Zn are the most enriched elements in the Black River and overall the river is moderately polluted. Applying the coarse grain fraction XRF results to the I-Geo with the mud fraction XRF results implies Cd, Cu and Zn are the most enriched elements and overall the river is severely polluted. Grouping of I-Geo results using the coarse grain fraction was conducted using Wards method Euclidean distances and is shown in Figure 7 below.

This method revealed that samples collected from close proximities contained statistically similar element enrichment quantities, with the most apparent being GS.21, GS.22 and GS.02 in one close linkage distance group and GS.03, GS.04 and GS.05 in another close linked distance group. These two groups are located before and after the Athlone WWTW respectively. It is expected these two sections of the river receive little sediment disturbance in order to accumulate and contain geochemically similar sediments. However the remainder of the samples were randomly grouped, suggesting there has been disturbance of the sediment. Other groups formed using this method held a linkage of further distance and were not collected from similar localities along the river. GS01, GS.10 and GS.27 belonged to the same linkage group and are the least toxic samples however they are from differing locations. GS.19, GS.23 and GS.26 were grouped and were deemed by all three indexes as being the most polluted samples.

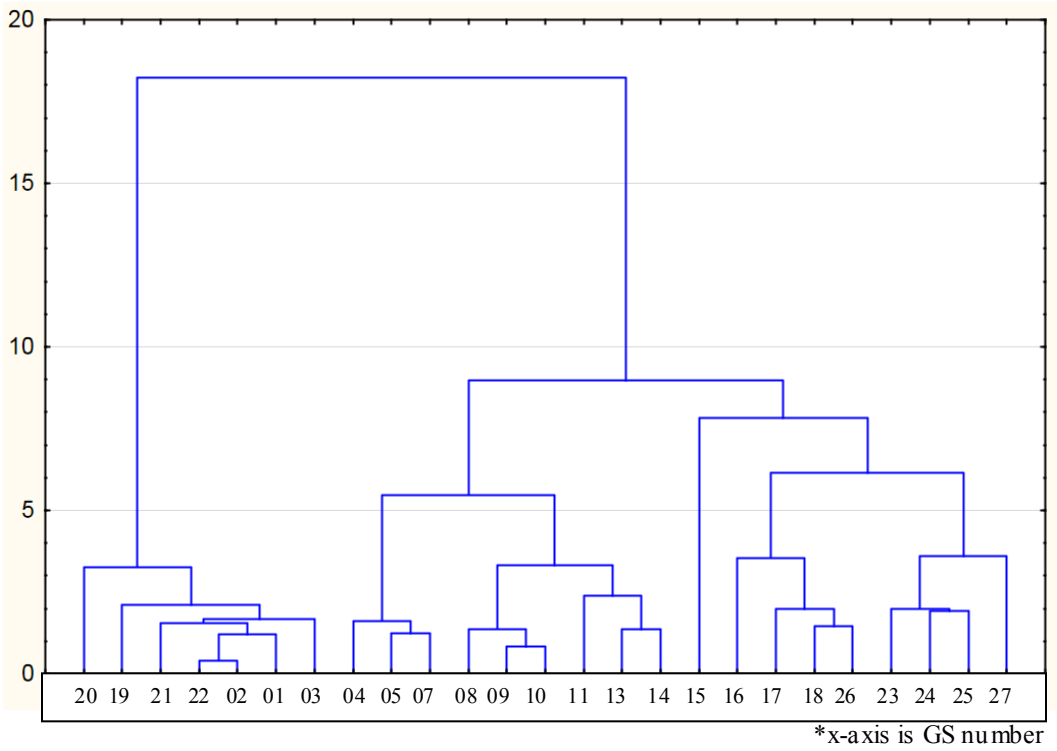



**Figure 7** Wards method Euclidean distances of I-Geo results

The EF provides a similar interpretation to the I-Geo results, as the NBC suggest Cd, Pb and Zn are the most enriched elements and the river is moderately enriched, whilst the coarse fraction XRF results suggest Cd, Cu and Zn are the most enriched and the river holds significant/ very high enrichment.

### 8.8. Water hyacinth

The abundance of the water hyacinth species in the Black River and its known abilities as a phyto-remediator makes it an ideal candidate to remediate the sediments (indirectly by up-taking heavy metals from the water column), and small changes to the extraction method would make it a relatively economic and energy efficient method of remediation by removing heavy metals. It was therefore briefly investigated as part of this study to identify its phyto-remediating potential in the Black River and results were shown in Table 12 in section 7.8.

The Bio-accumulation Factor (BAF) (Otti, 2015) was used to interpret the results (BAF=concentration in plant/ concentration in sediment). Those figures in red in Table 12 are greater than a BAF of 1, suggesting they are efficient in the uptake of the particular analyte. The results suggest efficient up-take of As, Cd, Hg, Ni, Pb and Sb. All four water hyacinth samples contained high concentrations of Cd, and high concentrations of As, Ni and Sb were present in three samples. Merucry was present (albeit at low concentrations) in 3 out of the 4 plant samples yet was not detected in any of the sediment samples, thus suggesting that the plant is efficient at up-taking Hg from the water column, or suggesting that Hg does not settle out into the sediment.

# 9. CONCLUSIONS AND RECOMMENDATIONS

## 9.1. Current contamination status of the Black River

Results from all statistical indicators used for the mud fraction signify the river is most enriched with Cd, Cu, Pb and Zn. Short-term fluctuations in heavy metal presence and kinetic components cannot be accurately determined due to complexities within river system inputs and the ever changing environmental conditions, and so the findings are based on equilibrium status and conditions at the time of sampling.

The distribution of metals in sediments of the Black River if not controlled by dredging is controlled by the association of metals with fine grained and organic-rich sediment, mainly between the locations of GS.15 and GS.26. In addition, contamination hotspots reflect river inputs draining various areas of the Cape Flats, with highest concern being the Elsieskraal River. The XRF results of GS.22 and GS.02 suggest the Athlone WWTW now significantly improves sediment quality compared with results from 2002, when the treatment works appeared to be depositing significant quantities of As, Cu, Ni and Pb between H.06 and H.01. Unfortunately the improvement of sediment quality appears to be short lived due to subsequent polluted river inputs downstream.

It is important to note that the CBSQG were applied to the mud fraction which is undoubtedly the fraction of sediment that holds the highest heavy metal concentrations (Bately & Maher, 2001). The toxicity results are therefore based on worst case scenario as the sand and gravel within the sediment buffer these concentrations. Bio-availability of the heavy metals was also not taken into account; again concluding a worst case scenario as it was assumed all heavy metal partitions have the ability to become bio-available at any given time.

Using background concentrations collected from the area of the river that is under investigation is more reliable than globally recognised ASV or concentrations established for regions elsewhere as past studies deduce a higher level of certainty is reached when regional geological data are used as opposed to global averages (Gałuszka & Migaszewski, 2011: Sakan et al, 2015: Amorosi et al., 2014).

However, although the coarse grain fraction of the Black River sediments would have (theoretically) been site specific, it was concluded that the heavy metal concentration from this sediment fraction could not successfully establish precisive NBC due to sediment disturbances and windblown coastal sand inputs in the Black River. It is possible this method of establishing NBC could be used for urban river sediments which are less frequently disturbed and are more shielded from geological input outside of the river catchment.

### 9.2. Proposed remediation strategy for the Black River

Dredging the sediments of the Black River undoubtedly needs to continue due to the near impossible task (at least in the short term) of transforming Cape Town's urban areas into sustainable low impact systems which do not overload the river with pollution as they do at current, along with the need to relieve flood risk. It has been established that dredging and the current water hyacinth removal techniques can cause the remobilization of heavy metals into the water column from sediment disturbance (Eggleston, 2012). Fly-ash or waste material of a similar level of inertness could be applied to the surface of the sediments in the area prior to the Athlone WWTW and at river convergences. This would not only put use to inert waste but would also reduce remobilization of heavy metals. Once dredged the mixture of inert waste and contaminated sediments would reduce the toxicity of the contaminated sediment waste.

Water hyacinth is a problematic invasive species found in the Black River however it is also a known phyto-remediator (Buta et al., 2011). Water hyacinth can act as a highly useful tool for indirectly removing heavy metals from sediments. This phyto-remediation strategy is occurring in the Black River due to the removal of the invasive species, particularly in locations close to Athlone WWTW. Heavy metal concentrations in water hyacinth collected from the Black River were applied to the BAF which revealed the plant has high affinity for As, Cd, Hg, Pb, Ni and Sb. An improvement to the current water hyacinth clearing strategy occurring in the Black River would be to ensure the plant is fully removed as the majority of heavy metals up-taken remain in the root system (Hasan, 2007). The roots themselves do not sit within the sediments but are suspended in the water.

It was noted during the fieldwork that anoxic sediments located between GS.16 and GS.23 were heavily loaded with trapped gases; most probably methane and hydrogen sulphide. Due to the influence sulphides have on the mobility of heavy metals, it is likely that any physical or chemical disturbances which result in oxidizing conditions within the sediments can cause a severe loading of heavy metals being re-mobilized into the water column. The benefit of optimizing the use of water hyacinth as a phyto-remediator is that the roots are suspended in the river, which limits sediment disturbances.

Gas control and release pipes could be placed in the sediments in order to relieve the sediments from accumulated gases, which would gradually allow conditions to stabilize. Combined with fly-ash and controlled water hyacinth growth, this revised remediation method could be cost-efficient and effective to control the remobilization of the point-source pollution that is the Black River sediment itself. This method would reduce the impact of dredging by reducing heavy metal loads entering the above water column from disturbance.

### 9.3. Further research

The next stage in this investigation would be to run a control (pure quartz) in the same laboratory conditions in order to identify whether the coarse grain fraction in the sediment is region specific, or whether the sediment fraction is not representative of local weathered bedrock but is from an external source.

Further research of NBC in other South African rivers is required in order to produce intervention limits for sediments, and performing intrusive investigations can bridge gaps between the different research fields working towards the improvement of urban river quality. Further investigation of the effectiveness of using the coarse grain fraction of sediments to produce NBC could be conducted. Establishing a benchmark beneath which grain sizes can no longer effectively portray NBC would be beneficial.

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# APPENDIX I

Sample log

| | |
|---|---|
| **Date** | Thursday 5th February 2015 |
| **Temperature (°C)** | 21 - 27 |
| **Precipitation (mm)** | Last occurrence of precipitation in the region was 4th February 2015; very light rain of 0.7 mm [1]. Precipitation within two months prior to sampling has been minimal. |
| **Pressure (mb)** | 1011[1] |
| **Sampling locations on Day 1** |  (Google Earth, 2015) |

| | |
|---|---|
| **Date** | Saturday 28th February 2015 |
| **Temperature (°C)** | 25 – 31 [1] |
| **Precipitation (mm)** | Last occurrence of precipitation in the region was 4th February 2015; very light rain of 0.7 mm (World Weather Online, 2015). Precipitation within the month prior to sampling has been minimal. |
| **Pressure (mb)** | 1015[1] |
| **Sampling locations on Day 2** |  (Google Earth, 2015) |

*Photographs captured for samples GS.19-27 on day two were lost

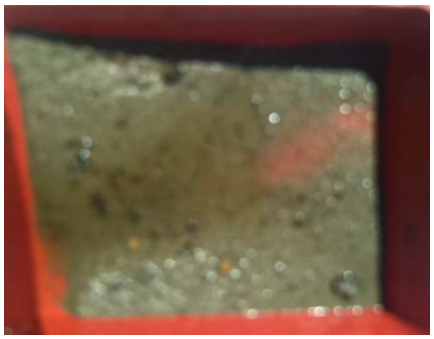
[1] World Weather Online. 2015. Cape Town Historical Weather, South Africa. Available http://www.worldweatheronline.com/Cape-Town-weather-history/Western-Cape/ZA.aspx [February 8, 2015]

| Sample name | SG.01 | Coordinates | -33.95056, 018.50753 | Time | 09:50 |
|---|---|---|---|---|---|
| Sediment description | Clayey silt, dark in colour, little organic matter visible and a slight hydrocarbon odour present when sediments brought to surface. Compact and relatively dry sediment. | | | | |
| Comments | Sample included large pieces of broken glass and other waste materials (shards of plastic and clothing). Tyres and large household items present in the section of the river. 0.5 m water depth with medium-slow moving current. | | | | |

**Figure** SG.01

| Sample name | SG.02 | Coordinates | -33.95058, 018.50893 | Time | 10:15 |
|---|---|---|---|---|---|
| Sediment description | Homogenised sandy silt. Light in colour and containing rounded stones. | | | | |
| Comments | Sample collected 5 m from pipeline depositing clear running water and before concrete section beneath bridge. Fast moving river flow with accumulation of plastics and plant matter on ridge of concrete base. | | | | |

**Figure** SG.02

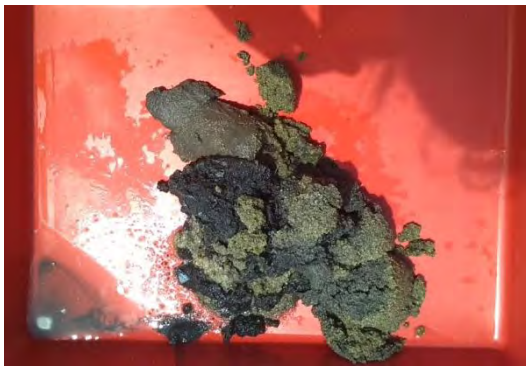


| Sample name | SG.03 | Coordinates | -33.95029, 018.50652 | Time | 10:32 |
|---|---|---|---|---|---|
| Sediment description | Green algal covering on the surface of the sediments. Underlain with sticky textured clayey silt, brown in colour with sub-angular and rounded stones. | | | | |
| Comments | Shallow, wide stretch of the river with slow moving river flow. | | | | |

**Figure** SG.03

| Sample name | SG.04 | Coordinates | -33.95018, 018.50513 | Time | 10:44 |
|---|---|---|---|---|---|
| Sediment description | Sandy silt texture. Surface layer green in colour underlain with very dark black sediment, subsequently underlain with a green banded layer. Relatively dense and dry. | | | | |
| Comments | Running alongside N2 with steep bank up to the road. Wide stretch of river, shallow in the centre with large sediment accumulation. | | | | |

**Figure** SG.04



| Sample | SG.05 | Coordinates | -33.95025, 018.50410 | Time | 11:01 |
|---|---|---|---|---|---|
| Sediment description | Very thin layer of green algae on the surface of the sediments. Once disturbed the covering dispersed in the water. Dark brown with green tint silt with few small suspended stones. Waste materials in the vicinity included tyres and household waste. | | | | |
| Comments | Close to N2 with steep bank leading down to the river from the road. | | | | |

**Figure** SG.05

| Sample name | SG.06 | Coordinates | -33.95076, 018.50213 | Time | 11:14 |
|---|---|---|---|---|---|
| Sediment description | Brown and green banded dry silt with large pieces of organic matter. | | | | |
| Comments | Shallow and slow moving water in wide stretch of river. Few large waste items present in this vicinity due to clear up operation occurring. | | | | |

**Figure** SG.06

| Sample name | SG.07 | Coordinates | -33.95053, 018.50204 | Time | 11:20 |
|---|---|---|---|---|---|
| Sediment description | Sheen on surface sediments. Black in colour and various particle sizes throughout. | | | | |
| Comments | Black oily water released from sub-horizon when sediments disturbed. Sample collected close to bridge and upstream in the adjoining Elsieskraal River. Large amount of bird activity expected on the nearby banks due to the quantity of faunal waste present and the strong odour. | | | | |

**Figure** SG.07

| Sample name | SG.08 | Coordinates | -33.95137, 018.50019 | Time | 11:36 |
|---|---|---|---|---|---|
| Sediment description | Sandy silt dark brown on surface and underlain with a green, less organic rich layer. | | | | |
| Comments | Lots of large items in the vicinity including tyres, traffic signs and household waste. | | | | |

**Figure** SG.08

| Sample name | SG.09 | Coordinates | -33.95251, 018.49821 | Time | 11:46 |
|---|---|---|---|---|---|
| Sediment description | Homogenised dense material of greeny brown silt with organic matter. | | | | |
| Comments | Wide stretch of river, slow moving relatively clear water. | | | | |

**Figure** SG.09

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.10 | **Coordinates** | -33.95310, 018.49632 | **Time** | 11:57 |
| **Sediment description** | Organic rich, sticky clayey silt. Green/ brown in colour. | | | | |
| **Comments** | Close to golf course, relatively well-kept stretch of river with little waste present. | | | | |

**Figure** SG.10

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.11 | **Coordinates** | -33.95308, 018.49532 | **Time** | 12:13 |
| **Sediment description** | Silty sand with some gravel present. Light surface sediments becoming darker with depth. Some 200 mm deep the sediments are very dark brown/black. | | | | |
| **Comments** | Sample taken from a relatively deep section of the river, (600 mm) with very large sediment accumulation at the base. Large tree debris material present at the bottom of the river and some waste materials. | | | | |

**Figure** SG.11

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.12 | **Coordinates** | -33.95206, 018.49368 | **Time** | 12:32 |
| **Sediment description** | Light green surface becoming brown with depth. Dense and compact silt. | | | | |
| **Comments** | River becoming deeper and more consistent in depth and width. Sample taken close to footbridge with litter scattered in the vicinity. | | | | |

**Figure** SG.12

| Sample name | SG.13 | Coordinates | -33.95078, 018.49189 | Time | 12:45 |
|---|---|---|---|---|---|
| Sediment description | Compacted dark brown silt becoming green/lighter with depth. | | | | |
| Comments | Water depth estimated to be 600 mm. High turbidity in the water with green colour and slight sheen on the surface. | | | | |

**Figure** SG.13

| Sample name | SG.14 | Coordinates | -33.94908, 018.48963 | Time | 12:57 |
|---|---|---|---|---|---|
| Sediment description | Organic rich sediment. Very fine, loose particles. | | | | |
| Comments | (Most likely) hydrocarbons present in the sub-horizon which were released when the sediments were disturbed. Remnants shown in figure below. | | | | |

**Figure** SG.14

| Sample name | SG.15 | Coordinates | -33.94752 018.48717 | Time | 13:16 |
|---|---|---|---|---|---|
| Sediment description | Dark brown compacted sediment of clayey silt turning green and loose with depth. Organics minimal. | | | | |
| Comments | River depth some 650 mm. Slow flowing and murky. | | | | |

**Figure** SG.15

| Sample name | SG.16 | Coordinates | -33.94638, 018.48617 | Time | 13:27 |
|---|---|---|---|---|---|
| Sediment description | Organic rich silty sediment. Very black on surface turning brown/green with depth (past 150 mm). | | | | |
| Comments | Once disturbed the sediments released a significant quantity of bubbles from the sub-horizon. Strong possibly hydrogen sulphide (egg smell) and methane odour. | | | | |

**Figure** SG.16

| Sample name | SG.17 | Coordinates | -33.94496, 018.48505 | Time | 13:49 |
|---|---|---|---|---|---|
| Sediment description | Dark loose sediments rich in organic matter and held more water. | | | | |
| Comments | Odours of methane and hydrogen sulphide stronger at this location than SG.16. More bubbles released from disturbances. Water depth of 700 mm. | | | | |

**Figure** SG.17

| Sample name | SG.18 | Coordinates | -33.94243, 018.48491 | Time | 14:00 |
|---|---|---|---|---|---|
| Sediment description | Anoxic; black organic matter. Very little sand, mostly consisting of organics. Strong hydrogen sulphide odour. | | | | |
| Comments | This section of the riverbed had a very deep layer of loose materials, thought to have not been disturbed/ dredged recently. | | | | |

**Figure** SG.18

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.19 | **Coordinates** | -33.95138, 018.52138 | **Date** | 05/02/2015 |
| | | | | **Time** | 14:00 |
| **Sediment description & comments** | Very dark in colour with some light green/ brown shine to the surface of the sediments. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.20 | **Coordinates** | -33.95191, 018.52007 | **Time** | 14:43 |
| **Sediment description & comments** | Black, loose sediment with a shine to the surface. Little organic matter present. Fine sand and lots of suspended sediment in murky, slow moving water. Large quantity of larger litter materials. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.21 | **Coordinates** | -33.95124, 018.51736 | **Time** | 15:05 |
| **Sediment description & comments** | Light medium sand on the surface. Finer sand beneath the lighter sediment on the surface. River bed level varies greatly across the river. Medium speed of water flow, no visible output of water from AWTW. Large household waste items present in the river. Large pile of loose material some 20 m from the river inside AWTW. No impermeable boundary preventing this material being carried into the river with precipitation. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.22 | **Coordinates** | -33.95089, 018.51626 | **Time** | 15:50 |
| **Sediment description & comments** | Light sand overlain with a darker sediment (200 mm below sediment surface). Black solubles/ small particles were released on very slight disturbance . Bubbles also released. The river water at this point was shallow and had a slow flow. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.23 | **Coordinates** | -33.93459, 018.48041 | **Time** | 16:12 |
| **Sediment description & comments** | Black surface to the sediments. Sticky clayey texture beneath with large quantity of detrital material. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.24 | **Coordinates** | -33.93196, 018.47950 | **Time** | 16:23 |
| **Sediment description & comments** | Anox- black sediments with a shiny tint. Large quantity of organics and also large stones present at the size- possibly industrial/ building waste. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.25 | **Coordinates** | -33.92924, 018.47844 | **Time** | 16:44 |
| **Sediment description & comments** | Sample collect just downstream of the joining of the Lisebeek River. Very fast flowing, murky and deep water. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.26 | **Coordinates** | -33.93913, 018.48512 | **Time** | 17:15 |
| **Sediment description & comments** | Very murky water with strong odours. Large quantity of waste both in the water and stacked underneath the bridge. Sediments dark brown, compact mostly sand. | | | | |

| | | | | | |
|---|---|---|---|---|---|
| **Sample name** | SG.27 | **Coordinates** | -33.93290, 018.47263 | **Time** | 17:52 |
| **Sediment description & comments** | Taken from the side of Lisebeek River. Deep water, with a lot of aquatic plants growing. Light red/ yellow sediments, very densely compact with a high clay content. | | | | |

| Sample Name | Coordinates | Comments |
|---|---|---|
| WH.01 | -33.951071, 018.51776 | All water hyacinth samples were collected from the river stretch prior to the release of treated wastewater from AWTW. The river is relatively shallow, and slow moving with large and small household waste materials present. The water hyacinth had already been cut and was awaiting removal. |
| WH.02 | -33.950944, 18.515760 | |
| WH.03 | -33.950928, 18.514411 | |
| WH.04 | -33.950790, 18.512606 | |

# APPENDIX II

Particle size & Microscope images of sediment

Distribution of grain size in each sample as a percent.

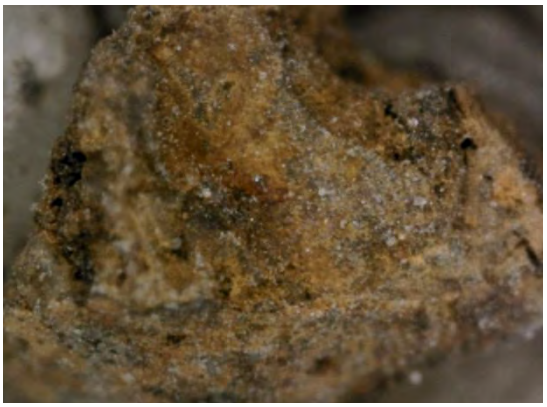
| Sample | Gravel | Very coarse sand | Coarse sand | Medium sand | Fine sand | Very fine sand | Mud |
|---|---|---|---|---|---|---|---|
| **GS.20** | 0.2 | 0.5 | 6.2 | 39.2 | 48.2 | 2.9 | 2.8 |
| **GS.19** | 1.2 | 1.6 | 14.8 | 51.1 | 30.6 | 0.4 | 0.2 |
| **GS.21** | 12.2 | 5.4 | 29.1 | 39.5 | 13.0 | 0.6 | 0.2 |
| **GS.22** | 2.8 | 6.4 | 45.4 | 34.0 | 10.9 | 0.4 | 0.1 |
| **GS.02** | 8.7 | 3.0 | 39.0 | 45.7 | 3.4 | 0.1 | 0.1 |
| **GS.01** | 18.3 | 7.3 | 25.0 | 32.0 | 13.6 | 1.1 | 2.6 |
| **GS.03** | 5.5 | 7.3 | 41.0 | 38.9 | 7.0 | 0.2 | 0.1 |
| **GS.04** | 14.3 | 5.4 | 33.0 | 39.7 | 7.2 | 0.2 | 0.2 |
| **GS.05** | 1.9 | 3.2 | 27.4 | 52.4 | 14.7 | 0.3 | 0.1 |
| **GS.06** | 0.2 | 0.6 | 8.4 | 61.5 | 28.5 | 0.6 | 0.2 |
| **GS.07** | 11.6 | 12.7 | 40.6 | 29.3 | 5.3 | 0.2 | 0.2 |
| **GS.08** | 1.1 | 2.5 | 29.2 | 50.5 | 16.3 | 0.3 | 0.1 |
| **GS.09** | 0.4 | 0.8 | 6.2 | 25.3 | 65.5 | 1.4 | 0.2 |
| **GS.10** | 1.7 | 1.0 | 2.1 | 9.4 | 78.9 | 6.3 | 0.6 |
| **GS.11** | 15.9 | 22.5 | 40.6 | 18.4 | 2.5 | 0.1 | 0.1 |
| **GS.12** | 3.1 | 6.1 | 11.9 | 32.6 | 45.0 | 1.2 | 0.2 |
| **GS.13** | 0.5 | 3.4 | 22.9 | 49.3 | 23.3 | 0.4 | 0.2 |
| **GS.14** | 1.2 | 1.0 | 5.2 | 19.8 | 69.5 | 2.7 | 0.6 |
| **GS.15** | 1.6 | 2.7 | 19.3 | 53.4 | 22.4 | 0.6 | 0.1 |
| **GS.16** | 5.5 | 2.4 | 4.8 | 9.3 | 73.5 | 3.5 | 1.0 |
| **GS.17** | 5.1 | 3.8 | 4.6 | 12.6 | 67.2 | 5.1 | 1.6 |
| **GS.18** | 1.5 | 7.1 | 8.6 | 24.7 | 53.4 | 3.6 | 1.0 |
| **GS.26** | 24.0 | 8.8 | 11.8 | 23.1 | 20.8 | 5.7 | 5.8 |
| **GS.23** | 26.0 | 13.0 | 17.9 | 13.0 | 16.2 | 7.3 | 6.7 |
| **GS.24** | 24.9 | 6.7 | 16.0 | 21.7 | 23.8 | 4.6 | 2.2 |
| **GS.25** | 49.2 | 5.1 | 8.6 | 15.5 | 16.3 | 3.9 | 1.5 |
| **GS.27** | 2.7 | 2.1 | 5.4 | 14.0 | 10.8 | 14.5 | 50.6 |

## Visual observations of gravels and sands using digital microscope

A visual analysis of larger grain sizes allowed for the identification of minerals within the sands and gravels. Samples of significance were captured using the digital microscope and descriptions of the sands are described in the table below. It is apparent that the very large majority of sands consist of well-rounded stained quartz which stays true throughout the course of the river samples.

| Sample | Description |
|---|---|
| **GS.01** | Large dark stones in gravels. Sand mostly well rounded quartz with some conglomerates with small quartz stones visible within the matrix. |
| **GS.03, 11** | Large individual grains of well rounded and stained quartz. Some small household waste materials present in gravels. All sand fractions mostly well rounded quartz |
| **GS.04, 15** | Large dark stones. Conglomerates with small quartz stones visible in the matrix. Sand mostly quartz (stained) |
| **GS.05** | Small marine shells and quartz suspended in dark metallic like matrix- similar to tarmac. Separate well rounded and stained quartz present. |
| **GS.06** | Very little gravel present. Little/ no organics. |
| **GS.08** | Small marine shells present. Little organic matter or waste materials present. |
| **GS.12** | Gravel sized quartz grains present. Well rounded and stained. Small fractions of broken glass also present. |
| **GS.13** | Tarmac like conglomerates with rounded quartz suspended in dark matrix. |
| **GS.09,10,14,16,17,18** | Mostly large particles of decaying organics. Very dark in colour. |
| **GS.19** | Mostly small marine shells. |
| **GS.21** | Large variation in size and colours of small gravels. Little organic material present and little waste materials present. |
| **GS.23** | Large variation in well rounded gravel sized minerals present. Appeared to hold onto clay particles. |

GS.11 Coarse sand fraction



GS.11 Coarse sand fraction

GS.11 Coarse sand fraction

GS.11 Medium sand fraction

GS.11 Medium sand fraction

GS.11 Fine sand fraction

GS.11 Fine sand fraction

GS.15 Coarse sand fraction

GS.15 Medium sand fraction

GS.15 Fine sand fraction

GS.15 Medium sand fraction

# APPENDIX III

XRF results

Coarse fraction major element by XRF (mg/kg)

| | SiO2 | TiO2 | Al2O3 | Fe2O3 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | SO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.22** | 299504 | 480 | 7198 | 8184 | 155 | 844 | 6146 | 0 | 1577 | 742 | 68 | 1402 |
| **GS.02** | 259536 | 839 | 13654 | 22382 | 155 | 1387 | 2073 | 890 | 3570 | 698 | 68 | 881 |
| **GS.01** | 186285 | 240 | 5081 | 1049 | 77 | 543 | 9362 | 445 | 0 | 916 | 0 | 3764 |
| **GS.04** | 188622 | 120 | 4710 | 4057 | 77 | 784 | 4717 | 74 | 996 | 960 | 0 | 1882 |
| **GS.11** | 236163 | 1619 | 18894 | 24900 | 310 | 2593 | 10363 | 0 | 8551 | 785 | 68 | 1362 |
| **GS.13** | 167072 | 599 | 7039 | 5246 | 77 | 844 | 17510 | 0 | 1411 | 1527 | 0 | 3524 |
| **GS.15** | 283891 | 540 | 7568 | 8463 | 155 | 905 | 6075 | 890 | 1660 | 785 | 0 | 1482 |
| **GS.21** | 197971 | 300 | 7409 | 909 | 77 | 603 | 1644 | 668 | 332 | 611 | 0 | 1842 |
| **GS.23** | 182779 | 240 | 3863 | 1329 | 77 | 784 | 9148 | 0 | 332 | 960 | 0 | 1722 |
| **GS.25** | 169175 | 2458 | 27097 | 90019 | 310 | 1869 | 27802 | 223 | 10460 | 873 | 137 | 2082 |

*Due to limitations of XRF when measuring very small quantities of oxidised major elements, the results are elusive particularly for Cr in the instance of the Black River.

Coarse fraction trace elements by XRF (mg/kg)

| | As | Ba | Bi | Cd | Ce | Cl | Co | Cs | Cu | Ga | Ge | Hf | Hg | La | Lu | Mo | Nb | Nd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.22** | 1.72 | 61.57 | 0.94 | 0 | 54.17 | 734.7 | 0 | 1.12 | 0 | 0 | 1.74 | 3.46 | 0.02 | 7.45 | 0.27 | 5.31 | 2.12 | 29.02 |
| **GS.02** | 8.57 | 68.8 | 0.96 | 0 | 55.43 | 700.99 | 0 | 1.17 | 0 | 1.54 | 1.3 | 3.59 | 0.02 | 12.03 | 0.27 | 4.73 | 4 | 31.94 |
| **GS.01** | 0 | 49.99 | 0.89 | 0.8 | 61.71 | 460.99 | 0 | 1.68 | 0 | 0 | 4.95 | 3.69 | 0.02 | 26.76 | 0.27 | 7.73 | 2.8 | 30.83 |
| **GS.04** | 0 | 51.77 | 0.9 | 0 | 59.93 | 684.89 | 0 | 1.61 | 0 | 0 | 2.2 | 3.28 | 0.02 | 0 | 0.27 | 7.35 | 2.4 | 30.41 |
| **GS.11** | 6.63 | 101.55 | 0.96 | 0 | 40.25 | 678.9 | 0 | 1.21 | 0 | 5.81 | 4.06 | 3.87 | 0.02 | 45.11 | 0.27 | 6.56 | 5.35 | 35.94 |
| **GS.13** | 0 | 60.57 | 0.95 | 0 | 55.42 | 805.59 | 0 | 1 | 0 | 0.16 | 6.45 | 3.25 | 0.02 | 0 | 0.27 | 8.1 | 3.76 | 29.71 |
| **GS.15** | 4.03 | 65.78 | 0.96 | 0 | 56.49 | 601.18 | 0 | 0.84 | 0 | 0 | 3.01 | 3.5 | 0.02 | 6.41 | 0.27 | 5.88 | 3.28 | 30.46 |
| **GS.21** | 0 | 55.63 | 0.91 | 0 | 63.87 | 353.02 | 0 | 1.21 | 0 | 0 | 2.54 | 3.02 | 0.02 | 0.86 | 0.27 | 7.29 | 2.44 | 28.69 |
| **GS.23** | 0 | 51.86 | 0.85 | 0.12 | 52 | 1125.41 | 0 | 1.61 | 0 | 0 | 5.11 | 3.38 | 0.02 | 0 | 0.27 | 8.14 | 2.51 | 30.47 |
| **GS.25** | 1.3 | 170.47 | 0.92 | 0.79 | 39.01 | 168.93 | 92.46 | 0.33 | 59.45 | 7.83 | 4.68 | 6.63 | 0.01 | 5.45 | 0.26 | 3.51 | 8.67 | 29.27 |

Coarse fraction trace elements by XRF continued. (mg/kg)

| | Ni | Pb | Rb | Sb | Sc | Se | Sm | Sn | Sr | Ta | Te | Th | Tl | U | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.22** | 9.87 | 28.84 | 4.03 | 0.28 | 13.18 | 0 | 12.61 | 0.73 | 44.35 | 1.95 | 8.75 | 11.1 | 0 | 1.15 | 14.2 | 5.85 | 3.12 | 17.98 | 84.74 | 59.09 |
| **GS.02** | 24.32 | 35.77 | 16.04 | 0.36 | 13.33 | 0.03 | 10.15 | 0 | 25.74 | 1.75 | 3.17 | 13.47 | 0 | 0.52 | 49.88 | 4.98 | 4.99 | 19.54 | 56.16 | 66.64 |
| **GS.01** | 0.93 | 5.68 | 0 | 1.48 | 13.55 | 0.12 | 14.19 | 9.87 | 30.38 | 1.86 | 7.98 | 8.29 | 0 | 0.34 | 13.71 | 4.52 | 0.7 | 29.12 | 94.11 | 41.95 |
| **GS.04** | 2.73 | 4.93 | 0 | 2.33 | 12.87 | 0.06 | 13.07 | 13.37 | 11.41 | 1.9 | 7.12 | 8.2 | 0 | 0.49 | 2.23 | 4.65 | 0 | 28.73 | 41.38 | 29.25 |
| **GS.11** | 31.03 | 44.51 | 47.78 | 0.37 | 15.28 | 0 | 9.78 | 1.28 | 90.56 | 1.6 | 10.22 | 14.92 | 0.14 | 2.07 | 53.7 | 5.97 | 11.5 | 20.93 | 115.16 | 135.82 |
| **GS.13** | 5.39 | 27.75 | 11.66 | 1.74 | 3.53 | 0.23 | 13.1 | 0 | 75.67 | 1.86 | 22.83 | 11.5 | 0.01 | 0.53 | 21.92 | 4.14 | 3.09 | 27.29 | 145.99 | 65.84 |
| **GS.15** | 9.98 | 36.98 | 5.67 | 0 | 12.54 | 0.15 | 12.63 | 0 | 64.31 | 2 | 9.78 | 12.3 | 0 | 1 | 19.13 | 5.5 | 3.55 | 18.74 | 114.16 | 64.08 |
| **GS.21** | 3.53 | 15.55 | 0 | 0 | 14.73 | 0 | 14.29 | 7.38 | 9.2 | 1.89 | 0.28 | 9.14 | 0 | 0.13 | 8.1 | 4.55 | 0 | 29.73 | 41.39 | 38.28 |
| **GS.23** | 1.57 | 7.41 | 0 | 0.91 | 11.28 | 0 | 14.09 | 11.23 | 27.88 | 1.72 | 8.84 | 6.66 | 0 | 0.2 | 4.59 | 4.54 | 0.61 | 29.25 | 98.01 | 33.25 |
| **GS.25** | 74.73 | 183.24 | 64.4 | 1.21 | 7.54 | 1.87 | 1.7 | 17.85 | 156.31 | 1.92 | 27.77 | 25.4 | 1.14 | 2.82 | 147.35 | 2.03 | 10.87 | 5.4 | 236.31 | 175.58 |

Mud fraction major element by XRF (% g/g)

| Analyte | SiO2 | TiO2 | Al2O3 | Fe2O3 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | SO3 | Loss on ignition | Total (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.20** | 54.74 | 0.63 | 6.82 | 4.10 | 0.03 | 0.63 | 5.23 | 0.24 | 0.61 | 0.64 | 0.02 | 1.09 | 22.53 | 97.30 |
| **GS.19** | 52.95 | 0.65 | 5.65 | 5.72 | 0.04 | 0.65 | 6.77 | 0.59 | 0.61 | 0.92 | 0.03 | 1.44 | 21.57 | 97.60 |
| **GS.21** | 63.13 | 0.81 | 5.79 | 4.96 | 0.03 | 0.41 | 3.61 | 0.04 | 0.43 | 1.21 | 0.02 | 1.28 | 16.72 | 96.12 |
| **GS.22** | 64.56 | 0.79 | 5.58 | 4.03 | 0.03 | 0.53 | 4.15 | 0.18 | 0.51 | 1.09 | 0.04 | 1.49 | 16.00 | 96.73 |
| **GS.02** | 37.02 | 0.45 | 3.95 | 2.63 | 0.02 | 0.20 | 1.12 | <0.01 | 0.27 | 0.64 | 0.01 | 0.27 | 15.18 | 59.27 |
| **GS.01** | 75.74 | 0.89 | 9.27 | 2.46 | 0.02 | 0.25 | 0.58 | <0.01 | 0.52 | 0.11 | <0.01 | 0.27 | 9.89 | 98.39 |
| **GS.03** | 61.76 | 0.80 | 4.42 | 3.55 | 0.04 | 0.36 | 2.59 | 0.13 | 0.44 | 1.47 | 0.02 | 0.66 | 14.9 | 88.98 |
| **GS.04** | 67.01 | 0.75 | 5.27 | 4.60 | 0.03 | 0.31 | 2.25 | 0.16 | 0.45 | 0.75 | 0.01 | 0.94 | 12.62 | 93.12 |
| **GS.05** | 82.53 | 1.29 | 5.57 | 6.95 | 0.05 | 0.48 | 3.70 | 0.41 | 0.57 | 2.45 | 0.03 | 1.55 | 12.12 | 116.04 |
| **GS.06** | 70.14 | 2.55 | 2.96 | 2.54 | 0.04 | 0.24 | 2.60 | <0.01 | 0.28 | 5.13 | 0.02 | 0.73 | 7.21 | 93.55 |
| **GS.07** | 42.71 | 0.36 | 4.96 | 4.34 | 0.05 | 0.81 | 18.74 | 0.37 | 0.48 | 0.30 | 0.02 | 1.96 | 25.56 | 98.58 |
| **GS.08** | 67.58 | 0.66 | 3.87 | 2.77 | 0.03 | 0.41 | 9.43 | 0.09 | 0.41 | 0.56 | 0.02 | 0.79 | 13.67 | 99.06 |
| **GS.09** | 77.80 | 1.61 | 2.47 | 2.28 | 0.04 | 0.25 | 4.82 | 0.01 | 0.31 | 1.83 | 0.02 | 0.45 | 5.58 | 97.43 |
| **GS.10** | 83.42 | 0.84 | 2.99 | 1.89 | 0.03 | 0.27 | 3.33 | 0.06 | 0.41 | 0.61 | 0.02 | 0.32 | 5.49 | 99.19 |
| **GS.11** | 56.83 | 0.59 | 5.90 | 6.44 | 0.04 | 0.62 | 6.77 | 0.29 | 0.56 | 0.59 | 0.02 | 2.26 | 18.15 | 96.75 |
| **GS.12** | 73.89 | 1.78 | 3.08 | 2.93 | 0.04 | 0.30 | 4.19 | 0.13 | 0.34 | 2.47 | 0.03 | 0.79 | 8.94 | 97.42 |
| **GS.13** | 77.07 | 1.30 | 3.38 | 2.56 | 0.03 | 0.30 | 3.62 | 0.13 | 0.40 | 1.34 | 0.01 | 0.95 | 8.23 | 98.08 |
| **GS.14** | 78.33 | 0.98 | 3.39 | 1.92 | 0.02 | 0.37 | 3.78 | <0.01 | 0.43 | 0.88 | 0.01 | 0.35 | 8.51 | 97.68 |
| **GS.15** | 75.12 | 1.03 | 4.36 | 3.37 | 0.03 | 0.25 | 3.04 | <0.01 | 0.49 | 0.97 | 0.01 | 1.20 | 8.26 | 97.09 |
| **GS.16** | 81.79 | 0.96 | 4.04 | 2.24 | 0.03 | 0.31 | 1.98 | 0.19 | 0.49 | 0.67 | 0.01 | 0.38 | 7.43 | 99.45 |
| **GS.17** | 63.65 | 0.70 | 6.02 | 3.27 | 0.03 | 0.51 | 4.60 | 0.28 | 0.63 | 0.64 | 0.01 | 0.41 | 18.3 | 96.59 |
| **GS.18** | 69.50 | 0.82 | 5.30 | 3.10 | 0.03 | 0.74 | 3.25 | 1.18 | 0.70 | 0.59 | 0.02 | 0.22 | 14.38 | 97.34 |
| **GS.26** | 53.43 | 0.80 | 12.61 | 5.89 | 0.04 | 0.82 | 2.45 | 0.04 | 1.22 | 0.82 | 0.03 | 0.44 | 16.97 | 91.69 |
| **GS.23** | 57.25 | 0.71 | 10.34 | 5.04 | 0.03 | 0.62 | 2.08 | 0.22 | 1.00 | 0.64 | 0.02 | 0.28 | 20.87 | 96.99 |
| **GS.24** | 67.40 | 0.77 | 7.56 | 4.58 | 0.03 | 0.53 | 2.19 | 0.31 | 0.82 | 0.57 | 0.02 | 0.33 | 14.3 | 96.85 |
| **GS.25** | 64.06 | 0.90 | 11.15 | 5.70 | 0.04 | 0.48 | 2.74 | 0.10 | 0.87 | 0.39 | 0.02 | 0.68 | 12.43 | 98.22 |
| **GS.27** | 53.54 | 1.13 | 19.90 | 6.81 | 0.03 | 0.47 | 0.45 | <0.01 | 1.33 | 0.08 | 0.01 | 0.17 | 11.87 | 94.41 |

Mud trace elements by XRF (mg/kg)

| Analyte | As | Ba | Bi | Cd | Cr | Ce | Cl | Co | Cs | Cu | Ga | Ge | Hf | Hg | La | Lu | Mo | Nb | Nd |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.20** | 30.8 | 122 | 1.45 | 8 | 115.7 | 26.8 | 2,109 | <0.56 | 0.84 | 179 | 9.74 | 42.09 | 9.3 | <1.00 | 0 | <0.61 | 12.69 | 9.24 | 37.08 |
| **GS.19** | 29.3 | 102 | 1.09 | 2.96 | 229.2 | <3.08 | 10,989 | <0.56 | 1.06 | 325 | 9.05 | 57.79 | 13 | <1.00 | 0 | <0.61 | 12.9 | 7.17 | 34.2 |
| **GS.21** | 19.4 | 114 | 0.93 | 0 | 147.7 | <3.08 | 2,296 | <0.56 | 1.28 | 196 | 8.6 | 39.22 | 26.8 | <1.00 | 13.4 | <0.61 | 21 | 13.6 | 33.9 |
| **GS.22** | 21.3 | 92.2 | 1.02 | 0.96 | 240.9 | <3.08 | 2,807 | <0.56 | 0.98 | 265 | 9.53 | 38.7 | 28.6 | <1.00 | <0.62 | <0.61 | 13.3 | 9.64 | 34 |
| **GS.02** | 8.62 | 66.3 | 0.89 | 0 | 77.4 | <3.08 | 3,195 | <0.56 | 0.86 | 121 | 8.1 | 17.7 | 24.2 | <1.00 | 11.4 | <0.61 | 7.79 | 8.97 | 35 |
| **GS.01** | 5.9 | 77.9 | 0.95 | 0 | 49.3 | <3.08 | 543 | <0.56 | 0.93 | 23 | 9.58 | 7.83 | 5.76 | <1.00 | 24.39 | <0.61 | 11.1 | 15.7 | 35.81 |
| **GS.03** | 14.3 | 88.7 | 0.87 | 0.8 | 154.6 | <3.08 | 3,195 | <0.56 | 0.6 | 508 | 10.3 | 25.71 | 25 | <1.00 | <0.62 | <0.61 | 11.7 | 12.9 | 36.1 |
| **GS.04** | 15.7 | 101 | 0.82 | 1.85 | 77.2 | <3.08 | 3,096 | <0.56 | 1.11 | 525 | 10.4 | 38.65 | 15.5 | <1.00 | 10.1 | <0.61 | 16.7 | 14.5 | 36.2 |
| **GS.05** | 16 | 149 | 0.72 | 1.53 | 171.9 | <3.08 | 8,786 | 711 | 1.37 | 377 | 12.1 | 32.41 | 40.2 | <1.00 | <0.62 | <0.61 | 58.3 | 12.6 | 36.7 |
| **GS.07** | 23.4 | 108 | 1.03 | 4.85 | 112.3 | 45.4 | 3,016 | <0.56 | 0.88 | 333 | 5.34 | 45.8 | 4.8 | <1.00 | <0.62 | <0.61 | 14.1 | 6.82 | 30.6 |
| **GS.08** | 12.7 | 96.8 | 0.92 | 2.77 | 124.1 | 13.5 | 7,285 | <0.56 | 0.69 | 200 | 9.22 | 43.9 | 13.9 | <1.00 | <0.62 | <0.61 | 15.4 | 11.6 | 35.6 |
| **GS.09** | 13.1 | 109 | 0.83 | 1.63 | 122.2 | <3.08 | 3,658 | <0.56 | 0.93 | 53.9 | 3.7 | 18.4 | 27.1 | <1.00 | <0.62 | <0.61 | 30.1 | 21.7 | 36 |
| **GS.10** | 5.72 | 82.8 | 0.93 | 0.71 | 103.5 | 13.2 | 2,723 | <0.56 | 1.11 | 62.7 | <3.21 | 22 | 10.6 | <1.00 | <0.62 | <0.61 | 14.3 | 9.72 | 33.7 |
| **GS.11** | 27.8 | 92.8 | 1.11 | 2.6 | 123.0 | <3.08 | 3,714 | <0.56 | 1.09 | 373 | 8.72 | 40.6 | 11.1 | <1.00 | <0.62 | <0.61 | 14.2 | 9.04 | 36.2 |
| **GS.13** | 14.8 | 95.5 | 0.83 | 3.1 | 87.9 | <3.08 | 3,875 | <0.56 | <0.49 | 144 | 8.28 | 24.5 | 35 | <1.00 | <0.62 | <0.61 | 21.7 | 16.5 | 34.7 |
| **GS.14** | 9.48 | 95.7 | 0.77 | 0.92 | 100.1 | <3.08 | 823 | <0.56 | 1.28 | 62.5 | 6.55 | 24.6 | 26.3 | <1.00 | <0.62 | <0.61 | 20.6 | 17.3 | 34.1 |
| **GS.15** | 56.8 | 125 | 1.55 | 0.51 | 94.0 | <3.08 | 2,165 | <0.56 | 0.85 | 65.2 | 9.73 | 32.6 | 36.2 | <1.00 | <0.62 | <0.61 | 14.1 | 16.1 | 34.3 |
| **GS.16** | 11.2 | 86.4 | 0.93 | 0.53 | 69.7 | <3.08 | 1,326 | <0.56 | 0.98 | 61.9 | 7.8 | 28.1 | 22.3 | <1.00 | <0.62 | <0.61 | 11 | 14.5 | 35.8 |
| **GS.17** | 19.7 | 102 | 1.03 | 3.51 | 89.3 | <3.08 | 3734 | <0.56 | 1.26 | 159 | 11.9 | 56.88 | 10.2 | <1.00 | <0.62 | <0.61 | 17.1 | 11.1 | 32.9 |
| **GS.18** | 16.5 | 116 | 1 | 1.84 | 111.3 | <3.08 | 33581 | <0.56 | 1.4 | 135 | 10.9 | 44.09 | 14.7 | <1.00 | <0.62 | <0.61 | 15.4 | 11.4 | 33.8 |
| **GS.26** | 41.2 | 243 | 1.26 | 3.51 | 185.7 | <3.08 | 984 | <0.56 | 1.41 | 172 | 30.31 | 43.44 | 4.7 | <1.00 | <0.62 | <0.61 | 9.9 | 14.1 | 42.2 |
| **GS.23** | 28.3 | 157 | 0.93 | 1.17 | 135.0 | <3.08 | 1276 | <0.56 | 0.81 | 210 | 17.2 | 54.4 | 6.06 | <1.00 | <0.62 | <0.61 | 10.7 | 11.6 | 37.4 |
| **GS.24** | 22.7 | 131 | 1.1 | 1.23 | 105.4 | <3.08 | 2338 | <0.56 | 1.27 | 144 | 10.8 | 40.37 | 6.99 | <1.00 | <0.62 | <0.61 | 11.7 | 13.5 | 36.0 |
| **GS.25** | 17.7 | 139.4 | 1 | 1.27 | 131.7 | <3.08 | 1402 | <0.56 | 0.98 | 123 | 15.9 | 27.49 | 9.64 | <1.00 | 59.3 | 0.26 | 11.12 | 14.69 | 42.0 |
| **GS.27** | 20.7 | 111.9 | 0.87 | 0 | 59.9 | <3.08 | 784 | <0.56 | 1.23 | 4.4 | 27.9 | 7.08 | 4.57 | <1.00 | 46.03 | 0.27 | 6.73 | 24.47 | 38.8 |

Mud trace elements by XRF continued (mg/kg)

| Analyte | Ni | Pb | Rb | Sb | Sc | Se | Sm | Sn | Sr | Ta | Te | Th | Tl | U | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.20** | 42.4 | 269 | 29.92 | 1.8 | <2.63 | 1.43 | 9.31 | 1.88 | 263 | 1.69 | 52.56 | 28.56 | 0.97 | 1.76 | 58.23 | 4.31 | 30.2 | 27.56 | 1430 | 2085 |
| **GS.19** | 64.7 | 226 | 25.8 | <1.48 | <2.63 | 2.43 | 7.73 | <0.08 | 293 | 1.72 | 70.12 | 23.9 | 1.27 | 1.48 | 61.45 | 2.86 | 31.3 | 22.03 | 2193 | 3160 |
| **GS.21** | 58.7 | 135 | 17.3 | 2.74 | 5.57 | 1.79 | 8.06 | 23.3 | 204 | 1.68 | 35.86 | 19.2 | 1.41 | 4.17 | 42.53 | 4.44 | 68.7 | 29.55 | 1286 | 8397 |
| **GS.22** | 51.6 | 149 | 17.2 | <1.48 | <2.63 | 1.46 | 10.2 | <0.08 | 180 | 1.28 | 47.71 | 21.5 | 0.96 | 4 | 57.14 | 3.52 | 58.4 | 26.49 | 1225 | 6819 |
| **GS.02** | 50.9 | 78.1 | 9.78 | <1.48 | 11.5 | 1.44 | 9.29 | <0.08 | 85.3 | 1.13 | 15.63 | 15.2 | 0.77 | 2.78 | 41.59 | 3.33 | 41.7 | 27.41 | 496 | 4239 |
| **GS.01** | 24.04 | 41 | 26 | <1.48 | 13.5 | 2.35 | 12.17 | 1 | 54 | 1.5 | 7.4 | 17.1 | 0.59 | 2.19 | 51.2 | 4.37 | 37 | 30.45 | 166 | 1007 |
| **GS.03** | 56.1 | 104 | 11.3 | <1.48 | 3.92 | 1.87 | 8.9 | <0.08 | 147 | 0.9 | 29.5 | 14.6 | 0.83 | 3.1 | 45.7 | 4.11 | 51.5 | 30.4 | 752 | 6519 |
| **GS.04** | 60.1 | 147 | 17.6 | 1.91 | 7.85 | 2.48 | 9.76 | 10.9 | 134 | 0.96 | 27.3 | 16.3 | 0.99 | 2.7 | 32.4 | 4.6 | 47.7 | 29.8 | 1221 | 4924 |
| **GS.05** | 60.1 | 171 | 14.9 | <1.48 | 2.86 | 1.18 | 7.2 | 16 | 179 | 0.25 | 33.3 | 15.8 | 1.79 | 7.44 | 37.7 | 4.41 | 124 | 32.9 | 1013 | 17877 |
| **GS.07** | 36 | 177 | 24.7 | 1.52 | <2.63 | 0.96 | 8.6 | <0.08 | 586 | 2.14 | 115 | 16.4 | 0.86 | 1.68 | 43.4 | 3.25 | 16.4 | 17.9 | 1958 | 796 |
| **GS.08** | 25.8 | 115 | 20.4 | 1.49 | <2.63 | <0.36 | 10.1 | 3.53 | 380 | 1.06 | 73.6 | 13 | 1.42 | 3.41 | 30.6 | 4.24 | 40.2 | 26.6 | 1569 | 4362 |
| **GS.09** | 13 | 67.3 | 11.6 | 1.77 | <2.63 | 0.9 | 11.4 | 9.51 | 243 | 1.87 | 56.4 | 13.8 | 0.77 | 6.25 | 39.2 | 4.11 | 101 | 24.8 | 541 | 13910 |
| **GS.10** | 16.4 | 63 | 13.8 | 2.96 | <2.63 | 0.4 | 11.8 | <0.08 | 147 | 1.49 | 28.4 | 13.4 | 0.47 | 3.05 | 21.9 | 4.32 | 35.2 | 27.9 | 626 | 3992 |
| **GS.11** | 54.5 | 305 | 27 | <1.48 | <2.63 | 1.26 | 6.03 | 3.81 | 274 | 1.46 | 66.3 | 26.5 | 1.68 | 1.09 | 54.8 | 3.08 | 31.2 | 21.4 | 1564 | 2679 |
| **GS.13** | 22.5 | 142 | 13.9 | 1.5 | <2.63 | 1.14 | 11 | 7.83 | 180 | 1.42 | 45.6 | 19.5 | 1.3 | 7.51 | 41.9 | 3.91 | 110 | 27.5 | 671 | 14058 |
| **GS.14** | 23.9 | 72 | 14.1 | 1.81 | <2.63 | <0.36 | 11.9 | 5.42 | 168 | 1.44 | 36 | 10.4 | 0.54 | 4.05 | 25.9 | 4.21 | 77.8 | 30.2 | 660 | 8962 |
| **GS.15** | 33.8 | 728 | 15.7 | <1.48 | 7.72 | 1.02 | 8.83 | 1.77 | 138 | 1.36 | 32.3 | 63.3 | 1.02 | 4.98 | 49 | 3.59 | 91.9 | 26.3 | 966 | 11629 |
| **GS.16** | 27.6 | 84.9 | 17.2 | <1.48 | 5.47 | <0.36 | 11.6 | <0.08 | 92.8 | 1.18 | 25.2 | 18 | 0.72 | 2.95 | 40.6 | 4.38 | 48.7 | 29.9 | 780 | 5790 |
| **GS.17** | 46.8 | 159 | 30.5 | <1.48 | <2.63 | 1.02 | 10.4 | <0.08 | 213 | 1.21 | 47.2 | 20.6 | 1.04 | 2.74 | 49.25 | 4.22 | 41.9 | 29.2 | 1898 | 2748 |
| **GS.18** | 43.2 | 156 | 32.5 | 2.28 | 7.12 | <0.36 | 10.1 | 0.18 | 170 | 1.16 | 29.4 | 22.1 | 1.17 | 4.06 | 54.47 | 4.96 | 59.2 | 31.3 | 1428 | 4469 |
| **GS.26** | 75.1 | 441 | 75.3 | 2.14 | 15.8 | 2.3 | 8.03 | 22.96 | 289 | 1.72 | 18.59 | 43.37 | 1.23 | 1.72 | 96.31 | 3.16 | 35 | 23.4 | 1442 | 625 |
| **GS.23** | 60.5 | 226 | 63.6 | 2.81 | 12 | 1.38 | 8.33 | 3.29 | 160 | 1.84 | 19.87 | 24.95 | 1.17 | 1.75 | 81.16 | 3.98 | 30.69 | 25 | 1839 | 779 |
| **GS.24** | 51.3 | 183 | 43.5 | <1.48 | 11.1 | 1.27 | 9.49 | 2.48 | 137 | 1.89 | 24.63 | 24 | 1.15 | 0.7 | 68.81 | 3.72 | 29.85 | 26.3 | 1314 | 1703 |
| **GS.25** | 59.15 | 212 | 44.5 | 1.11 | 8.17 | 0.7 | 7.32 | 1.99 | 139.5 | 1.43 | 26.13 | 25.78 | 1.42 | 1.85 | 61.01 | 3.92 | 40.31 | 26.88 | 893 | 2277 |
| **GS.27** | 51.59 | 71.4 | 90.02 | 1.15 | 16.75 | 1.17 | 7.64 | <0.08 | 51.06 | 1.73 | 0.41 | 23.1 | 0.11 | 6.32 | 115.75 | 3.6 | 32.9 | 24.14 | 124 | 332 |

Major element results and Omnian results for GS.06 and GS.12 (% g/g)

| Analyte | $SiO_2$ | $TiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $P_2O_5$ | $Cr_2O_3$ | $SO_3$ | Loss on ignition | Total (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.06** | 70.14 | 2.55 | 2.96 | 2.54 | 0.04 | 0.24 | 2.60 | <0.01 | 0.28 | 5.13 | 0.02 | 0.73 | 7.21 | 93.55 |
| **GS.12** | 73.89 | 1.78 | 3.08 | 2.93 | 0.04 | 0.30 | 4.19 | 0.13 | 0.34 | 2.47 | 0.03 | 0.79 | 8.94 | 97.42 |

| Analyte | As | Bi | Cl | Cu | Hf | Nb | Pb | Rb | Sn | Sr | V | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **GS.06** | 0.001 | 0.004 | 0.602 | 0.01 | 0.161 | 0.006 | 0.011 | 0.01 | 0.021 | 0.02 | 0.01 | 0.041 | 0.059 | 5.813 |
| **GS.12** | 0.001 | 0 | 0.584 | 0.015 | 0.062 | 0.003 | 0.014 | 0.002 | 0.007 | 0.026 | 0.007 | 0.02 | 0.082 | 2.547 |

Water hyacinth major elements by XRF (% g/g)

| I.D | SiO2 | TiO2 | Al2O3 | Fe2O3 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | SO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **WH.01** | 0.48 | 0.06 | 0.19 | 1.44 | 0.04 | 56.77 | 139.21 | 1.12 | 0.48 | 0.03 | 0.5 | 0.02 |
| **WH.02** | -0.13 | 0.02 | 0.11 | 0.19 | 0 | 13.96 | 33.08 | 0.18 | -0.08 | 0.02 | 0.07 | 0 |
| **WH.03** | 0.99 | 0.05 | 0.65 | 0.61 | 0 | 0.18 | 59.94 | 0.43 | -0.16 | 1.34 | 0.01 | 88.39 |
| **WH.04** | 2.33 | 0.08 | 1.18 | 2.09 | 0.01 | 0.25 | 73.51 | 1.51 | 0.15 | 1.42 | 0.08 | 92.9 |

Water hyacinth trace elements by XRF (mg/kg)

| I.D | As | Ba | Bi | Cd | Ce | Cl | Co | Cs | Cu | Ga | Ge | Hf | Hg | La | Lu | Mo | Nb | Nd | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **WH.01** | 41.2 | 274.1 | 0.9 | 8.7 | -176.8 | 157.7 | 92.7 | 16.8 | 52.2 | 0.3 | 1.3 | -35.7 | 0.01 | -0.6 | 1.3 | 9.8 | 6.3 | 85.5 | 1558.3 |
| **WH.02** | -0.3 | 53.9 | 1.5 | 6.0 | -22.6 | 167.1 | 66.8 | 4.7 | 18.1 | 1.3 | 1.3 | -5.2 | 0.02 | 87.3 | 1.6 | 1.7 | 3.3 | 52.4 | -6.3 |
| **WH.03** | 4.5 | 59.3 | 2.0 | 8.1 | 35.0 | 5285.2 | 78.0 | 9.2 | 24.6 | 1.1 | 1.3 | -2.5 | 0.01 | 124.5 | 1.6 | 3.1 | 3.6 | 49.4 | 11.3 |
| **WH.04** | 122.7 | 178.7 | 2.6 | 12.4 | 19.9 | 6007.1 | 111.1 | 5.6 | 142.0 | -0.1 | 1.4 | -33.8 | 0.0 | 120.4 | 1.6 | 16.8 | 5.5 | 49.5 | 657.2 |

| I.D | Pb | Rb | Sb | Sc | Se | Sm | Sn | Sr | Ta | Te | Th | Tl | U | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **WH.01** | 109.6 | 3.0 | 29.2 | -74.9 | -1.2 | -55.4 | -220.1 | 559.1 | 3.3 | -26.4 | 3.5 | 0.0 | 2.7 | 32.1 | -5.2 | 0.5 | 20.5 | 122.6 | 14.4 |
| **WH.02** | -46.0 | -0.5 | -0.2 | 154.7 | -2.0 | -8.8 | -2.9 | 141.5 | 1.8 | -0.3 | -1.2 | 0.2 | 2.2 | 16.5 | 1.2 | -0.9 | 10.6 | 40.2 | -0.5 |
| **WH.03** | -20.1 | 0.7 | 9.5 | 84.3 | -0.3 | -11.1 | -42.3 | 631.5 | 2.2 | 12.5 | -0.3 | 0.3 | 5.5 | 15.6 | 1.8 | 8.6 | 18.7 | 46.1 | 19.0 |
| **WH.04** | 821.8 | 13.3 | 192.7 | 83.2 | 15.8 | -12.0 | -55.6 | 749.6 | 1.5 | 31.4 | -5.9 | 2.0 | 9.5 | 72.8 | 6.0 | 12.1 | 78.5 | 123.1 | 45.4 |

**APPENDIX IV**
Statistical test results

T-test to identify significantly similar concentrations between the coarse fraction results and NBC major elements

| | SiO2 | TiO2 | Al2O3 | Fe2O3 | MnO | MgO | CaO | Na2O | K2O | P2O5 | Cr2O3 | SO3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **tcalc** | 4.8438 | 13.9013 | 29.5604 | 2.8991 | 9.3056 | 72.6582 | 3.6856 | 51.2659 | 17.2253 | 1.4279 | 2.6006 | 4.6210 |
| **tcrit** | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 | 2.2622 |
| | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | PASS | FAIL | FAIL |

T-test to identify significantly similar concentrations between the coarse fraction results and NBC minor elements

| | As | Ba | Bi | Cd | Ce | Cl | Co | Cs | Cu | Ga | Ge | Hf | Hg | La | Lu | Mo | Nb | Nd | Ni |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **tcalc** | 10.35 | 0.43 | 3.09 | 0.09 | 0.61 | 0.84 | 1.00 | 0.06 | 4.80 | 0.01 | 4.30 | 0.54 | 1.00 | 0.35 | 1.00 | 3.50 | 0.42 | 1.92 | 3.07 |
| **tcrit** | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 |
| | FAIL | PASS | FAIL | PASS | PASS | PASS | PASS | PASS | FAIL | PASS | FAIL | PASS | PASS | PASS | PASS | FAIL | PASS | PASS | FAIL |

| | Pb | Rb | Sb | Sc | Se | Sm | Sn | Sr | Ta | Te | Th | Tl | U | V | W | Y | Yb | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **tcalc** | 1.01 | 0.15 | 4.48 | 1.36 | 1.19 | 1.17 | 2.94 | 1.95 | 2.49 | 21.11 | 5.29 | 117.87 | 3.32 | 2.38 | 128.31 | 0.85 | 7.21 | 1.74 | 0.98 |
| **tcrit** | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 | 2.26 |
| | PASS | PASS | FAIL | PASS | PASS | PASS | FAIL | PASS | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | FAIL | PASS | FAIL | PASS | PASS |