The partitioning and mobility of metals in the Blesbokspruit

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ABSTRACT

The Blesbokspruit is situated south-east of Johannesburg on South Africa's East Rand, famous for its prolific gold and uranium deposits. With the onset of mining in the region around 1930, the Blesbokspruit was altered from a non-perennial to a perennial stream and a wetland due to the construction of roads and embankments as well as the discharge of mine effluent. Various studies have highlighted the detrimental impact South African gold mines and their slimes dams have on the environment especially the release of metals into aquatic ecosystems. Unable to degrade naturally, metal pollution accumulates within aquatic ecosystems with the potential to move up the biologic chain.

Water and sediment samples were taken from throughout the Blesbokspruit in an attempt to characterise the aqueous and sediment geochemistry of the stream. Filtered and acidified water samples were analysed for major cations and anions using Atomic Absorption Spectrophotometry and Ion Chromatography respectively. The waters were found to have elevated levels of Cl^-, SO_4^{2-}, Na^+ and Ca^{2+}. These elevated salt concentrations are derived from the discharge of saline effluent into the Blesbokspruit by the Grootvlei Proprietary Mines Ltd and are responsible for the increase in electrical conductivity downstream of the mine. The generally mildly alkaline nature of the Blesbokspruit is the result of the underlying dolomites of the Chuniespoort Group.

ICP-MS was used to quantify aqueous and sediment metal enrichment relative to natural concentrations reported in the literature. The results of the ICP-MS indicate aqueous and sediment enrichment in chalcophile metals derived from the oxidation of sulphide minerals. U is also enriched within the water and is derived from the ore minerals mined from the underlying Witwatersrand Supergroup. However, total metal concentrations are not indicative of bioavailable metal concentrations. For this reason it is important to determine how metals are partitioned within the sediment.

A sequential extraction was performed on sediment samples from the Blesbokspruit as a method of determining metal partitioning and mobility

under various possible environmental conditions. The sequential extraction extracted metals from the following five operationally defined fractions: the *exchangeable* fraction, sensitive to changes in ionic concentration; the pH-sensitive *bound to carbonates* fraction; the redox-sensitive *bound to Fe and Mn oxides* and *bound to organic matter* fractions and essentially inert and unavailable *residual* fraction. Metal extracts from the five fractions were analysed by ICP-MS. The results of the sequential extraction indicate that only minor proportions of metals are *exchangeable,* while a significant proportion of many of the metals analysed for were hosted in the *residual* phase and are therefore not bioavailable under most natural conditions. Varying amounts of the metals analysed were partitioned within the *carbonates, Fe and Mn oxides and organic matter.*

CONTENTS

1 *INTRODUCTION*

1.1 *MOTIVATION*

Metal pollution of aquatic systems is important for two main reasons. Firstly, metals are not usually eliminated from aquatic ecosystems by natural processes, in contrast to most organic pollutants. Secondly, most metal pollutants are enriched in mineral and organic substances resulting in their accumulation in bottom sediments (Förstner and Wittman, 1981). Various processes of remobilisation may release metals from the sediment allowing them to move up the biologic chain to ultimately reach humans, producing both chronic and acute ailments (Förstner and Wittman, 1981).

Förstner and Wittman (1976) found metal enrichment in sediment effluent from a number of Witwatersrand gold mines which they ascribed to the presence of ore minerals, containing Cr, Zn, Pb, Co or processing additives containing Hg, Zn, Pb. Wade *et al.* (2000) reported accumulations of U in the Mooi River on the West Rand also as a result of mining in the area. Waste produced, both currently and historically, by gold mines surrounding the Blesbokspruit includes solid processed residues disposed on tailings dumps as well as water pumped from flooded underground workings and discharged into the Blesbokspruit. Both of these waste types are potential sources of metals, suggesting accumulation of metals within the Blesbokspruit.

The total concentration of metals in sediments does, however, not accurately determine the potential effects of sediment contamination, as not all forms of a given metal have equal impacts on the environment (Tessier *et al.*, 1979). For this reason, a sequential extraction was performed on the sediment of the Blesbokspruit. Sequential extractions provide details on the origin, mode of occurrence, biological and physiochemical availability, mobilisation and transport of metals (Tessier *et al.*, 1979). However, sequential extractions do have limitations (Kheboian and Bauer, 1987). These include the inability of the extraction to simulate natural processes, the effects of sample pre-treatment and preservation as well as the selectivity and specificity of the reagents used (Martin *et al.*, 1987; Rapin *et al.*, 1986).

1.2 OBJECTIVES

Coetzee (1993) reports that metal speciation data for South African natural water resources are practically non-existent. This study therefore aims to make a contribution in this regard with following objectives:

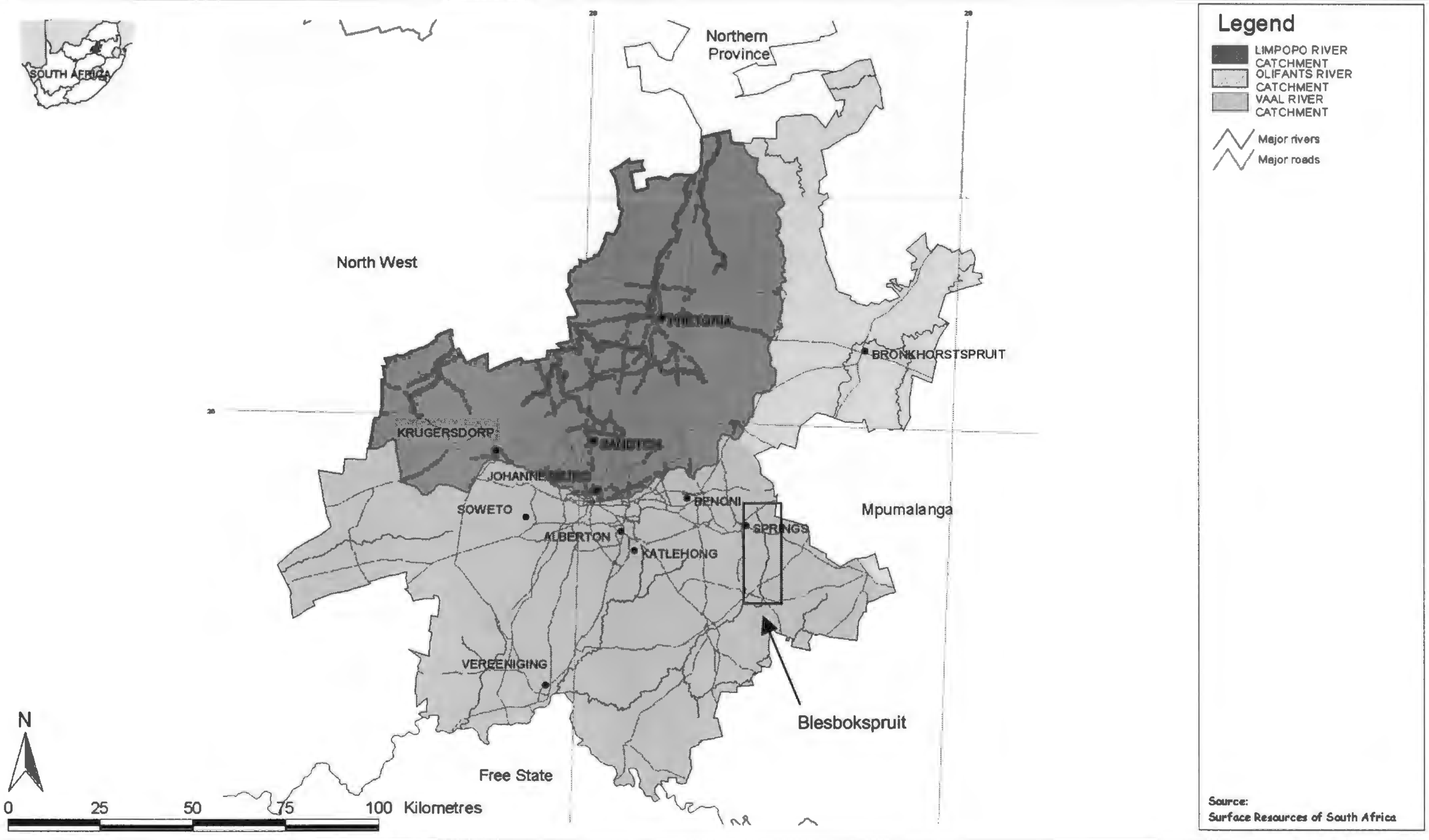
- to characterise the aqueous and sediment geochemistry of the Blesbokspruit;
- to determine the partitioning of metals within the Blesbokspruit using the sequential extraction method of Tessier *et al.* (1979) and;
- to investigate how the sediment metal partitioning affects metal availability during potential environmental conditions within the Blesbokspruit.

1.3 STUDY AREA

1.3.1 Site Description

Prior to 1930, the Blesbokspruit was a narrow meandering non-perennial stream with an associated "wet meadow" wetland (Haskins, 1998). This all changed with the onset of gold mining in the area circa 1930. The construction of roads and embankments created artificial barriers to the natural flow and caused flooding of upstream areas. With the growth of reeds and the continued daily input of water from the mine, the once meandering Blesbokspruit developed into a perennial river with a significant wetland. The wetland ultimately became important for a number of different bird species, leading to its designation, in October 1996, as a Ramsar site (Haskins, 1998). The Blesbokspruit is situated on the industrially developed East Rand of South Africa's Highveld at an elevation of approximately 1600 m above mean sea level. Figure 1.1 is a map of Gauteng showing the location of the Blesbokspruit within the Vaal Catchment.

Figure 1.1 ***Location of the Blesbokspruit within the Vaal Catchment of Gauteng (published in 2003 by the Department of Environmental Affairs and Tourism)***

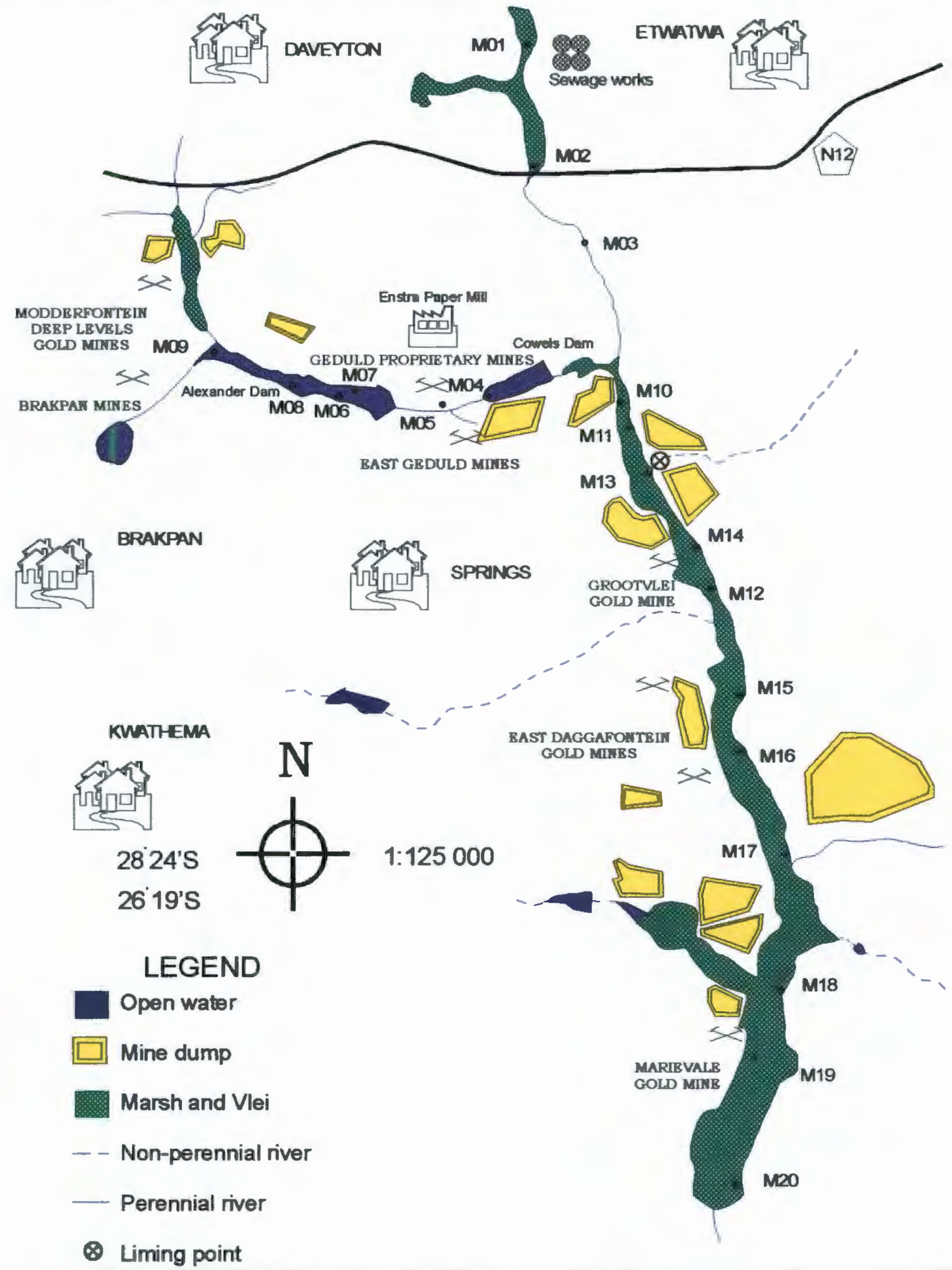


Source:
Surface Resources of South Africa

The Blesbokspruit has its headwaters in Koppiesfontein to the north and flows for approximately 40 km in a southerly direction through the Vaal catchment. The Blesbokspruit has a number of tributaries including a partly canalised furrow flowing westwards through the Alexander and Cowles Dams. The Blesbokspruit is shallow due to the region's flat topography resulting in the development of a wetland covering an area of approximately 1858 hectares. A dense *Typha* and *Phragmites* reed habitat predominates the wetland (Haskins, 1998). Grootvlei Proprietary Mines Ltd pumps between 80 000 and 100 000 m^3 of underground mine water daily into the Blesbokspruit (Schoeman and Steyn, 2001). Water flow is therefore maintained throughout the year with any variation expressed as a lateral shift in the water body rather than a change in depth because of the area's flat topography (Haskins, 1998). Figure 1.2 shows a schematic map of the Blesbokspruit and surrounding area.

The surrounding land usage includes suburban settlements, informal settlements, agriculture, industry as well as gold mining and associated rock dumps and slimes dams. Approximately 45% of the 60 km^2 Blesbokspruit catchment is urbanised with mining, industry and agriculture making up the rest (Haskins, 1998).

Figure 1.2 *Schematic layout of the Blesbokspruit and surrounding areas after the 1:250 000 4th Edition map of the East Rand (2628) published in 1996.*



1.3.2 *Climate*

Air temperature varies from a minimum of -10°C in winter to a maximum of 35°C in summer (Haskins, 1998). The average annual rainfall, recorded over 31 years, is 670 mm (Haskins, 1998). More than 80% of this annual rainfall occurs between October and March (Tyson, 1988). The winter months of April to September are dominated by anticyclonic atmospheric circulation causing a subsidence of air. The effect of this subsidence is, amongst others, to suppress precipitation (Tyson, 1988).

1.3.3 *Geology and Geohydrology*

Rocks of the Witwatersrand Triad (Dominion Reef, Witwatersrand Supergroup and Venterdsdorp Supergroup) overlie basement in the area and represent the source of both the gold and uranium being mined (Kent, 1980). The Transvaal Supergroup overlies the Witwatersrand Triad and is in turn overlain by the basal unit of the Karoo Supergroup, namely the glacial tillites of the Dwyka Formation. Overlying the Dwyka Formation are the sandstones, shales and subordinate coal beds of the Vryheid Formation (Kent, 1980). The Blesbokspruit has eroded through both the Vryheid and Dwyka Formations exposing the Chuniespoort Group Dolomites which outcrop at surface. The dolomites alternate between being chert-rich and chert-poor (Barnard, 2000).

Groundwater beneath the Blesbokspruit occurs within the Varkfontein/East Rand Basin compartment and is associated with the karst aquifers of the Chuniespoort Group. Large scale groundwater abstraction occurs with annual abstraction of more than 10 million m^3 of groundwater by the mining industry, 2-5 million m^3 for irrigation and another 1-2 million m^3 for domestic purposes (Barnard, 2000). The Chuniespoort dolomites represent the most important aquifer in South Africa due to the generally high to very high storage capacity and often highly permeable characteristics of this rock type (Barnard, 2000).

1.4 *SOURCES OF METAL POLLUTION IN THE BLESBOKSPRUIT*

Gold mine waters become enriched in metals as saline groundwaters interact with minerals of the surrounding lithologies (Duane *et al.*, 1997). The surrounding gold mines of the Blesbokspruit therefore represent the most significant source of metals in this stream. Metal enriched water accumulated in these underground gold mines is continuously discharged into the Blesbokspruit. Another source of metals are the surface slimes dams. Here, the fine-grained solid waste of ore processing is pumped as a slurry onto slimes dams, of which there a number surrounding the Blesbokspruit. The water pools on the dump surface before evaporating or leaching downwards towards the river. The majority of these dumps are not significantly vegetated also allowing aeolian erosion and transport of material into the river.

1.5 *METAL CYCLING IN AQUATIC ENVIRONMENTS*

Metal concentrations in natural waters are often much lower than expected on the basis of equilibrium solubility calculations or supply from various sources (Drever, 1997). The reason for this is that the majority of dissolved metals transported by natural water systems are, under normal physiochemical conditions, rapidly adsorbed onto, or co-precipitated with, particulate material (Förstner, 1981b). Adsorption occurs when a dissolved ion or molecule becomes attached to the surface of a pre-existing solid substrate. Co-precipitation occurs when a dissolved species is incorporated as a minor component in a solid phase as that phase itself is precipitated (Drever, 1997). Metals immobilised in bottom sediments do not necessarily remain there, but may be released following chemical changes in the aquatic environment (Förstner, 1981b). Gibbs' (1973) proposed mechanisms of metal transport in rivers are:

- in solution or adsorbed on solids, where they are readily available;
- with metallic hydroxides where chemical changes are required before they are released;
- with organic materials where chemical changes are required before they are released and;
- in detrital crystalline material where they are nearly unavailable.

1.5.1 *Precipitation*

If the solubility product of a particular substance is exceeded it will precipitate until the numeric product of its aqueous ion concentrations no longer exceeds the solubility product. The concentration of a metal ion in the initial stages of precipitation is a function of the type and activity of the anionic species in solution and the pH. The chlorides and sulphates of most metals are readily soluble, while the hydroxides, sulphides and carbonates dissolve with difficulty and are therefore of greater interest in terms of immobilisation (Förstner, 1981b).

The precipitation of metal hydroxides results in various forms which behave differently in terms of the effects of coprecipitation and/or dissolution. Strongly oversaturated solutions produce amorphous or very fine crystalline precipitates with disordered lattices. Such precipitates may persist in metastable equilibrium with the solution, while slowly converting into more stable forms. Slightly oversaturated solutions produce stable solid phases with ordered crystals (Stumm and Morgan, 1996). The minimum solubility for metal hydroxides lies within the pH range of 9 to 12, with an increase in solubility as pH is lowered. In neutral solutions the solubilities are increased by several orders of magnitude, while at pH 4, complete dissolution is largely achieved (Förstner, 1981b).

Within the Me^{2+}-H_2O-CO_2 system, in contact with the earth's atmosphere, carbonates are frequently more stable as solid phases than oxides or hydroxides. In natural water systems, the concentration of some metal ions is therefore controlled by the solubility of their carbonates (Stumm and Morgan, 1996). Carbonate solubility in aqueous solutions is highly dependent on the partial pressure of CO_2. With increasing aqueous CO_2 concentrations, carbonate solubility increases releasing metal ions into solution according to the reaction, where M is the metal cation (Förstner, 1981b):

$$M(II)CO_{3(s)} + H_2O + CO_2 \Leftrightarrow M^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$$

The aqueous HCO_3^- concentration is therefore important in determining the stability of metal carbonates. Any increase in HCO_3^- shifts the above reaction to the left favouring metal carbonates, while a decrease in HCO_3^- concentration favours the release of metal ions into solution. More metal carbonates will therefore dissolve under open system conditions in which CO_2 is replenished from the atmosphere (Drever, 1997).

To determine the cycling and fate of metals in the environment it is important to have an understanding of their association with sedimentary sulphides. However, there are fundamental questions concerning the extent of interaction between sulphides and metals. According to Huerta-Diaz (1998), little is known about how metals are associated with sulphides, are they coprecipitated/adsorbed on Fe sulphides or precipitated as discrete metal sulphides? Furthermore, the generally low concentrations of Fe sulphides in sediments, their susceptibility to rapid oxidation and the difficulties involved with their separation from bulk sediment inhibit understanding (Huerta-Diaz, 1998).

The type of precipitation product, hydroxide, carbonate or sulphide, can be determined from stability associations in an Eh-pH diagram. In the presence of free oxygen, M^{2+} is stable at pH values of less than approximately 7 to 8. With increasing pH, first the carbonate and then the hydroxide becomes the stable phase. For negative redox potentials, the sulphide remains the stable phase over a wide pH range (Förstner, 1981b). Figure 4.6 depicts the stability fields of the main minerals controlling metal solubility in relation to pH and Eh.

1.5.2 *Cation Exchange and Adsorption*

All fine-grained materials with large surface areas are capable of adsorbing metal ions at the solid-liquid interface as a result of intermolecular forces. Exchange processes at the particle surface involve the release of H^+ ions or other cations and the adsorption or surface complexation of metal ions (Förstner, 1981b). The surface complexation model accounts for all the metal adsorption competing processes; including the effect of pH on adsorption and surface charge (Bourg, 1995):

$$M + Surf\text{-}H^+ \Leftrightarrow Surf\text{-}M + H^+$$

As pH decreases metals become more mobile, except for Mo which is more mobile under alkaline conditions. A state of equilibrium exists between the number of cations accumulated by an adsorptive substance and their concentration. If the metal content of the solution is increased, the quantity of adsorbed cations increases. Desorption occurs if the solution concentration is lowered, since a new equilibrium must be attained. The rate at which cation exchange takes place depends on the exchange capacity of the material as well as the cation species and their concentrations (Förstner, 1981b). Metal mobilisation can also occur if there is an increase in the occurrence of natural or synthetic complexing agents that can form soluble metal complexes. Increased dissolved salt concentrations result in more competition for sorption sites on solid surfaces, also promoting the release of metals (Förstner, 1981b).

1.5.3 *Clay Minerals*

The concentration of H^+ ions may dominate metal adsorption onto clay minerals. H^+ ions compete with metal cations for exchange sites in the system, releasing metal cations with complete release under extreme acidic conditions. The exchange capacity of clay minerals increases markedly in the order kaolinite<chlorite<illite<montmorillonite. This increase corresponds as a result of the reduction of particle size and related increase in surface area. The selective affinity of clay minerals for certain metals is not fully understood, however, the following sequence has been established (Förstner, 1981b):

Pb>Ni>Cu>Zn

1.5.4 *Carbonates*

The surface energy of carbonates is sufficient to effect metal adsorption with at least the same intensity as kaolinite. Co-precipitation with carbonate minerals at higher pHs is a potentially important mechanism of metal immobilisation (Förstner, 1981b). The mixing of different water bodies can initiate $CaCO_3$ precipitation. If an alkaline water body comes into contact with and mixes in neutral river water with normal concentrations of Ca^{2+} and HCO_3^-, pH will increase. The solubility product of $CaCO_3$ is reduced, causing it to precipitate in the mixing zone and thus removing metals from solution (Förstner, 1981b).

1.5.5 *Fe and Mn Oxyhydroxides and Fe-Sulphides*

Fe and Mn oxyhydroxides commonly occur as mineral coatings and finely dispersed particles and with high specific surface areas and are significant metal sinks in aquatic systems (Förstner, 1981b). In oxidising environments with neutral to alkaline pH, amorphous and crystalline Fe and Mn solids are strong adsorbents or co-precipitating matrices (Bourg, 1995). As a result, minor concentrations of $Fe(OH)_3$ and MnO_2 are able to control metal distribution in aquatic systems (Förstner, 1981b). When the environment is only slightly reducing or slightly oxidising with neutral to acidic pH, the surface reactive Fe and Mn oxyhydroxides are solubilised as Fe^{3+} and Mn^{4+} are reduced releasing any co-precipitated metals into solution (Bourg, 1995). Accumulations of Fe and Mn oxyhydroxides can therefore also act as major sources of dissolved metals in natural waters especially in the presence of high levels of dissolved organic matter (Förstner, 1981b).

The adsorptive sites of Fe and Mn oxyhydroxides are valence-unsatisfied OH^- or H_2O ligands bound to Fe^{3+}, Mn^{3+} or Mn^{4+}. A metal, M, may bind to iron oxides according to the following reaction which tends towards irreversibility (McBride, 1994):

$$\text{Surface}{>}\text{Fe-OH}]^{-1/2} + \text{M}(\text{H}_2\text{O})_6^{n+} \rightarrow {>}\text{Fe-O-M}(\text{H}_2\text{O})_5]^{(n-3/2)+} + \text{H}_3\text{O}^+$$

Metal sorption onto Fe and Mn oxyhydroxides is characterised by a high degree of specificity shown by particular minerals for particular metals (McBride, 1994).

There are only limited data on the significance of metal co-precipitation with iron sulphides. Since most metals generally occur in substantially lower concentrations compared to ferrous iron in interstitial and other anoxic waters, these metals may be expected to co-precipitate with iron sulphides rather than as discrete sulphide crystals (Förstner, 1981b). Förstner (1981b) concluded that co-precipitation of metals with iron sulphides is less effective in concentrating metals than their incorporation into hydrous iron oxides.

1.5.6 *Organic Matter*

The presence of organic matter and its decomposition products influences the behaviour of metals in aquatic systems (Förstner, 1981b). Organic matter and metals probably form chelate-type complexes (Drever, 1997). The attractive forces between metal ions and soluble, colloidal or particulate organic material range from weak, leaving the ions easily replaceable, to strong making them undistinguishable from chemical bonds (Förstner, 1981b). Organic matter with which natural waters come into contact ranges from relatively small soluble molecules to insoluble polymeric material like coal and wood (Drever, 1997). Singer (1977, in Förstner, 1981b) reported that dissolved organic substances are capable of influencing metals by:

- complexing metals thereby increasing their solubility;
- changing the distribution between oxidised and reduced metal species;
- reducing metal availability to aquatic life;
- influencing the extent of metal adsorption onto suspended matter and;
- influencing the stability of metal-containing colloids.

Metals can also be removed from the system by adsorption onto solid organic matter. However, very little is known about the details of this adsorption, making quantitative predictions difficult (Drever, 1997). Saxby (1973) suggested three possible processes leading to the incorporation of a particular metal-organic species in sediment:

1. Reaction between a metal ion and an organic ligand in solution leading to a species which can either precipitate directly or be adsorbed on sedimentary material.
2. Incorporation into sediments of all or part of an organism containing biological coordination compounds.
3. Adsorption on sediment of molecules resulting from the solubilisation of minerals (sulphides, carbonates, etc.) by natural waters containing organic ligands.

1.5.7 Detrital Minerals

Metals can occur as major, minor or trace components within the mineral substances of natural rock debris. They frequently occur in inert lattice positions and as a result are virtually unavailable to the environment (Förstner, 1981b).

2 METHODS

2.1 WATER SAMPLING AND ANALYSIS

A total of twenty sites chosen for their geographic spread, were sampled from the Blesbokspruit between the 5th and 13th of August 2003. Figure 1.2 presents the locations of these sample sites (labelled M01 to M20). At each site, two water samples were taken. Both were filtered through 45mm, 0.45µm nylon membrane filters using a hand-held vacuum pump. One of the samples was acidified with 3M HNO_3 to a pH of approximately 2 to prevent metal precipitation. The water samples were stored in plastic bottles pre-rinsed with HNO_3 and de-ionised water. The bottles were sealed and stored at 4°C before analysis.

2.1.1 *Field Measurements*

The pH, electrical conductivity (EC), dissolved oxygen (DO), redox potential (Eh) and temperature were measured at each site. The pH was measured using a Wiessenschaftlic-Technishe Werstätten (WTW) Sentix 41 pH-electrode. The EC was measured using a WTW TetraCon® 325 sensor while dissolved DO measurements were made with a WTW galvanic CellOx 325 sensor. The respective probes were connected to a WTW Multi 340i Universal Pocket Meter. The Eh of the water was measured using a SENTEK combination platinum electrode.

2.1.2 *Alkalinity*

The spectrophotometric method of Sarazin *et al.* (1999) was used to determine the total alkalinity of all the filtered but unacidified water samples. The advantages of this method are its accuracy, rapidity and the small sample volume required (Sarazin *et al.*, 1999). This method uses a weak acid (10 mM $HCHO_2$) and a pH sensitive dye (50 mg/ L Bromophenol-Blue) to neutralise all basic species taken into account in the alkalinity expression. The product of the neutralisation reaction is a coloured complex with an absorbance at 590 nm as a function of the original alkalinity of the sample. Using a Sequia-Turner Model 340 Spectrophotometer, the alkalinity of all twenty samples was determined by comparison with 1.0 – 7.0 mM $NaHCO_3$ standard solutions.

The alkalinity of the water at 10 of the sites was also determined by the potentiometric titration of Clesceri *et al.* (1998) to ascertain any error associated with the method of Sarazin *et al.* (1999). Clesceri *et al.* (1998) define the alkalinity of water as its acid-neutralising capacity equal to the sum of all the titratable bases. In this procedure, the alkalinity was determined from the volume of standard acid (0.02M HCl) required to titrate 100 mL of unfiltered water sample to an end-point of pH 4.5.

2.1.3 *Ions*

The aqueous concentrations of the anions Cl^-, SO_4^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, and Br^- in filtered, unacidified water were determined using a Dionex Ion Chromatograph (IC). Prior to analysis samples were diluted to an EC of ~100 µS/cm and filtered through Dionex OnGuard® IIP 1cc cartridges to remove any remaining organic and particulate matter. A 4 mm High Performance Ion Chromatography (HPIC)-AG14 guard column was used in conjunction with a 4 mm HPIC-AS14 separator column. The eluent flow rate was 1.2 mL/min and suppression was achieved using an ASRS-I-4 mm suppressor. A mixed eluent of 2.4 mM Na_2CO_3 and 1 mM $NaHCO_3$ was used.

Aqueous cationic concentrations were determined by Atomic Absorption Spectrophotometry (AAS) on filtered, unacidified water. Ca^{2+} and Mg^{2+} concentrations were analysed using a Varian AA10 while Na^+, K^+ and Fe concentrations were measured with a Varian AA 110 Automatic.

2.1.4 *Metals*

The metal concentrations of filtered and acidified water samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Perkin Elmer/Sciex Elan 6000 Inductively Coupled Plasma Mass Spectrometer equipped with an acid resistant cross flow nebuliser. Samples were diluted 10 times with an internal standard of 10 ppb In, Re, Rh and Bi in 5% HNO_3, to correct for instrumental drift. The U.S. National Institute of Standards and Technology's (NIST) Standard Reference Material® (SRM) 1640 for trace elements in natural water was analysed to quantify analytical error and the results included in Table 3.4. The calibration standards used in this study were the:

1. Claritas PPT™ Multi-element Solution 2A which contains 10 mg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V, Zn in 5% HNO_3.
2. PE Pure Plus Atomic Spectroscopy Multi-element Calibration Standard 2 which contains 10 µg/mL Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Th, Tm, Y, Yb in 5% HNO_3.
3. PE Pure Plus Atomic Spectroscopy Multi-element ICP-MS Calibration Standard 5 which contains 10 µg/ml of B, Ge, Mo, Nb, P, Re, S, Si, Ta, Ti, W, Zr in H_2O/trace HF.
4. Specpure® Precious Metals Plasma Standard Solution which contains 100 µg/ml Au, Ir, Os, Pt, Pd, Re, Rh, Ru in a matrix of 20% HCl.

2.2 *SEDIMENT SAMPLING AND ANALYSIS*

At each of the 20 sample sites, sediment was sampled from the sediment-water interface using a 50 ml plastic vial. Care was taken to prevent sample exposure to the atmosphere. Sediment samples were stored at 4°C before being transported back to the University of Cape Town under anoxic conditions for further analyses. Anoxic conditions were maintained using an anaerobic jar and a BBL gas pack.

2.2.1 *Metals*

The metal concentrations of the sediment were determined by ICP-MS. Samples were prepared and analysed in the same way as the residual fraction of the sequential extraction discussed below.

2.2.2 *Sequential Extraction*

A sequential extraction was performed on wet sediment according to the method of Tessier *et al.* (1979). This method sequentially extracts metals from five fractions chosen for their likelihood of being affected by various environmental conditions (Tessier *et al.*, 1979). The five fractions and their methods of extraction are reported below.

1. *Exchangeable*: Approximately 1g of sediment was extracted with continuous agitation at room temperature for 1 h with 8 mL of 1M $MgCl_2.6H_2O$ stabilised to pH 7 with 1M NaOH and 0.1M HCl.

2. *Bound to carbonates:* The residue from step 1 was leached at room temperature with 8mL of 1M CH_3COONa adjusted to pH 5 with CH_3COOH. Continuous agitation was maintained for the 5 h extraction.
3. *Bound to iron and manganese oxides:* The residue from step 2 was extracted with 20 mL of 0.04M $NH_2OH.HCl$ in 25% (v/v) CH_3COOH at 96 ± 3°C with occasional agitation for 6 hours.

The first 3 fractions were extracted under anaerobic conditions to prevent any oxidation of metals within the sediment.

4. *Bound to organic matter:* To the residue from step 3 were added 3 mL of 0.02M HNO_3 and 5 mL of 30% H_2O_2 adjusted to pH 2 with HNO_3. The mixture was kept at 85 ± 2°C for 2 h with occasional agitation. A second 3 mL aliquot of 30% H_2O_2, adjusted to pH 2 with HNO_3, was added and the sample heated again to 85 ± 2°C for 3 h with intermittent agitation. After cooling, 5mL of 3.2M CH_3OONH_4 was added before diluting the sample to 20 mL with de-ionised water and agitating continuously for 30 min. CH_3OONH_4 is added to prevent adsorption of extracted metals onto the oxidised sediment (Tessier *et al.*, 1979).

5. *Residual:* To approximately 50 mg of dry residue from step 4, 4 ml of a 4:1 mixture of 28M HF and 14M HNO_3 were added. Samples were digested for 48 hours at 50-60°C with occasional agitation before evaporation to complete dryness. A further 2 ml of 14M HNO_3 were added and samples digested at 50-60°C until complete dissolution followed by evaporation to dryness at approximately 75 °C. This latter procedure was repeated. After cooling, samples were diluted 1000 times with the internal standard. A syenite geostandard, STM-1, from the United States Geological Survey (USGS) was analysed with the residual fraction to determine the percentage analytical error. Values

for this geostandard were published by Gladney and Roelandts (1988) and are included in Table 3.5.

The metal concentrations of the five extracts were measured by ICP-MS. The presence of the extractive reagent within the extract of the first four fractions may have significant matrix effects during ICP-MS (pers comm., Coetzee, 2003). In order to minimise these matrix effects, the calibration standards for each of the first four fractions were matrix matched to the samples. This was achieved by including the respective extractive reagent during the preparation of the calibration standards.

2.2.3 *Particle Size Distribution*

The analysis of the particle size distribution performed in this study was adapted from the Non-Affliated Soil Analysis Work Committee (1990) and Moore and Reynolds (1997). A 50 mL wet sediment sample was air-dried and sieved through a 2 mm sieve. Approximately 10 g was weighed out from the < 2mm fraction and wet sieved through a 63 µm sieve. $(NaPO_3)_6$ was added to the < 63 µm fraction and the solution dispersed using a Vitris Virsonic 475 ultrasonic cell disrupter. Using Stoke's Law:

$$t = \frac{18\eta h}{g(d_p - d_l)D^2}$$

where η = viscosity (1.002×10^{-2} g/cm/s at 20°C), h = height of water (cm), g = gravity (cm/s^2), d_p-d_l = difference in density between particle (2.65 g/cm^3) and liquid (1.0 g/cm^3) and D = particle diameter in cm; the amount of time required for the silt sized fraction (63 μm<2 μm) to settle out can be calculated, leaving the clay fraction (<2 μm) in suspension. The silt was then decanted, dried and weighed while the clay content was calculated by subtracting the silt content from the initial weight.

2.2.4 *Organic Carbon*

The organic carbon content of the sediment was determined using a CHN analyser. Approximately 0.5 g of wet sediment was treated with 2 mL of 50% (v/v) 12M HCl to dissolve any carbonate. The carbonate free sediment was washed with 5 mL of 1M $HCOONH_4$ and dried at 40°C. A known weight of dried and ground sediment was encapsulated in aluminium foil and placed in the auto sampler. The auto sampler dispensed the sample into a furnace at the same time as a dose of oxygen arrived, causing the sample to combust. The CO_2 produced by the combustion of the organic carbon was transported through the system by He to the non-dispersive infrared adsorption detection system, where it is measured. Adjustments for blanks, calibration and weight were made.

3 RESULTS

3.1 AQUEOUS GEOCHEMISTRY

3.1.1 Field Measurements

The values obtained from the field measurements are reported in Table 3.1. The Blesbokspruit is an alkaline stream with the pH values recorded ranging between 5.6 and 9.2 with a mean of 7.9. The average pH of samples M01 to M03 is 7.3. For M04 to M09 the average of the pH is 7.8 while for samples M10 to M20 the pH average is 8.1. Samples M10 to M20 show a more consistent pH of around 8 with less variation compared to the other samples.

The EC increases remarkably from the uppermost portion of the Blesbokspruit to the lower stretches. Samples M01 to M03 have an average EC of 579 μS/cm, while samples M04 to M09 (excluding M05) have an average EC of 744 μS/cm. M05 has an extremely high EC of 9,700μS/cm. The EC of samples M10 to M20 increases downstream from 1393 μS/cm at M10 to 2300 μS/cm at M20.

The Blesbokspruit waters were found to be oxic with between 2.5 mg/L and 15.1 mg/L DO. The DO value at M12 of 2.5 mg/L is lower than all the other measurements and may reflect localised stagnant conditions with sluggish flow. The average DO for samples M01 to M03 is 6.8 mg/L, for M04 to M09 it is 9.1 mg/L while for M10 to M20 it is 8.2 mg/L.

The Eh values obtained from the Blesbokspruit are positive and range from 54 mV to 538 mV with an average of 248 mV. The average Eh of M01 to M03 is 351 mV, while for M04 to M09 it equal to 205 mV. Downstream of the point where these two tributaries join, the average Eh is equal to 241 mV.

Using the method of Sarazin *et al.* (1999) the alkalinity was found to range between 0.0 meq/L and 6.5 meq/L and is generally lower in the upper portions (Samples M01 to M09), increasing within the main portion of the Blesbokspruit. At alkalinities greater than 5 meq/L the error between the method of Sarazin *et al.* (1999) and the potentiometric titration performed in the field are within the acceptable limit of 10%. The error between the two methods at alkalinities below 5 meq/L is greater than the acceptable limit of 10%.

Table 3.1 ***Field measurements***

Sample	pH	DO (mg/L)	Eh (mV)	EC (μS/cm)	Alkalinity (meq/L)	Temp (°C)
M01	9.2	6.1	297	521	0.3	11.0
M02	7.1	8.4	470	630	0.0	15.9
M03	5.6	5.8	187	586	0.4	11.3
M04	7.2	3.7	538	698	1.6	11.4
M05	6.9	6.6	108	9660	2.1	12.4
M06	7.0	5.4	118	787	1.5	14.1
M07	9.2	15.1	108	670	1.2	14.8
M08	9.0	15.1	203	790	1.5	18.5
M09	7.4	8.5	155	733	2.1	10.6
M10	8.1	7.1	190	1393	4.7	16.1
M11	8.1	6.1	200	1344	5.8	16.3
M12	7.5	2.5	na	2250	6.4	9.2
M13	8.2	11.8	187	1395	5.0	13.0
M14	7.9	9.8	218	2120	6.4	17.0
M15	8.1	6.8	54	2300	6.2	24.2
M16	8.0	9.3	454	2400	6.5	5.7
M17	8.1	9.3	180	2220	5.8	11.1
M18	8.2	8.6	279	2240	5.9	16.0
M19	8.2	10.3	462	2220	5.7	15.0
M20	8.4	9.1	192	2300	6.0	17.7

na not analysed

3.1.2 ***Ions***

The results of the IC are reported in Table 3.2 and indicate that the Blesbokspruit is dominated by the major anions Cl$^-$ and SO$_4^{2-}$. The high NO$_3^-$ concentration found in the trip blank, M21, indicates some NO$_3^-$ contamination, most likely due to the use of HNO$_3$ during the pre-rinsing of the sample bottles. In some samples, there were minor quantities of Br$^-$ and NO$_2^-$. Low concentrations of F$^-$ and PO$_4^{2-}$ are each detected in only one sample, M04 and M10 respectively. The Cl$^-$ concentrations of the Blesbokspruit range between 31 mg/L to 177 mg/L with a general downstream increase. NO$_3^-$ concentrations in the Blesbokspruit range from 1.0 mg/L at M14 to a high of 187.5 mg/L at M01. SO$_4^{2-}$ values in the Blesbokspruit range between 72.6 mg/L and 702.1 mg/L with an exceptionally high value at M05 of 4194.2 mg/L. SO$_4^{2-}$ values in the Blesbokspruit range between 72.6 mg/L and 702.1 mg/L with an exceptionally high value at M05 of 4194.2 mg/L. SO$_4^{2-}$ concentrations are generally highest in the main portion of the wetland, alongside the current mining operations. The majority of the samples do not show any detectable NO_2^- although the highest concentrations were found at M05, the most polluted site.

The results of the AAS are presented in Table 3.2. The dominant cations in the Blesbokspruit are Na^+ and Ca^{2+} with lesser amounts of K^+ and Mg^{2+}. The Na^+ content of the Blesbokspruit ranges from 69.1 mg/L to 285.0 mg/L with an exceptional value of 855.0 mg/L at M05. There is a trend of increasing Na^+ downstream with the highest concentrations in the main portion of the system. Concentrations of K^+ range from 9.4 mg/L to 20.5 mg/L with a high value of 32.0 mg/L at M05. The Ca^{2+} content of the Blesbokspruit ranges between 20.7 mg/L and 195.3 mg/L with a trend of increasing concentrations downstream. Mg^{2+} concentrations in the Blesbokspruit range between 8.7 mg/L and 56.0 mg/L. The samples with lower Mg^{2+} concentration are upstream of the mines' impact while those with higher concentrations are within the main portion of the Blesbokspruit alongside the mining operations.

Table 3.2 ***Aqueous ionic concentrations (mg/L)***

	Anions							Cations			
Sample	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}
M01	-	28.1	-	-	187.5	-	111.4	69.1	14.3	33.2	16.7
M02	-	89.0	-	-	26.3	-	125.8	80.0	12.6	23.2	10.0
M03	-	83.8	-	-	9.6	-	109.2	75.3	9.4	20.7	8.7
M04	0.1	73.7	-	-	12.9	-	81.9	86.7	13.3	35.1	10.0
M05	-	66.9	28.3	-	73.1	-	4194.2	855.0	32.0	171.0	43.0
M06	-	106.2	-	-	16.6	-	105.1	114.6	20.5	33.8	10.6
M07	-	80.7	-	-	42.2	-	89.9	78.4	13.7	33.6	10.0
M08	-	113.5	-	-	23.5	-	100.3	110.4	16.7	36.3	10.4
M09	-	99.5	-	-	4.2	-	72.6	108.9	15.9	29.1	9.7
M10	-	140.1	3.1	-	68.8	-	129.7	245.0	15.8	49.5	16.5
M11	-	149.9	-	-	18.9	-	128.8	237.5	15.4	48.5	15.9
M12	-	148.4	-	-	16.6	-	627.9	275.0	18.3	157.5	50.0
M13	-	154.7	-	-	25.8	-	101.6	225.4	15.2	55.2	18.3
M14	-	138.6	-	8.2	1.0	-	508.5	270.0	15.8	158.0	46.0
M15	-	136.7	2.1	2.1	9.6	-	602.2	258.8	17.5	179.3	50.8
M16	-	161.4	-	-	3.8	-	702.1	285.0	19.0	195.3	54.0
M17	-	148.3	-	-	42.2	-	646.9	276.3	16.8	188.0	50.0
M18	-	153.8	-	-	16.3	-	674.5	256.3	17.3	186.0	50.8
M19	-	140.2	2.2	2.2	26.3	-	613.2	246.0	16.6	183.4	56.0
M20	-	154.7	-	-	5.4	-	699.6	253.0	18.0	193.4	56.0
M21	-	-	-	-	34.9	-	-	2.7	0.1	-	-

- below detection limits

3.1.3 *Analytical appraisal*

A fundamental principle of solution chemistry is that solutions are electrically neutral. The total number of positive charges carried by cations must therefore equal the total number of negative charges carried by anions (Drever, 1997). The percentage difference between the total number of positive charges and negative charges can be calculated using the formula defined by Clesceri *et al.* (1998):

$$\%difference = 100\frac{\sum cations - \sum anions}{\sum cations + \sum anions}$$

Table 3.3 presents the results of this appraisal. There are two possible sources of error in this appraisal. Either there is inaccuracy in the analytical procedure or certain ions have been omitted from the calculation. Where the anion sum is between 3.0 and 10.0 meq/L then the acceptable difference is ± 2% while at higher anion sums of between 10.0 and 800.0 meq/L the acceptable difference increases to 5% (Clesceri *et al.*, 1998). The two most inaccurate charge balances are calculated to be samples M05 and M21. Due to M05's very high EC (9660 µS/cm) it was diluted 100 times for IC analysis. This significant dilution may be responsible for inaccurate SO_4^{2-} concentrations. M21 was a trip blank of de-ionised water from the Council for Geoscience's laboratory in Pretoria. Results of IC analyses show NO_3^- contamination, probably by the 3M HNO_3 used to acid wash the water sample vessels prior to a triple rinse with de-ionised water. The percentage difference between the total number of positive and negative charges slightly exceeds Clesceri *et al.*'s (1998) acceptable criteria in the case of samples M04, M06, M08, M09, M10 and M13. This probably reflects dilution inaccuracies or possible minor analytical error rather than the omission of specific ions from the calculation. In general, the samples with a higher anion sums have a lower percentage difference between the total number of positive and negative charges, with the exception of M05.

Table 3.3 ***Analytical appraisal by charge balance***

Sample	Anion sum (meq/L)	Cation sum (meq/L)	% Difference
M01	6.4	6.4	0.1
M02	5.6	5.8	2.5
M03	5.2	5.4	2.0
M04	5.6	6.7	8.8

Sample	Anion sum (meq/L)	Cation sum (meq/L)	% Difference
M05	93.1	50.2	29.9
M06	6.9	8.1	7.7
M07	6.0	6.3	1.9
M08	7.2	7.9	4.7
M09	6.5	7.4	6.6
M10	12.5	14.9	8.7
M11	13.0	14.5	5.4
M12	23.9	24.4	1.0
M13	11.9	14.5	9.8
M14	21.0	23.8	6.3
M15	22.8	24.8	4.4
M16	25.7	27.1	2.6
M17	24.2	26.0	3.6
M18	24.6	25.1	1.0
M19	22.9	24.9	4.3
M20	25.2	25.7	1.1
M21	0.6	0.1	64.6

3.1.4 *Metals*

The results of the ICP-MS on the filtered and acidified water samples are presented in Table 3.4. The results of the analysis of the NIST's SRM 1640 are also presented in this table. The SRM 1640 concentrations obtained can be compared to the reported values which are certified by the NIST unless denoted with an asterisk in which case they are reference values only. Reported values are considered to be more accurate than reference values. The analysed values obtained for the SRM 1640 were compared to the NIST values and the percentage analytical error calculated. For all but two of the metals with either certified or reference values the analytical error was calculated to be within the acceptable range of less than 10%. The low concentrations of Ag may be responsible for the higher analytical error. In the case of Zn, the higher metal concentration may have caused greater analytical error. Analytical matrix effects are the most likely cause of the large error associated with the Fe results.

Table 3.4 ***Dissolved aqueous metal concentrations (µg/L)***

Samples	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	Nd	30.8	0.6	1.5	71.4	197.8	12.2	6.8	3.8	157.5	2.0	0.5	118.8	0.3	6.6	0.9	0.1	64.8	0.5	1.1	2.1	0.0	2.0
M02	Nd	28.7	0.6	1.2	1711.0	481.5	4.4	3.7	Nd	155.9	0.2	0.2	81.7	0.1	0.1	1.2	0.0	45.1	0.3	0.8	0.1	0.0	Nd
M03	Nd	26.5	0.6	0.7	3128.5	559.6	2.6	2.4	2.0	272.7	0.0	0.2	88.7	0.1	0.1	1.3	0.1	79.0	0.3	0.6	0.3	Nd	Nd
M04	Nd	39.7	1.0	3.5	23.7	103.5	6.5	44.7	2.5	69.8	8.0	1.3	150.7	0.2	4.7	1.3	0.1	26.3	0.2	0.4	0.3	Nd	23.2
M05	Nd	324.3	1.2	4.3	2634.6	356.6	4250.0	41495.1	267.1	1118.9	4.4	41.3	484.7	0.3	6.6	1.7	1.5	31.0	0.5	0.3	0.4	0.0	15.5
M06	Nd	39.9	1.0	5.2	253.5	146.9	18.3	60.5	3.1	68.8	3.1	1.2	143.4	0.3	7.5	1.8	0.2	15.8	0.0	0.1	0.7	Nd	20.0
M07	Nd	39.9	1.2	2.2	101.3	88.0	2.9	37.9	3.1	10.1	8.2	0.7	147.1	0.3	4.8	1.8	0.1	14.4	0.0	0.1	7.6	Nd	24.3
M08	Nd	38.9	1.3	2.6	40.7	56.8	6.6	24.2	1.9	8.3	4.1	0.9	138.7	0.3	9.6	1.5	0.1	13.0	0.1	0.4	0.5	Nd	22.4
M09	Nd	34.1	2.3	3.6	31.3	73.5	8.1	19.5	0.8	21.2	7.1	1.8	170.9	0.3	15.6	1.3	0.2	16.7	0.1	0.3	1.0	Nd	2.8
M10	Nd	47.2	6.5	7.0	928.1	154.2	123.0	294.2	3.3	54.1	9.9	6.5	155.9	0.4	16.8	2.0	0.1	16.7	0.5	2.1	1.7	0.0	28.9
M11	Nd	40.2	7.2	2.0	275.7	152.5	14.7	65.6	2.1	25.4	8.0	5.9	141.7	0.3	12.5	1.6	0.1	25.0	0.3	1.3	2.3	0.0	10.6
M12	Nd	170.4	3.4	5.6	298.6	505.6	9.1	50.4	3.0	39.1	6.0	4.8	337.3	0.4	6.6	1.0	0.3	16.4	0.3	1.0	0.6	0.0	27.3
M13	Nd	47.6	5.8	5.8	282.5	151.1	14.6	65.6	5.4	20.7	9.4	5.9	156.1	0.4	11.6	1.4	0.2	20.9	0.4	0.7	1.8	0.0	15.9
M14	0.0	158.2	4.5	6.9	419.5	429.9	9.7	50.3	2.7	29.7	6.3	5.5	308.1	0.3	7.4	1.3	0.2	17.8	0.4	0.7	0.6	0.0	26.8
M15	0.1	179.1	3.1	3.2	365.9	464.5	11.3	41.7	0.1	28.1	5.4	3.4	323.5	0.3	3.8	1.4	0.3	25.0	0.2	0.5	0.3	Nd	32.6
M16	0.2	186.8	3.7	4.6	581.9	499.5	8.0	35.8	0.3	32.2	4.9	3.6	357.1	0.4	4.3	1.2	0.3	20.8	0.1	0.2	0.4	Nd	38.1
M17	Nd	186.6	4.4	4.6	686.4	487.4	11.0	48.4	0.9	32.0	4.8	4.3	340.2	0.3	5.6	1.2	0.3	32.7	0.1	0.4	0.5	Nd	34.9
M18	0.2	178.7	4.6	6.7	557.9	470.2	9.5	36.7	5.1	29.8	4.1	4.4	338.7	0.5	4.9	1.3	0.3	29.3	0.0	0.2	0.4	Nd	36.2
M19	Nd	192.2	3.3	4.4	395.8	496.8	6.4	30.9	4.1	31.9	4.0	4.4	341.1	0.4	4.4	1.2	0.3	25.5	0.0	0.2	0.3	Nd	39.9
M20	Nd	200.2	5.1	11.3	272.5	491.2	5.1	24.6	0.1	28.4	3.5	3.4	366.3	0.4	4.3	1.0	0.3	26.7	0.8	2.5	0.4	0.1	36.7
M21	Nd	Nd	0.3	7.6	0.0	10.6	1.7	0.1	Nd	3.5	0.0	0.6	0.0	0.1	0.1	1.3	0.0	0.2	0.4	1.3	0.4	0.0	Nd
SRM 1640	35.4	7.8	13.1	38.2	123.7	43.3	20.3	29.2	93.3	70.7	27.1	22.1	121.8	0.7	49.0	9.5	23.7	141.8	0.6	1.9	30.4	0.1	0.8
SRM 1640 value	34.9	Na	13.0	38.6	121.5	34.3	20.3	27.4*	85.2*	53.2*	26.7	22.0	124.2	Na	46.8	7.6	22.8	148.0	Na	Na	27.9	Na	Na
% Error	1.4	Na	0.8	1.0	1.8	26.2	0.0	6.6	9.5	32.9	1.5	0.5	1.9	Na	4.7	25.0	3.9	4.2	Na	Na	8.9	Na	Na

Nd below detection limits

Na certified or reference value not available

3.2 *SEDIMENT GEOCHEMISTRY*

3.2.1 *Metals*

The metal concentrations of the bulk sediment as determined by ICP-MS are reported in Table 3.5. Also reported are the concentrations obtained for the USGS's STM-1 geostandard. STM-1 concentrations obtained can be compared to the certified values of STM-1 which are underlined for recommended values while other values are proposed except those preceded by a "(" which are only information values (Govindaraju, 1994). These published comparative values can be ranked in order of decreasing accuracy from the recommended values, followed by the proposed values and finally the information values. The percentage analytical error is calculated for each metal where comparative values are available and ranges from below the acceptable limit of 10% up to 100%. Analytical error, analytical matrix effects and the accuracy of the comparative values are possible reasons for the high percentage errors.

Table 3.5 *Dry sediment metal concentrations (mg/kg)*

Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	3924.4	118.9	191.5	2551.3	40174.0	54.3	86.9	62.6	202.2	8.2	0.9	96.7	109.7	1.3	0.7	0.2	1160.5	0.1	0.2	38.7	11.1	2.4
M02	3427.1	89.6	155.0	1469.9	58346.7	22.4	52.2	38.4	181.7	8.3	0.9	67.7	83.4	1.6	0.6	0.1	483.8	0.3	0.9	36.1	9.5	2.1
M04	1314.1	32.8	79.4	67.8	10462.2	33.8	134.9	48.1	91.9	32.5	0.9	9.1	26.5	0.8	0.3	0.2	59.8	0.4	0.8	11.6	2.3	14.5
M05	1905.8	53.2	219.1	111.4	18005.9	11.6	79.6	54.2	35.8	77.8	1.3	41.5	51.2	1.2	0.3	0.0	139.3	0.1	Nd	25.4	4.3	7.7
M06	2928.6	93.5	164.2	159.9	33929.8	28.4	117.6	71.4	182.4	20.0	0.1	14.7	74.2	1.3	0.3	0.4	117.3	0.2	Nd	19.3	5.9	35.5
M07	5358.6	237.6	339.1	902.3	56936.4	40.0	163.2	91.7	155.9	6.0	0.4	17.6	97.1	1.9	0.5	0.2	138.1	0.2	0.5	12.3	6.8	2.8
M08	2567.6	68.3	110.6	89.3	15943.9	7.6	67.3	21.9	100.2	24.3	1.8	13.0	58.6	0.7	0.3	0.1	113.6	0.2	0.3	8.2	4.9	2.4
M11	3636.7	82.2	217.7	530.1	28562.4	19.7	65.3	39.6	102.9	8.0	1.0	47.3	106.5	1.0	0.5	0.1	162.8	0.2	0.2	22.3	10.1	4.4
M12	5107.7	102.8	130.0	1207.1	41925.7	14.4	71.9	47.8	150.6	7.3	1.4	49.4	125.9	1.4	0.6	0.1	249.0	0.1	0.2	20.6	11.5	3.3
M13	4016.7	152.5	304.2	908.0	46084.2	81.5	233.1	361.6	225.6	130.7	1.3	52.5	103.1	1.4	1.2	0.1	644.5	0.3	0.1	24.4	12.2	62.4
M16	4435.9	104.6	178.0	1245.8	38417.6	22.0	54.3	39.5	107.7	3.9	2.9	45.1	120.2	0.5	0.6	0.1	245.8	0.1	0.0	16.0	9.1	1.9
M18	4252.2	84.9	124.3	409.3	26400.2	12.6	32.2	30.2	81.9	3.7	1.2	25.8	124.0	0.7	0.5	0.1	149.1	0.1	0.1	15.2	9.7	1.7
M19	4868.2	108.5	210.0	998.3	48472.9	101.8	343.4	61.6	330.0	10.3	2.0	43.1	135.5	1.4	0.7	0.2	221.2	0.6	0.2	17.5	11.5	44.9
M20	2336.9	47.9	62.3	146.3	11732.6	3.6	16.2	14.4	43.2	2.5	1.1	16.4	66.0	0.5	0.3	0.1	110.7	0.1	Nd	7.4	5.0	1.4
STM1	675.7	0.3	2.3	1374.9	25150.9	0.8	1.8	3.1	229.4	1.4	nd	616.8	1184.4	5.2	5.0	0.3	566.7	0.7	0.2	15.7	29.7	8.6
Certified	Na	(8.7	(4.3	Na	Na	0.9	(3	(4.6	235	4.6	0.0077	700	1210	5.2	0.079	0.27	560	(0.0004	(0.015	17.7	31	9.06
% Error	Na	96.6	46.5	Na	Na	11.1	40.0	32.6	2.4	69.6	100.0	11.9	2.1	0.0	100.0	11.1	1.2	100.0	100.0	11.3	4.19	11.7

Nd below detection limits

Na certified, recommended or information value not available

3.2.2 *Sequential Extraction*

The metal concentrations extracted from the exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions of Tessier *et al.*'s (1979) sequential extraction are presented in the Appendix. In Figure 3.1 the average metal concentrations of the samples extracted from each fraction are presented as percentages of the total of the average concentrations. The use of average values was selected to reflect the general apportionment of metals within the Blesbokspruit sediment. The disadvantage of this method is that it obscures any between-site differences in metal partitioning that may exist. Due to time constraints between-site differences were not investigated as part of this study and represent an area of future investigation.

The exchangeable fraction contains generally low average metal concentrations with no exchangeable Be, Ti, Cr, Zn, Zr, Mo, Cd and Th extracted. Average metal concentrations extracted from this fraction range from 0 to 27.6%. Sr has the highest exchangeable average concentration while Ag, Au and Hg have approximately 20%. Only 1% of the total average U concentration is exchangeable.

Less than 10% of the total average Ti, V, Cr, Fe, Co, Ni, Cu, As, Se, Zr, Mo, Ag, Cd, Pb and Th is partitioned within the Fe and Mn oxide fraction. Mn, Zn, Sr, Ba, Au and Hg have between 10% and 20% of their total average concentrations partitioned within this fraction. While U has the highest Fe and Mn oxide fraction at 36%. Varying fractions of the metals analysed are bound to carbonates ranging from 0.1% to 70.6%. Metals Cr, Fe, Co, Cu, Sr, Ba and Th have less than 20% of their total average concentration bound to carbonates. While for elements Zn, Ag, Cd, and U greater than 40% is carbonate bound.

All the metals analysed have some percentage of their total average concentration bound to organic matter with the exception of Ti, Zr and Cd. The majority of metals analysed have less than 20% of their total average concentration bound to the organic fraction, including V, Cr, Mn, Fe, Zn, As, Sr, Mo, Ag, Ba, Au, Hg, Pb, Th and U. For Be, Co, Ni, Cu and Se between 38% and 51% of their total average concentration is bound to organic matter.

Almost all of the average Ti and Zr concentration is partitioned within the residual phase. All the metals analysed, except Se, Ag, Au and U, have greater than 20% of their total average concentration within the residual fraction, while V, Cr, Fe and Th have greater than 60% partitioned within the residual fraction. Coetzee's (1993) study on metal speciation in sediments from the Hartebeesport Dam, approximately 100 km north-west of the Blesbokspruit, found that 76% of the Cr occurred in the inert fraction, which compares well to the 78% Cr in the residual fraction of this study. Be, Mn, Co, Ni, Zn, Cd, Hg and Pb have between 20% and 40% of their total average concentrations bound to the residual fraction. Of all the metals analysed, U is the least partitioned within the residual phase.

Co and Ni partition almost identically between the five fractions. Au and Hg also partition in roughly the same way, although there is slightly more Hg in the residual fraction and slightly more Au in the carbonate fraction. Ti and Zr also have very similar partitioning.

Figure 3.1 *Metal partitioning within the sediment*

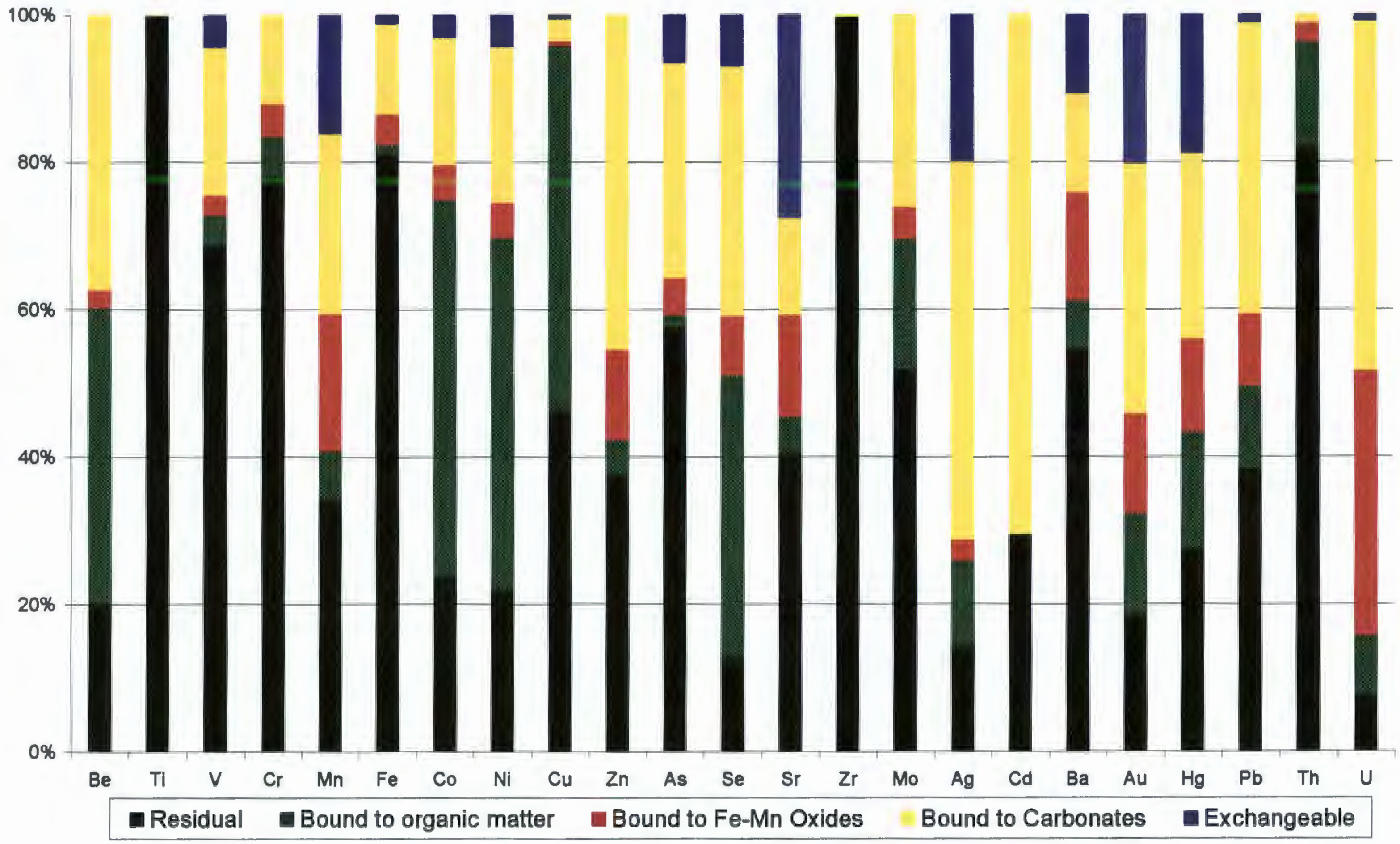
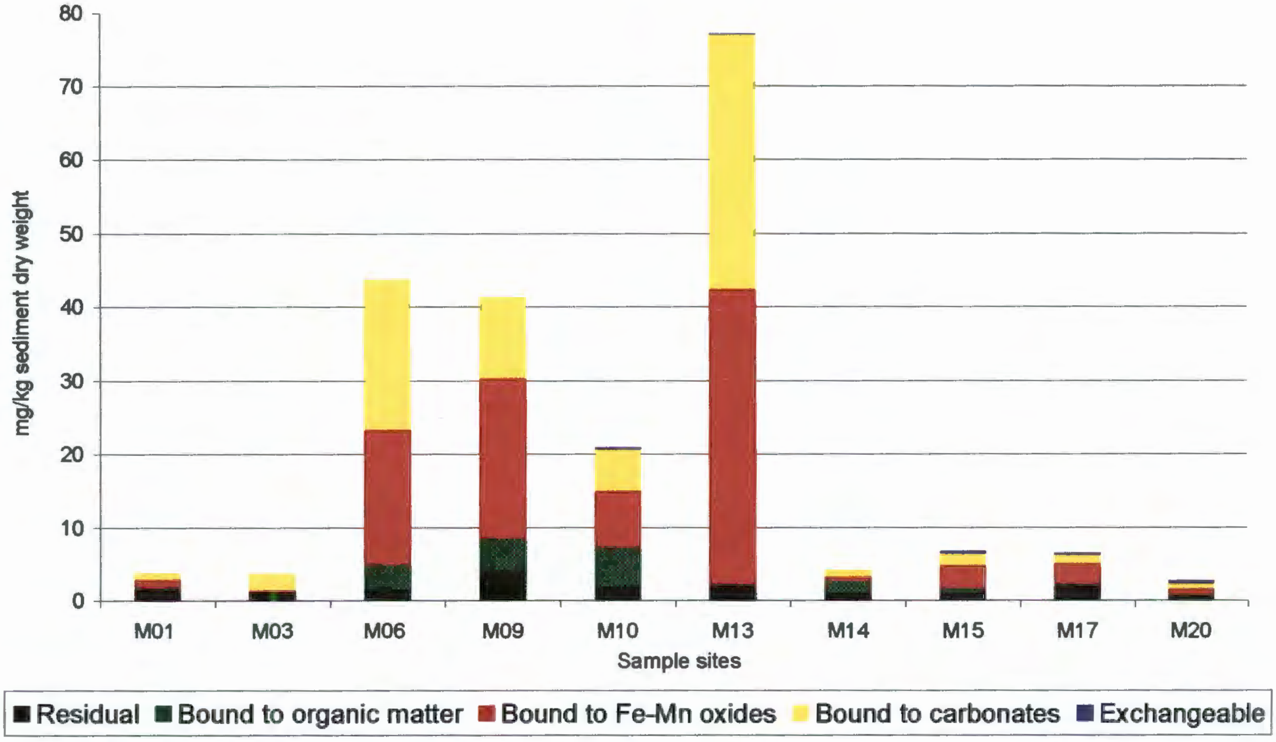


Figure 3.2 plots U concentrations at selected sample sites and their operationally defined partitioning. The carbonate and Fe-Mn oxide fraction together account for the majority of U within the Blesbokspruit sediments. Samples M01 and M03 represent relatively unpolluted sites taken upstream of any significant mining influence. They have low U concentrations with over 30% of the U in the inert residual phase. Samples M14, M15, M17 and M20, taken from the lower stretches of the main portion of the wetland, also have low relatively lower U concentrations with approximately 20% of the U in the residual phase. Samples M06, M09, M10 and M13 have higher concentrations of U with the majority of U bound to carbonates and Fe-Mn oxides and generally less than 10% in the residual fraction. This suggests that U has accumulated in the tributary flowing through the Alexander and Cowles Dams. Within the main portion of the wetland, the highest U accumulations occur just downstream of the point at which this tributary enters the main stream. However, the U appears to be relatively immobile within the sediment as downstream sample sites do not show the same levels of accumulation.

Figure 3.2 *Uranium partitioning*



3.2.3 *Particle Size Distribution*

The particle size distribution of the Blesbokspruit sediments is presented in Table 3.6. The sediments consist predominantly of sand and silt with minor amounts of gravel and clay. The upper portion of the system, M01 to M09, appears to be sandier with varying amounts of gravel, silt and clay. Downstream from sample M10, the sediments become siltier, with greater proportions of clay and less gravel. Overall, the Blesbokspruit appears to be generally coarser grained in the upper portions, becoming finer grained downstream.

Table 3.6 ***Particle size distribution***

Sample	% Gravel	% Sand	% Silt	% Clay
M01	44	33	18	5
M02	6	31	45	18
M03	27	61	8	4
M04	1	64	26	9
M05	8	52	37	4
M06	14	67	12	7
M07	2	31	29	38
M08	0	66	24	10
M09	0	85	9	6
M10	3	21	73	4
M11	3	32	59	6
M12	0	16	54	29
M13	0	11	47	43
M14	0	50	40	10
M15	0	21	73	6
M16	0	24	71	4
M17	3	21	47	30
M18	1	34	43	23
M19	1	17	56	26
M20	0	63	27	10

3.2.4 *Organic Carbon*

The sediment organic carbon content is presented in Table 3.7 and shows a range from 0.5% to 9.0% with an average of 2.3%. In general, there appears to be a higher organic carbon content in the main portion of the wetland, M10 to M20. This coincides with the establishment of major *Typha* and *Phragmites* reed beds within this portion of the river. M06 and M16 were analysed in duplicate to establish the precision of the CHN analyser. The percentage error between the original and duplicate samples is below the acceptable level of 10% for both M06 and M16.

Table 3.7 Organic carbon content of sediment

Sample	% Organic Carbon
M01	1.75
M02	9.00
M03	0.93
M04	0.87
M05	0.59
M06	1.21
M06 duplicate	1.27
M07	1.30
M08	0.91
M09	0.47
M10	2.94
M11	5.79
M12	2.38
M13	2.14
M14	1.28
M15	2.18
M16	1.71
M16 duplicate	1.54
M17	3.19
M18	1.38
M19	4.44
M20	0.88

4 *DISCUSSION*

4.1 *AQUEOUS GEOCHEMISTRY*

4.1.1 *Field Measurements*

pH is often termed the "master variable" that controls ion exchange, dissolution/precipitation, reduction/oxidation, adsorption and complexation reactions (McBride, 1994). It is defined as:

$$pH = -\log[H^+]$$

The underlying dolomites of the Chuniespoort Group are the probable cause of the relatively high pH values of the Blesbokspruit. Typical groundwater within the Chuniespoort Group has a pH of between 5.8 and 9.5 with a mean of 7.6 (Barnard, 2000). The downstream increase in average pH could be the result of discharge from flooded underground mine workings in contact with the Chuniepoort Group aquifer. The moderately reducing conditions of the downstream wetland also have the potential to contribute to higher pHs (Reddy *et al.*, 2000).

The Blesbokspruit waters were generally oxic. Oxygen is involved in or influences most chemical and biological process occurring within water bodies and is a function of temperature, salinity, turbulence, photosynthesis and atmospheric pressure (Chapman and Kimstach, 1992). Variations in these parameters may be responsible for the variable DO values measured in the Blesbokspruit, especially temperature and salinity which changed throughout the stream.

In relatively oxic waters, such as those encountered in the Blesbokspruit, Eh values measured are not necessarily related to a unique redox pair and are therefore not of much value in quantitative interpretations of natural water chemistry (Drever, 1997). Instead, the measured Eh values in this study represent a mixed potential resulting from a combination of two or more different redox processes (Stumm and Morgan, 1996). Stumm and Morgan (1996) suggest that these mixed potentials are of little worth in determining equilibrium Eh values. Given these limitations, the Eh measurements made are useful qualitative indicators of the overall oxidising nature of the stream water.

The downstream increase in EC is most likely caused by input from the surrounding gold mine's flooded underground workings. Grootvlei Proprietary Mines Ltd discharges between 80 and 100 ML of underground water into the Blesbokspruit every day (Schoeman and Steyn, 2001). This water contains high concentrations of dissolved salts with a TDS of 2700-3800 mg/L (Schoeman and Steyn, 2001). Using the approximate relationship reported by McBride (1994):

$$\text{TDS (mg/L)} \approx \text{EC (mS/cm)} \times 640$$

the EC of the water from the underground workings is calculated to be between 4200 μS/cm and 5900 μS/cm. This input of high TDS is likely to have an effect on the salinity of the Vaal River, of which the Blesbokspruit is a tributary. Davies and Day (1998) report that the concentration of total dissolved solids in the Vaal Dam is rising at a rate of 2.5 mg/L every year.

4.1.2 Alkalinity

The various processes affecting alkalinity according to Stumm and Morgan (1996) are summarised in Table 4.1. The alkalinity of the Blesbokspruit is lowest in the less polluted portions and increases downstream. This is probably the result of the discharge of groundwater from flooded underground workings in contact with dolomitic karst aquifers. In addition $CaCO_3$ dissolution during liming, SO_4^{2-} reduction as well as denitrification may also contribute to increased alkalinity in the wetland portion, according to processes 6, 5 and 3 in Table 4.1. Both denitrification and sulphate reduction consume organic matter. The higher organic carbon content of the main wetland portion of the Blesbokspruit may therefore promote these two processes.

In comparison, the method of Sarazin *et* al. (1999) is less time consuming than the potentiometric titration. The greater error between these two methods at alkalinities below 5 meq/L is probably the result of experimental error during the potentiometric titration.

Table 4.1 *Processes affecting alkalinity*

Process	Δ Alkalinity for forward reaction
1. *Photosynthesis*	
$n\mathrm{CO_2} + n\mathrm{H_2O} \Leftrightarrow (\mathrm{CH_2O})_n + n\mathrm{O_2}$	No change
2. *Nitrification*	
$\mathrm{NH_4^+} + 2\mathrm{O_2} \rightarrow \mathrm{NO_3^-} + \mathrm{H_2O} + 2\mathrm{H^+}$	Decrease
3. *Denitrification*	
$5\mathrm{CH_2O} + 4\mathrm{NO_3^-} + 4\mathrm{H^+} \rightarrow 5\mathrm{CO_2} + 2\mathrm{N_2} + 7\mathrm{H_2O}$	Increase
4. *Sulphide oxidation*	
$\mathrm{FeS_{2(s)}} + {}^{15}/_{4}\mathrm{O_2} + {}^{7}/_{2}\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_{3(s)}} + 4\mathrm{H^+} + \mathrm{SO_4^{2-}}$	Decrease
5. *Sulphate reduction*	
$\mathrm{SO_4^{2-}} + 2\mathrm{CH_2O} + \mathrm{H^+} \rightarrow 2\mathrm{CO_2} + \mathrm{HS^-} + \mathrm{H_2O}$	Increase
6. *$CaCO_3$ dissolution*	
$\mathrm{CaCO_3} + \mathrm{CO_2} + \mathrm{H_2O} \Leftrightarrow \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-}$	Increase

4.1.3 *Ions*

The results of the IC indicate that the dominant anions in the Blesbokspruit are Cl^-, SO_4^{2-} and NO_3^-. Concentrations of Cl^- in fresh water typically range from a few to a several hundred mg/L with inputs from irrigation return flows, sewage effluent discharges and various industrial processes (Department of Water Affairs and Forestry, 1996). The Cl^- concentration of the Grootvlei Proprietary Mines Ltd discharge is 190-240 mg/L (Schoeman and Steyn, 2001) suggesting significant Cl^- input from mine dewatering. This is confirmed by the high Cl^- concentrations in the vicinity of the current mining operations.

SO_4^{2-} concentrations in natural waters are usually between 2 mg/L and 80 mg/L, although levels may exceed 1000 mg/L near industrial discharges (Chapman and Kimstach, 1992). Schoeman and Steyn (2001) report that the water pumped out of Grootvlei Proprietary Mines Ltd has an SO_4^{2-} concentration of between 1700 mg/L and 2300 mg/L. During mining, the oxidation of pyrite releases SO_4^{2-} into solution according to process 4 in Table 4.1. SO_4^{2-} enriched water is then discharged into the Blesbokspruit. In the case of M05 the SO_4^{2-} enriched water is left to pool on the surface of the reworked mine dump.

Natural levels of NO_3^- seldom exceed 0.1 mg/L (Chapman and Kimstach, 1992). Municipal and industrial wastes, inorganic fertilisers as well as human and animal waste all contribute to higher aqueous NO_3^- concentrations

(Chapman and Kimstach, 1992). M01's high NO_3^- concentration was probably derived from the sewage plant nearby as well as surrounding informal settlements that often lack basic sanitation. Significant algal growth was evident at M01 indicating nutrient-rich eutrophic conditions. The high concentration of NO_3^- in the trip blank, M21, suggests possible NO_3^- contamination. This source of this contamination could be from an initial HNO_3 rinse of the sample bottles before a double rinse with de-ionised water.

Na^+ and Ca^{2+} are the dominant major cations. The concentrations of Na^+ in natural surface waters vary considerably depending on local geological conditions and wastewater discharges. Values range from 1 mg/L or less to 10^5 mg/L or more in natural brines (Chapman and Kimstach, 1992). The surrounding mining operations are the most likely source of this Na^+. The water discharged by Grootvlei Proprietary Mines Ltd has a Na^+ content of between 270 and 320 mg/L (Schoeman and Steyn, 2001).

Ca^{2+} concentrations in natural waters are typically less than 15 mg/L (Chapman and Kimstach, 1992). There are two possible major sources of Ca^{2+} in the Blesbokspruit. Firstly, there is a natural component derived from weathering of crustal material with an average Ca concentration of 3.85% (Wedepohl, 1995). Secondly, there is an anthropogenic load of Ca^{2+} derived from the dissolution of $CaCO_3$ used in AMD neutralisation as shown in process 6 in Table 4.1.

Chapman and Kimstach (1992) report concentrations of K^+ to be less than 10 mg/L in natural waters. The high K^+ concentration at M05 suggests that surrounding mine dumps are a source of K^+ in this system. The mine dumps contain mainly crushed silicates and shales which are high in K^+ (Turekian, 1972). The dump surfaces appeared insufficiently stabilised, allowing K^+ to be transported by wind and water into the Blesbokspruit.

Natural levels of Mg^{2+} in freshwaters range from 1 mg/L to >100 mg/L depending on rock types within the catchment (Chapman and Kimstach, 1992). Silicate rock weathering, both natural and mining enhanced, is the main source of Mg^{2+} in river water (Schlesinger, 1997). Grootvlei Mines Proprietary

Mines Ltd discharges water with 150-200 mg/L Mg^{2+} (Schoeman and Steyn, 2001).

Figure 4.1 ***Variation of Na/(Na+Ca) as a function of the total dissolved solids in the Blesbokspruit after Gibbs (1970) and Day and King (1995)***

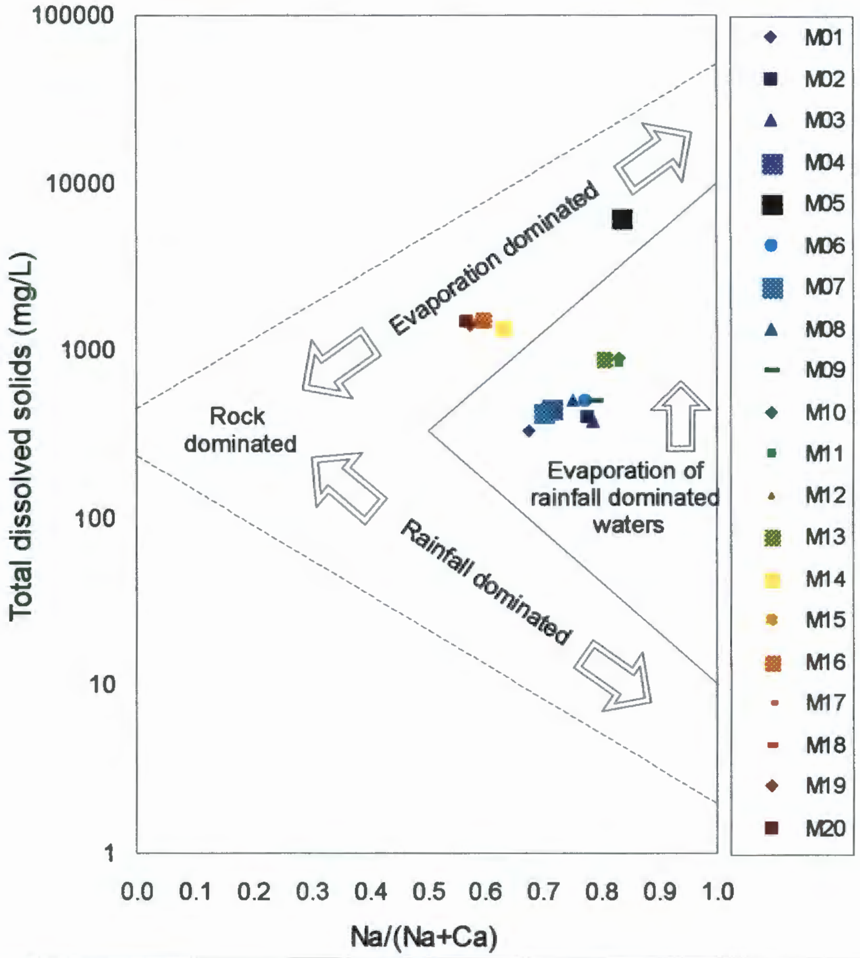


Figure 4.1. highlights the major mechanisms controlling water chemistry and their effect on the water quality of the Blesbokspruit, which can be divided into two distinct aquatic environments based on water chemistry. The first environment represents the upper, less mining-influenced portion of the stream and is made up of samples M01, M02, M03, M04, M06, M07, M08, M09, M10 and M11. The chemical composition of these waters is controlled by the evaporation of precipitation-dominated waters (Gibbs, 1970, Day and King, 1995). This environment represents the almost natural "background" signature of the Blesbokspruit.

The second environment is downstream of the first and is polluted by industrial discharge, mainly from dewatering of underground mine workings.

This environment is represented by samples M12 to M20 and has a rock-dominated signature with higher TDS. The shift towards the rock-dominance end-member is due to the groundwater interaction with surrounding rock before it is pumped out of the mine and into the Blesbokspruit. This interaction between rock and groundwater results in a mine discharge with high TDS (Schoeman and Steyn, 2001). Sample M05 was taken from a stagnant, flooded and partially reworked mine dump alongside a tributary into the Blesbokspruit. The interaction of water with the mine dump at this site as well as surface evaporation have resulted in water with a much higher TDS than the other background samples as shown in Figure 4.1.

4.1.4 *Metals*

The migration of contaminated seepage from tailings deposits of uranium and gold mining activities into underlying aquifers and adjacent streams is a major pathway for the rapid and extensive transport of dissolved metals into the environment (Winde, 2002). However, a distinction must be made between naturally occurring background metal concentrations and those that result from anthropogenic influences. This distinction was made by normalising the aqueous metal concentrations obtained in this study against data for natural systems reported in the literature. The elements Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Ag, Ba, Au, Pb and Th were normalised against world average river dissolved matter reported by Martin and Meybeck (1979). Se and Hg were normalised against typical concentrations in streams as reported by Drever (1997). Cd was normalised against normal concentrations in freshwater from Bowen (1979). Despite the problems associated with obtaining such "average" values (Martin and Meybeck, 1979) they provide a means of comparison. The naturally occurring aqueous metal concentrations used to normalise the respective concentrations obtained in the Blesbokspruit are reported in Table 4.2. The normalised aqueous metal concentrations are presented in Figure 4.2.

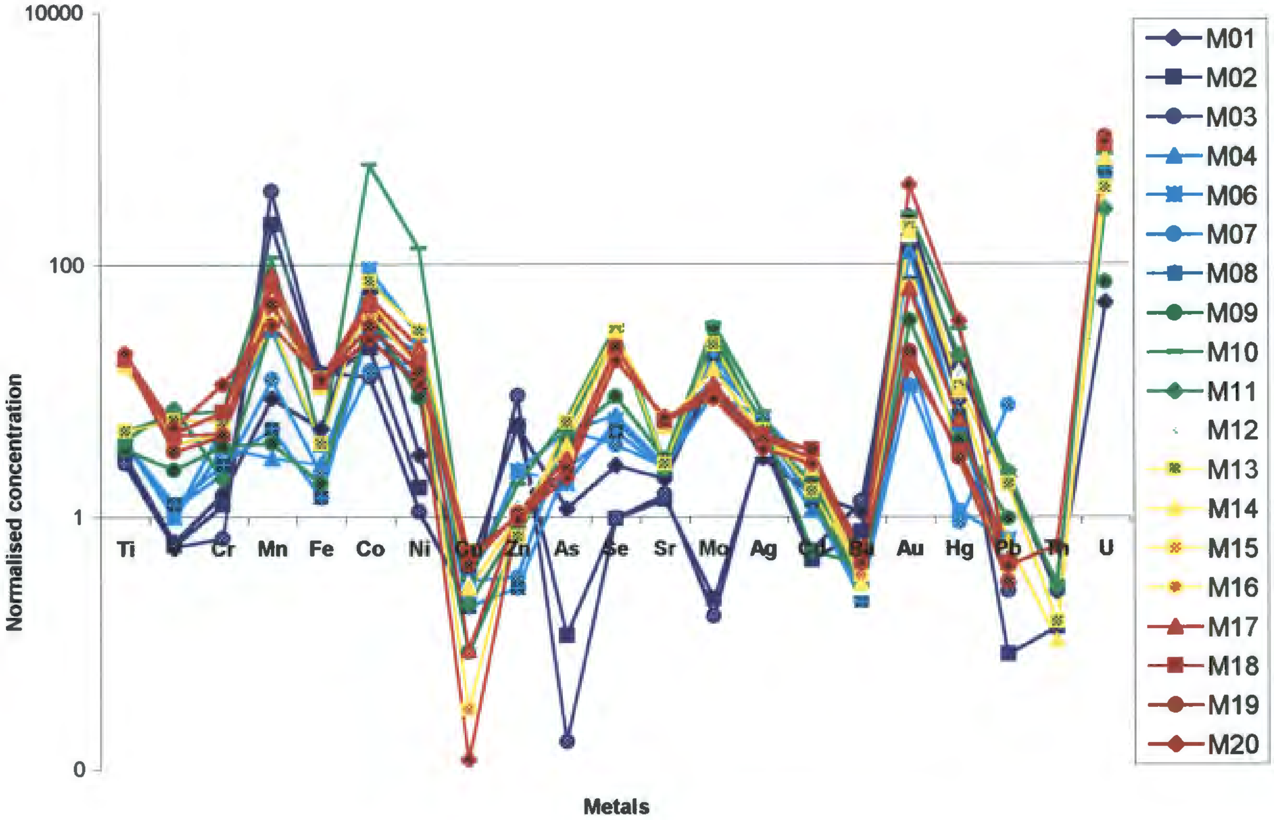
Table 4.2 ***Background dissolved metal concentrations used for normalisation of Blesbokspruit aqueous metal concentrations after Bowen (1979), Martin and Meybeck (1979) and Drever (1997).***

Metal	Concentration (µg/L)
Ti	10.0

Metal	Concentration (µg/L)
V	1.0
Cr	1.0
Mn	8.2
Fe	40.0
Co	0.2
Ni	2.2
Cu	10.0
Zn	30.0
As	1.7
Se	0.2
Sr	60.0
Mo	0.5
Ag	0.3
Cd	0.1
Ba	60.0
Au	0.002
Hg	0.07
Pb	1.0
Th	0.1
U	0.04

The dissolved metal concentrations of the Blesbokspruit are significantly influenced by the oxidation of sulphide minerals derived from the Witwatersrand Supergroup. These minerals include allogenic pyrite (FeS_2) and sphalerite (ZnS) as well as authigenic chalcopyrite ($CuFeS_2$) and pyrrhotite (Fe_7S_8) (Robb and Meyer, 1995). Hawley (1972, in Förstner, 1981b) reports some important metals in sulphides, namely: Co, Ni, Cu, Zn, As, Se, Ag, Cd, Te, and Pb. With the exception of Cu, all these metals show some degree of enrichment compared to natural or background values reported in the literature, aside from Te which was not analysed in this study. Cu is typically strongly associated with organic matter (Salomons and Förstner, 1980) which may be the cause of its lower aqueous concentrations. There is thus strong evidence that the oxidation of the sulphide minerals, pyrite, sphalerite, chalcopyrite and pyrrhotite mined from the Witwatersrand Supergroup has enriched the Blesbokspruit in chalcophile metals. This observation is supported by the work of Förstner and Wittmann (1976).

Figure 4.2 *Normalised dissolved aqueous metal concentrations*



In addition to those metals reported by Hawley (1972) as important in sulphides, Deer *et al.* (1992) report that V, Cr, Mn, Mo and Au also occur in sulphides. These metals also all show relative enrichment within the aqueous phase. Additional Mn enrichment may also result from the runoff of surrounding fertilised fields as Mn is a component of some fertilizers (Adriano, 2001). Mo may also be derived from fertilizers used on surrounding fields (Adriano, 2001). However, the fact that agriculturally influenced samples M01 and M02 are not enriched in Mo suggests that fertilisers are not a significant source of this metal within the Blesbokspruit. The enrichment in Ti is probably derived from the TiO_2 of the Witwatersrand Supergroup (Smits, 1984). Au and U are the most significantly enriched metals within the water and both occur within the minerals mined from the Witwatersrand Supergroup (Smits, 1984).

Figure 4.3 *Suggested mixing of natural uncontaminated water with mining contaminated discharge as represented by Sr and Ti concentrations*

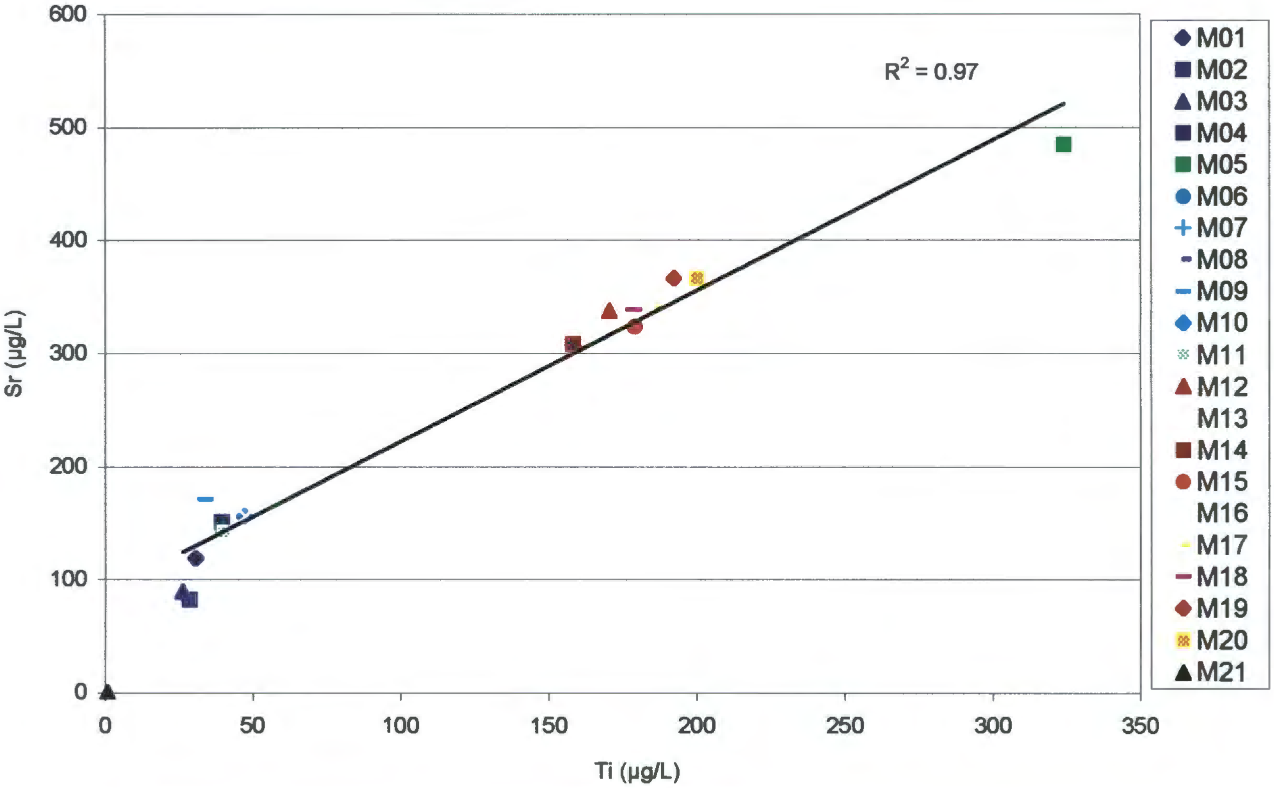


Figure 4.3 illustrates the strong positive correlation between Sr and Ti which is probably a function of source. Ti oxides are less common, but nonetheless important mineral components of the Witwatersrand Supergroup sediments (Smits, 1984). Together, Sr and Ti represent geochemical signatures of the subsurface geological environment. This signature has been transferred to the aqueous environment as water interacts with the geological environment, both underground and on surface. The relationship between Sr and Ti appears to represent a mixing line with contaminated and uncontaminated end-members. Sample M05 represents the rock-contaminated end-member, while samples taken upstream of Grootvlei Proprietary Mines Ltd are representative of more natural background concentrations. Samples downstream of Grootvlei Proprietary Mines Ltd suggest mixing of contaminated and uncontaminated waters.

A comparison was made between the results of the sequential extraction and that obtained by total analysis for the four samples with both data and is presented in Table 7.6 in the Appendix. This comparison suggests that in general the metal concentrations sequentially extracted were less than the total concentrations analysed. Experimental error during the extraction is the most probable cause of this discrepancy.

4.2 *SEDIMENT GEOCHEMISTRY*

4.2.1 *Metals*

In order to determine potential anthropogenic enrichment in metal concentrations of the Blesbokspruit sediment, measured concentrations were normalised to average metal concentrations for the Vryheid Formation determined by Azzie (2002). Over time, the Blesbokspruit has eroded through the Vryheid Formation (Haskins, 1998). The metal concentrations of this formation were therefore considered a useful representation of naturally occurring background metal levels. Azzie (2002) did not, however, report data for all the metals analysed in this study. Concentrations of Ti, Fe, As, Se, Ag, Cd, Au and Hg were therefore normalised to metal concentrations of average crustal shale reported by Turekian (1972). The values of Turekian (1972) are not necessarily representative of the Vryheid Formation, but in the absence of other data, serve as a proxy. The normalised data are plotted in Figure 4.4.

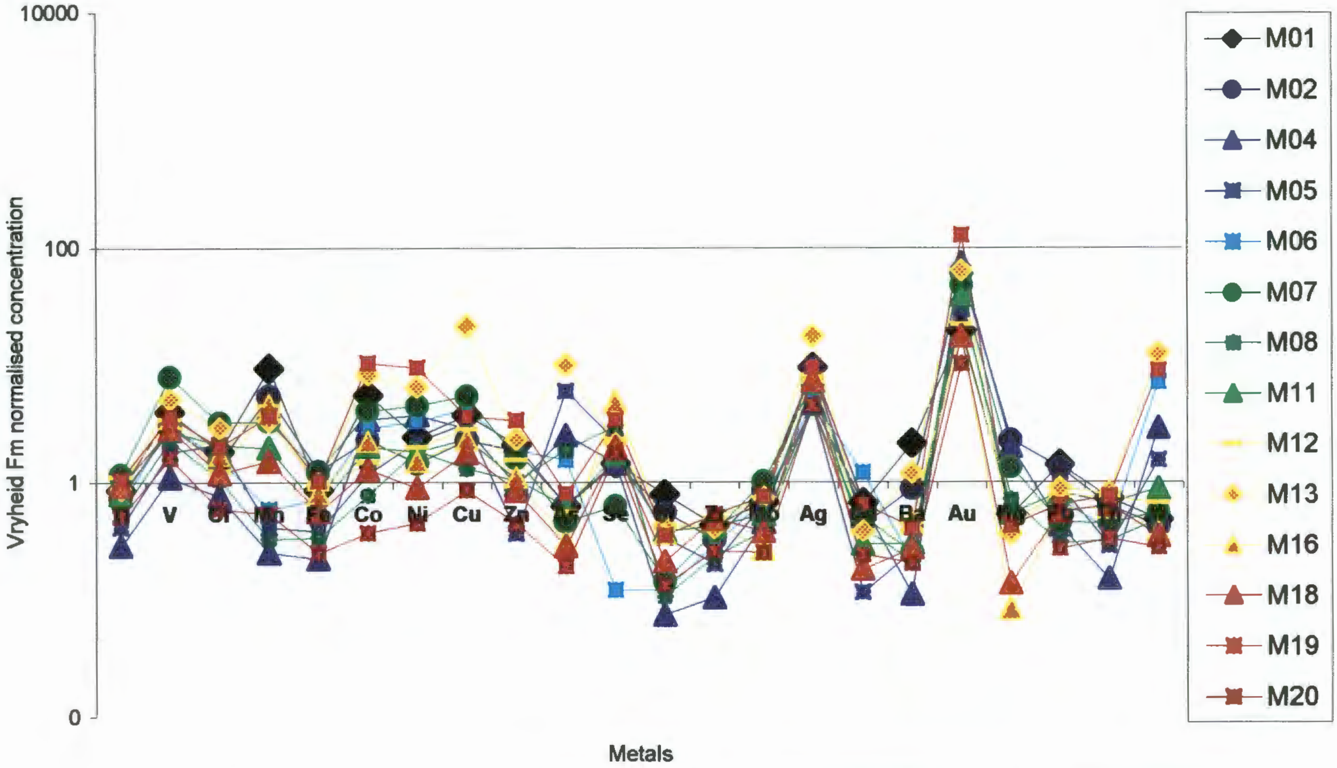
Table 4.3 ***Metal concentrations of average Vryheid Formation (Azzie, 2002) and average crustal shale (Turekian, 1972) used for normalisation of Blesbokspruit sediment metal concentrations***

Metal	Concentration (mg/kg)
Ti	4600.0
V	29.9
Cr	104.6
Mn	271.6
Fe	47200.0
Co	9.8
Ni	36.1
Cu	16.9
Zn	97.7
As	13.0
Se	0.6
Sr	123.6
Zr	256.6
Mo	1.9
Ag	0.07
Cd	0.3
Ba	547.6
Au	0.005

Metal	Concentration (mg/kg)
Hg	0.4
Pb	27.42
Th	15.3
U	5.1

The greatest influence on the sediment's metal composition is the oxidation and dissolution of sulphide minerals mined from the Witwatersrand Supergroup. The metals are transported into the Blesbokspruit via leachate from the mine dumps as well as discharge from the flooded underground workings. The elements V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Au, and Pb occur in varying trace amounts in pyrite, pyrrhotite, chalcopyrite and sphalerite (Deer *et al.*, 1992). All of these elements, except Cd and Pb show some degree of enrichment within the sediment, as seen in Figure 4.4. The metals Ti, Sr, Zr, Ba, Hg, Th and U are not usually associated with sulphides and are generally not enriched within the sediment, except for U. In the case of Pb, the two samples showing some enrichment were taken from upwind of a major motorway, the N12, with vehicle exhaust emissions the most likely source of this metal.

Figure 4.4 ***Metal concentrations of the Blesbokspruit sediment normalised to the Vryheid Formation (Azzie, 2002) and average crustal shale (Turekian, 1972)***



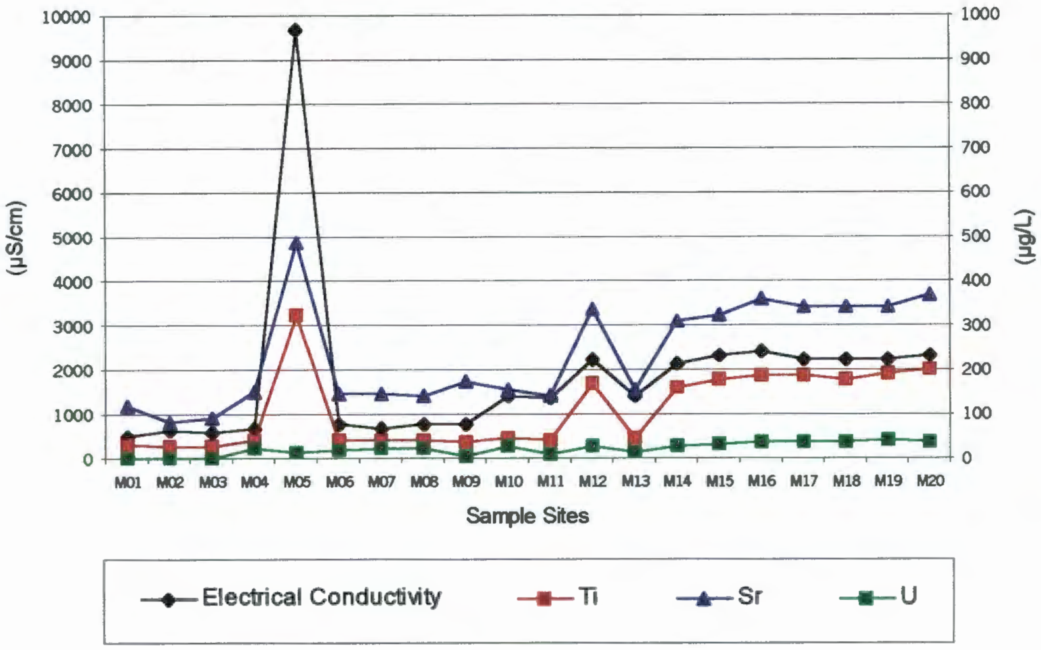
The two samples with highest U enrichment are from the main Blesbokspruit channel. M13 is situated in close proximity to three major slimes dams associated with the Grootvlei Proprietary Mines Ltd. M19 was taken adjacent to the Marievale Gold Mine. Samples taken downstream of M13 and M19 do not show U enrichment. The other three samples that show U enrichment are M04, M05 and M06. M06 was taken from the edges of Alexander Dam situated alongside Geduld Proprietary Mines and their slimes dump. M05 was sampled from a flooded reworked mine dump, while M04 was taken from Cowles Dam next to the East Geduld Mine and its slimes dam. The sediment contamination does not appear to migrate significantly downstream. This suggests that U enrichment within the sediment occurs in close proximity to the source of the element. Förstner (1981a) notes that metal levels in sediments play a key role in detecting pollution sources within aquatic systems as they can be detected long after input has taken place.

4.2.2 *Metal Partitioning and Mobility*

In defining the partitioning of metals Tessier *et al.* (1979) chose five fractions (*exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter* and *residual*) likely to be affected by various environmental conditions. The first environmental condition identified by Tessier *et al.* (1979) is an increase in the ionic composition of water and its likelihood to affect sorption-desorption processes, whereby the alkali and alkaline earth cations compete with metal ions sorbed onto solid particles (Förstner, 1981b). The fraction of metals within sediments affected by changes in ionic composition was defined by Tessier *et al.* (1979) as *exchangeable*. Förstner (1981b) notes that saline effluents have enriched the contents of Na^+, Ca^{2+}, Cl^- and SO_4^{2-} in some rivers and lakes. Such elevated salt concentrations compete with metal cations for sorption sites thereby increasing the solubility of metal compounds (Förstner, 1981b).

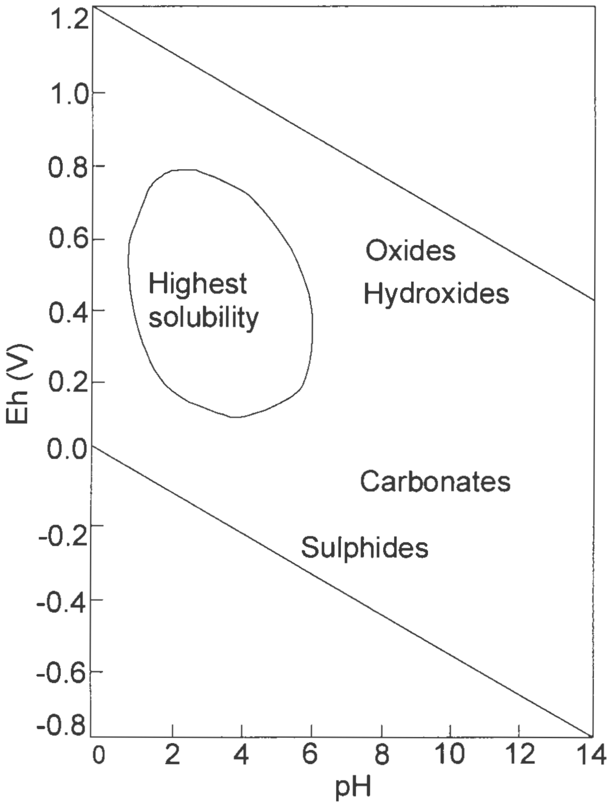
The results of this study indicate elevated levels of Na^+, Ca^{2+}, Cl^- and SO_4^{2-} downstream of the Grootvlei Proprietary Mines Ltd and at the flooded reworked mine dump, M05. These elevated salinity levels correspond with an increase in the aqueous concentrations of certain metals as shown in Figure 4.5 which graphs the variations in EC and the aqueous concentrations of Ti, Sr and U. This is evidence that the increase in the Blesbokspruit's ionic concentration, associated with the discharge of saline underground mine effluent and slimes dam leachate, is responsible for releasing certain metals into solution. However, within the Blesbokspruit, the *exchangeable* fraction does not host more than 20% of total average metal concentrations, with the exception of Sr. Increases in water ionic concentration within the Blesbokspruit therefore have a limited potential to release significant concentrations of these metals into solution. In the case of Sr, approximately 25% of its total average concentration is *exchangeable* and increases in ionic composition within the Blesbokspruit are shown to have resulted in the release of considerable concentrations of this metal into solution.

Figure 4.5 *Variations in EC (µS/cm) and Ti, Sr and U concentrations (µg/L) in the Blesbokspruit water*



The second environmental condition identified by Tessier *et al.* (1979) as likely to affect the partitioning of metals is a change in pH. A decrease in pH will lead to the dissolution of carbonates and hydroxides (as shown in Figure 4.6) as well as increased desorption of metal cations due to competition with H^+ ions (Förstner, 1981b). The fraction of metals affected by changes in pH was defined by Tessier *et al.* (1979) as *bound to carbonates.* Figure 3.1 shows that most of the metals analysed in this study have some fraction bound to carbonates, especially Zn, Ag, Cd and U which all have more than 40% of their total average concentration hosted within this fraction. As a result of the generally mildly alkaline pH values of the Blesbokspruit, carbonate minerals are stable and not expected to dissolve. It is therefore important that these mildly alkaline conditions of the Blesbokspruit are maintained to prevent metal mobilisation from the carbonate fraction, especially Zn, Ag, Zn, Cd and U.

Figure 4.6 *The stability fields of the main minerals controlling the solubility of metals in relation to Eh and pH (Förstner, 1987)*



The third environmental condition identified by Tessier *et al.* (1979) as likely to affect the partitioning of metals is the development of reducing conditions usually in conjunction with a decrease in the oxygen potential due to advanced eutrophication (Förstner, 1981b). Eutrophication results from the internal production of organic matter by primary producers as a result of excess amounts of nutrients available within the system (Thomas *et al.*, 1992). Fe and Mn oxides are excellent scavengers of metals and are thermodynamically unstable under anoxic conditions of low Eh (as shown in Figure 4.6) where they are partly or completely dissolved releasing part of the incorporated or sorbed metal load (Tessier *et al.*, 1979; Förstner, 1981b). The fraction of metals within the sediment affected by reducing conditions was defined by Tessier *et al.* (1979) as *bound to iron and manganese oxides.* A generally small percentage of the total average concentration of most of the metals analysed is partitioned within this fraction as evident from Figure 3.1. However, the results of the sequential extraction performed in this study indicate that of all the metals analysed, U has the largest percentage of its total average concentration bound to Fe and Mn oxides. Advanced eutrophication and the subsequent dissolution of oxides thus have the potential to release about 20% of the total average U concentration into solution. It is therefore important that the Blesbokspruit catchment is managed in such a way as to prevent excessive nutrient input. The sewage works close to M01 as well as surrounding agricultural lands need to be especially vigilant to prevent the release of excessive amounts of nutrient rich water into the Blesbokspruit.

The fourth environmental condition identified by Tessier *et al.* (1979) as likely to affect the partitioning of metals is the development of oxidising conditions. Metals in sediments affected by oxidising conditions were defined by Tessier *et al.* (1979) as *bound to organic matter*. An oxidising environment could develop if the Blesbokspruit sediments were, for example, exposed to the atmosphere during times of low water levels. The shallow and aerially extensive nature of the Blesbokspruit would result in the exposure of large surface areas with only a small drop in water levels. Under such oxidising conditions, the oxidation of organic matter and sulphide minerals (see Figure 4.6) would lead to the release of soluble metals (Tessier *et al.*, 1979; Förstner, 1981b). The results of the sequential extraction performed in this study and presented in Figure 3.1 show that approximately 40% of the Co, Ni, Cu and Se were released during this step of the extraction. These metals were most likely released from the oxidation of sulphide minerals. Cu typically associates with organic matter (Salomons and Förstner, 1980). Thus, the oxidation of organic matter may also represent a source of soluble Cu. The only other metal to be significantly released during this oxidative step was Be. Fairbridge (1972) reports that Be is concentrated by some plants. This occurs by the uptake of more mobile and therefore bioavailable $BeCl_2$ and $BeSO_4$, as free Be^{2+} readily complexes with organic compounds (Adriano, 2001). Coal combustion is the primary environmental source of Be (Adriano, 2001). South Africa's major coalfields and associated power stations are situated within 100 km east of the Blesbokspruit. Atmospheric fallout from power station emissions represents the most likely source of this metal.

Once the first four fractions, each representing specific environmental conditions, are sequentially extracted, the residual solid should contain mainly primary and secondary minerals which may hold metals within their crystal structure (Tessier *et al.*, 1979). These metals are not expected to be released into solution over a reasonable time span under the conditions normally encountered in nature (Tessier *et al.*, 1979). The results of the sequential extraction (Figure 3.1) indicate that a number of metals have a significant portion of their total average concentration partitioned within this residual fraction. Ti and Zr are almost entirely partitioned within this fraction. Zircon ($ZrSiO_4$) is a common accessory mineral in many types of sediment, often surviving more than one cycle of weathering and sedimentation (Deer *et al.*, 1992). This suggests that zircon is not easily weathered, preventing Zr from being released. Similarly, Ti oxide minerals are mostly resistant to weathering (Force, 1991) confirming the evidence of the sequential extraction. In general, the residual fraction contains the greatest percentage of the analysed metal's total average concentration.

5 CONCLUSIONS

As a result of the surrounding mining and industrial activities, the Blesbokspruit has been altered from a once meandering stream circa 1930 into an essentially artificial wetland with a high pollution load. The polluted status of the Blesbokspruit has potential negative consequences for its users which include a variety of important bird species as well as humans.

The water quality of the Blesbokspruit has been significantly influenced by the surrounding mining activities. The downstream increase in electrical conductivity is the result of massive daily discharge of saline effluent from the flooded underground workings of surrounding gold and uranium mines. This saline effluent has enriched the lower stretches of the Blesbokspruit in the anions Cl^- and SO_4^{2-} as well as the major cations, Na^+, K^+, Ca^{2+} and Mg^{2+}, imparting an artificial mining-induced rock dominated signature on the natural evaporation of rainfall-dominated waters signature. The naturally alkaline nature of the Blesbokspruit is the result of the underlying dolomites of the Chuniespoort Group but may be enhanced by the addition of lime to neutralise acid mine drainage.

The oxidation of sulphide minerals mined from the Witwatersrand Supergroup has enriched the sediments and waters of the Blesbokspruit in chalcophile metals as well as U. This enrichment was quantified relative to metal concentrations for natural water and the surrounding geology reported in the literature. The bioavailability of metals in the environment is dependent on their partitioning and mobility. For this reason the sequential extraction of Tessier *et al.* (1979) was performed on the sediments of the Blesbokspruit.

The results of the sequential extraction indicate that a relatively minor proportion of the metals analysed are *exchangeable* and subject to changes in the water's ionic composition. However, high salinity effluent discharged from the Grootvlei Proprietary Mines Ltd is responsible for displacing Sr, Ti and to a lesser extent U cations from their sorption sites resulting in their higher aqueous concentrations downstream of the mine's discharge.

The sequential extraction results show that most of the metals analysed in this study have some fraction of their total average concentration hosted by the pH-sensitive *bound to carbonate* fraction, especially Zn, Ag, Cd and U. Any decrease in pH from the mildly alkaline conditions measured at the time of sampling will release varying amounts of these and other metals into solution.

A generally small percentage of the total average concentration of most of the metals analysed is partitioned within the redox-sensitive *bound to iron and manganese oxides*. However, the results indicate that approximately 20% of the total average U concentration is partitioned within this fraction and would therefore be susceptible to changes in the redox conditions. The onset of reducing conditions and a decrease in oxygen potential can be caused by advanced eutrophication due to excessive nutrient input.

The development of oxidising conditions was the fourth environmental condition identified by Tessier *et al.* (1979) to affect the partitioning and mobility of metals. Approximately 40% of the total average concentrations of Co, Ni and Cu were released during this step of the sequential extraction. The development of oxidising conditions during times of low water levels would result in the release of Co, Ni and Cu as well as other metals into solution.

Some metals, especially Ti, V, Cr, Fe, Zr and Th, have a significant proportion of their concentration partitioned within the residual phase and are essentially unavailable to the environment over a reasonable time span and under conditions normally encountered in nature.

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7 *APPENDIX*

This appendix contains the results of the ICP-MS analyses on the extracts of the five fractions of Tessier *et al.*'s (1979) sequential extraction. Table 7.1 reports the exchangeable trace metal concentrations in mg/kg dry sediment. Table 7.2 reports the trace metal concentrations bound to carbonates in mg/kg dry sediment. Table 7.3 reports the trace metal concentrations bound to Fe-Mn oxides in mg/kg dry sediment. Table 7.4 reports the trace metal concentrations bound to organic matter in mg/kg dry sediment. Table 7.5 reports the trace metals concentrations in the residual fraction in mg/kg dry sediment. Table 7.6 presents a comparison between sequentially extracted and total metal concentrations (ppm).

Table 7.1 *Metal concentrations (in mg/kg dry sediment) extracted from the exchangeable fraction*

Sample	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	0.7	176.2	266.2	Nd	44491.0	26358.1	290.1	209.5	Nd	Nd	152.3	70.9	1471.3	Nd	Nd	258.7	1.8	4307.0	60.6	141.9	63.8	0.3	3.1
M03	1.3	25.9	386.4	Nd	21602.4	55190.0	86.2	83.8	Nd	Nd	244.7	79.9	310.0	Nd	Nd	241.8	0.7	3969.8	40.1	93.5	Nd	0.0	0.2
M05	Nd	10.4	148.7	Nd	105.5	16305.5	273.2	3190.2	340.9	Nd	99.4	51.2	43.5	Nd	Nd	13.4	1.4	Nd	23.8	61.3	61.7	0.1	2.1
M06	Nd	5.8	109.9	Nd	2791.4	66275.4	238.3	810.1	Nd	Nd	Nd	Nd	370.4	Nd	Nd	13.6	0.2	675.8	21.8	46.2	47.4	Nd	0.5
M09	Nd	5.3	326.7	Nd	2003.0	42913.3	139.0	464.5	Nd	Nd	134.2	82.0	261.8	Nd	Nd	7.8	0.4	Nd	15.8	41.7	10.3	Nd	1.7
M10	Nd	314.5	339.2	Nd	17627.2	17613.2	78.8	375.5	Nd	Nd	221.3	Nd	1151.8	Nd	Nd	5.8	0.6	3390.8	13.3	35.5	18.5	Nd	27.0
M13	0.1	203.4	358.3	Nd	15457.9	30931.6	37.5	126.3	Nd	Nd	258.8	29.0	1245.5	Nd	Nd	7.4	0.5	6982.4	10.9	19.5	16.8	Nd	4.9
M14	5.4	34.7	398.1	Nd	7487.7	61108.0	90.1	73.3	Nd	Nd	246.7	45.8	613.4	Nd	Nd	23.2	1.5	1257.6	10.6	12.4	19.1	Nd	Nd
M15	Nd	320.9	404.6	Nd	15763.7	9561.1	11.6	81.9	Nd	Nd	139.0	4.4	1086.9	Nd	Nd	15.9	0.4	4404.7	8.2	9.7	11.4	Nd	25.8
M17	15.4	231.5	254.8	Nd	10516.9	10766.9	23.5	6.4	Nd	Nd	167.8	131.4	1036.2	Nd	Nd	15.9	0.2	569.6	5.0	10.5	28.3	Nd	26.5
M19	1.8	225.9	364.3	Nd	16341.0	8546.0	7.1	29.4	Nd	Nd	224.1	30.4	714.5	Nd	Nd	17.9	1.1	160.3	3.1	6.2	5.4	Nd	120.6
M20	5.7	63.6	296.7	Nd	2801.4	10386.7	6.0	19.4	Nd	Nd	201.4	70.0	642.9	Nd	Nd	24.2	0.2		6.8	5.2	7.8	Nd	19.6

Nd below detection limits

Table 7.2 *Metal concentrations (in mg/kg dry sediment) extracted from the fraction bound to carbonate*

Sample	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	Nd	1246.5	305.4	942.4	39331.6	77794.1	510.9	505.1	4.7	6097.3	65.3	82.3	1939.7	Nd	10.4	6.1	4.2	7392.6	45.4	107.2	394.8	15.3	89.2
M03	20.0	2370.2	219.7	1286.4	25686.5	92375.6	186.1	813.7	261.0	2556.6	81.7	23.8	187.6	Nd	19.5	5.4	0.9	3234.3	27.8	66.5	265.4	4.4	152.0
M05	1.1	1491.8	6.5	151.9	75.0	Nd	46.2	565.7	137.8	Nd	27.2	48.2	34.3	Nd	6.6	5.8	Nd	461.3	16.0	46.8	33.0	2.3	123.5
M06	1.7	6137.7	56.2	776.4	755.0	27431.2	188.5	756.0	12.6	2346.5	60.8	68.6	129.5	Nd	3.5	5.5	5.0	2524.6	15.4	31.3	309.7	16.9	1419.6
M09	7.0	5329.2	52.6	663.1	2233.1	89505.3	159.3	384.3	Nd	2268.9	475.9	107.6	127.8	Nd	9.3	7.7	0.7	458.5	10.7	19.9	49.2	6.3	687.9
M10	4.8	2226.4	194.5	687.8	18461.1	93071.4	524.0	2469.4	Nd	4202.6	249.0	11.5	529.7	Nd	6.7	7.0	1.6	2787.2	10.1	14.3	198.2	17.2	562.5
M13	9.0	3137.3	322.9	652.9	5473.0	204536.3	144.2	646.3	Nd	2176.0	436.2	72.7	373.1	Nd	2.1	6.3	0.2	4994.7	6.9	13.0	160.7	27.5	2437.3
M14	5.5	4863.0	209.9	1061.1	9193.0	133649.3	184.3	276.8	8.5	2016.3	32.3	70.1	143.1	Nd	6.7	6.9	0.6	1786.5	4.4	6.4	359.1	28.2	51.2
M15	33.6	351.9	115.7	592.2	33167.2	7991.4	68.0	569.7	Nd	1246.5	54.1	81.8	349.8	Nd	5.2	9.7	1.4	4881.2	4.8	2.0	84.3	2.8	133.3
M17	9.8	937.1	409.5	760.9	16408.1	578403.5	115.0	430.6	30.7	149.6	54.5	115.2	442.9	Nd	5.5	12.8	0.4	2972.5	4.7	7.6	34.5	7.4	112.6
M19	Nd	455.6	88.4	450.5	9346.9	Nd	65.7	347.1	Nd	1468.9	78.5	Nd	203.9	Nd	2.5	16.1	0.5	2073.1	2.8	Nd	61.5	1.9	751.5
M20	17.0	798.4	289.6	583.6	13045.9	90255.0	12.5	106.5	Nd	1892.1	37.6	24.2	280.6	Nd	4.9	20.6	0.3	1511.2	1.0	Nd	114.4	9.4	38.7

Nd below detection limits

Table 7.3 ***Metal concentrations (in mg/kg dry sediment) extracted from the fraction bound to Fe-Mn oxides***

Sample	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	23.5	543.0	672.0	672.0	27574.7	108416.8	416.4	390.9	Nd	6803.6	30.9	177.8	647.5	4.7	17.8	8.2	7.4	3367.6	46.6	167.9	427.9	5.0	42.0
M03	58.2	74.4	305.2	305.2	25036.3	93302.4	369.3	862.4	Nd	952.4	11.8	53.3	87.0	Nd	15.8	381.3	0.6	2592.4	20.3	65.4	439.9	1.0	4.3
M05	42.8	93.0	123.0	123.0	3304.7	164764.0	194.9	1532.3	546.7	558.9	482.6	100.4	226.3	9.3	36.4	15.3	0.9	405.7	19.1	34.1	541.5	8.7	190.8
M06	26.9	52.5	466.1	466.1	451.7	145135.9	380.0	1612.4	6.0	3188.2	93.8	106.7	38.3	25.7	10.5	8.3	8.0	507.8	15.4	11.0	311.8	6.0	510.1
M09	37.0	11.4	100.4	100.4	498.7	148763.5	185.5	574.5	84.0	3109.0	1199.8	114.1	204.4	Nd	20.5	10.2	3.5	577.2	6.5	3.4	12.3	1.4	537.6
M10	26.4	45.6	719.0	719.0	2330.5	126502.7	790.6	5398.9	Nd	8849.3	394.6	83.2	71.0	1.7	24.6	6.7	9.4	609.6	15.7	11.4	234.7	1.6	309.5
M13	23.4	7.9	1281.9	1281.9	1770.8	185041.9	321.5	1172.6	187.7	4532.0	1150.6	65.6	179.1	24.3	19.7	7.9	2.0	1663.9	16.2	4.1	364.1	5.8	1126.7
M14	51.6	25.8	538.5	538.5	12563.8	167097.1	110.1	213.8	Nd	979.9	14.5	113.9	26.2	19.5	14.4	11.0	0.7	391.5	7.0	Nd	233.5	2.6	14.6
M15	34.1	10.3	464.4	464.4	5403.7	3643.2	120.1	1052.5	Nd	2055.9	22.5	76.3	36.1	28.6	6.3	9.0	4.7	879.1	4.9	Nd	160.9	1.3	96.7
M17	35.9	58.4	1170.7	1170.7	2578.4	276102.6	222.2	437.8	Nd	5274.2	93.9	66.6	54.3	13.2	10.9	10.8	14.5	657.6	6.4	Nd	337.2	5.2	104.9
M19	32.8	8.6	330.3	330.3	2723.7	3109.9	159.3	732.9	Nd	4141.9	40.3	144.1	28.5	Nd	5.2	12.1	3.1	500.8	14.0	Nd	105.2	0.9	484.6
M20	70.8	Nd	600.0	600.0	1231.3	51681.2	25.8	102.8	Nd	1666.0	25.0	65.8	38.1	9.9	9.0	57.4	1.3	456.9	3.1	Nd	132.3	1.7	17.7

Nd below detection limits

Table 7.4 ***Metal concentrations (in mg/kg dry sediment) extracted from the fraction bound to organic matter***

Sample	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	51.9	98.2	117.1	243.3	3151.4	1451.7	112.4	115.5	305.2	148.8	3.6	134.0	142.6	Nd	7.6	12.0	Nd	1286.9	11.2	71.8	93.3	12.7	6.4
M03	37.0	193.2	179.1	173.9	6687.1	Nd	68.2	170.2	90.0	Nd	4.3	132.7	81.0	Nd	18.8	12.4	Nd	1373.3	13.2	60.4	96.2	1.3	0.9
M06	29.9	221.5	438.4	739.1	73.4	818.9	276.5	587.5	1175.8	Nd	2.4	173.0	32.6	Nd	40.1	10.8	Nd	138.0	7.7	30.3	57.6	10.2	103.4
M09	45.8	71.1	43.2	65.0	49.2	2264.1	102.6	184.2	291.7	Nd	127.3	71.9	77.8	Nd	25.5	11.4	Nd	92.7	9.8	13.0	Nd	2.1	92.2
M10	13.7	49.2	73.0	641.9	884.8	24150.9	3711.7	10382.0	3893.2	1924.2	18.7	109.5	54.0	Nd	8.5	9.7	Nd	537.9	5.2	12.1	99.5	55.6	103.6
M13	51.8	47.9	13.7	536.1	563.1	17894.2	648.4	1488.4	11332.1	618.8	10.5	197.7	94.0	Nd	1.1	19.0	Nd	914.4	4.3	7.2	131.5	64.7	209.8
M14	93.9	223.8	310.8	421.7	1006.6	3578.1	39.6	63.1	Nd	Nd	4.0	101.2	9.9	Nd	33.8	11.0	Nd	121.3	1.1	Nd	31.7	13.9	4.1
M15	42.5	84.2	93.0	530.9	4327.9	14462.5	1734.9	7907.9	Nd	275.8	1.7	130.2	37.0	Nd	2.0	11.3	Nd	467.7	Nd	Nd	195.1	73.1	34.3
M17	52.8	67.4	154.3	308.2	491.2	42413.2	78.8	164.9	866.9	Nd	1.0	97.9	13.8	Nd	4.2	14.4	Nd	122.9	1.1	Nd	113.4	51.0	17.9
M20	87.4	71.5	118.8	392.3	344.3	14978.2	46.0	62.6	Nd	Nd	Nd	153.3	14.3	Nd	8.7	21.7	Nd	134.3	0.1	Nd	19.5	30.7	7.2

Nd below detection limits

Table 7.5 ***Metal concentrations (in mg/kg dry sediment) extracted from the residual fraction.***

Sample	Be	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U
M01	1.6	3762.1	97.9	217.3	170.8	58121.4	9.4	45.2	71.8	183.2	11.4	1.1	16.2	110.7	1.9	0.5	Nd	139.6	0.1	0.9	11.3	8.5	1.4
M03	0.9	1283.3	95.2	504.1	2475.6	49899.7	16.3	42.5	30.6	50.0	11.6	3.7	17.9	42.1	1.2	0.3	0.1	595.9	0.5	2.0	22.7	3.7	1.1
M06	0.9	3051.5	67.6	127.4	81.1	23283.5	5.6	33.5	27.1	56.4	10.1	0.9	10.1	97.1	0.9	0.4	0.0	49.9	0.1	0.2	4.0	4.5	1.4
M09	0.7	1393.9	32.6	115.7	32.7	10275.3	2.4	11.4	8.1	25.5	95.4	0.7	21.4	64.4	0.9	0.3	Nd	106.2	0.3	1.3	12.4	4.9	4.2
M10	0.7	3871.4	68.7	184.4	156.4	32378.2	28.7	99.8	121.6	174.4	26.2	0.8	15.0	118.1	2.0	0.7	0.0	95.1	0.4	1.1	12.6	9.7	1.9
M13	0.7	3838.0	86.4	181.2	119.5	31504.4	10.2	44.3	115.3	91.1	49.2	0.4	13.8	103.4	1.7	0.8	Nd	103.4	0.5	0.8	8.9	7.7	1.9
M14	0.6	3054.7	48.2	73.9	68.4	19463.4	3.3	20.6	12.9	45.5	3.8	0.5	11.0	103.4	1.0	0.4	0.0	85.5	0.1	0.7	5.2	6.4	0.9
M15	0.9	4262.0	62.6	144.6	220.3	33376.8	37.9	49.4	34.7	140.5	5.9	0.7	8.6	117.1	0.9	0.5	0.1	63.9	0.2	0.7	6.7	6.1	1.0
M17	0.9	5256.7	74.7	150.7	133.6	29404.0	7.3	41.4	32.9	115.7	4.2	2.5	19.6	175.5	1.1	0.8	Nd	139.0	0.4	0.6	10.0	9.1	1.9
M20	0.1	1945.9	21.6	40.6	37.6	6292.1	1.6	8.9	7.6	27.1	1.6	1.5	10.3	72.5	0.3	0.3	0.0	59.5	0.1	0.4	2.9	3.2	0.6
STM-1	9.1	670.0	0.5	3.8	1385.1	25313.2	0.8	2.0	3.1	235.4	1.7	Nd	603.7	1194.4	5.5	4.5	0.3	580.9	0.7	0.6	18.5	30.3	8.9
STM-1																							
Value	9.6	Na	(8.7	(4.3	Na	Na	0.9	(3	(4.6	235.0	4.6	0.0	700.0	1210.0	5.2	0.1	0.3	560.0	(0.0004	(0.015	17.7	31.0	9.1
% Error	5.2	Na	94.3	11.6	Na	Na	11.1	33.3	32.6	0.2	63.0	Nd	13.8	1.3	5.8	100.0	0.0	3.7	100.0	100.0	4.5	2.3	2.2

Nd below detection limits
Na certified, recommended or information value not available

Table 7.6 ***Comparison between sequentially extracted and total metal concentrations (ppm)***

Sample	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ag	Cd	Ba	Au	Hg	Pb	Th	U	Ti
Sequentially extracted																							
M01	3764.3	99.2	219.1	285.4	58335.4	10.8	46.4	72.1	196.2	11.6	1.6	20.4	110.8	1.9	0.7	0.0	156.0	0.2	1.4	12.2	8.5	1.6	1.4
M06	3051.8	68.6	130.1	85.2	23523.2	6.7	37.3	28.3	62.0	10.2	1.3	10.6	97.2	0.9	0.4	0.0	53.7	0.2	0.4	4.7	4.5	3.5	0.4
M13	3838.4	88.4	183.3	142.8	31942.8	11.4	47.7	126.8	98.5	51.1	0.8	15.7	103.4	1.8	0.9	0.0	118.0	0.6	0.9	9.6	7.8	5.7	0.9
M20	1946.2	22.9	42.1	55.0	6459.4	1.7	9.2	7.6	30.6	1.9	1.9	11.3	72.5	0.3	0.4	0.0	61.6	0.1	0.4	3.2	3.2	0.7	0.4
Total																							
M01	3924.4	118.9	191.5	2551.3	40174.0	54.3	86.9	62.6	202.2	8.2	0.9	96.7	109.7	1.3	0.7	0.2	1160.5	0.1	0.2	38.7	11.1	2.4	0.1
M06	2928.6	93.5	164.2	159.9	33929.8	28.4	117.6	71.4	182.4	20.0	0.1	14.7	74.2	1.3	0.3	0.4	117.3	0.2	*0.0*	19.3	5.9	35.5	0.2
M13	4016.7	152.5	304.2	908.0	46084.2	81.5	233.1	361.6	225.6	130.7	1.3	52.5	103.1	1.4	1.2	0.1	644.5	0.3	0.1	24.4	12.2	62.4	0.3
M20	2336.9	47.9	62.3	146.3	11732.6	3.6	16.2	14.4	43.2	2.5	1.1	16.4	66.0	0.5	0.3	0.1	110.7	0.1	*0.0*	7.4	5.0	1.4	0.1