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Trace Metal Accumulation in Urban Sediments, Black River, Western Cape, South Africa

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Submitted in partial fulfillment of the requirements of the degree of
MASTER OF SCIENCE
in the Department of Geological Sciences
Faculty of Science
University of Cape Town
December 2002

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Acknowledgements

Thank you to my two supervisors, Dr Alakendra Roychoudhury and Dr John Compton, for endless guidance and advice on document corrections, laboratory procedures, as well as for assisting with the sampling. Thank you to Mr Robert Siebritz and Mr Kallie Pienaar of the Cape Town Municipality Scientific Services for their great help with the sampling. Thank you to Shireen Govender, for always having the time to help with problem solving, and providing ideas and tips on how to get the job done, and to Fayrooza Rawoot, for performing a whole digestion procedure to a batch of sediment samples. Also, thank you to Malcolm Spurr for assisting with permission for printing and to Jill Marks for being thoughtful enough to find and scan maps for my benefit.

Abstract

The increase in urbanisation and the use of metal compounds and products domestically and in industry has resulted in the production of by-products and wastes, which needs to be evaluated in the urban environment. The discharge of some of these wastes into urban rivers should be evaluated to determine the potential effects, for example, toxicity and mobility. The effects may, in part, be determined by the chemical states in which these wastes manifest themselves, and by the chemical associations they have.

The sequential extraction technique of Tessier et al. (1979) was applied to the Black River and the Raapenberg riparian wetland sediments under nitrogen atmosphere, with a good level of accuracy, in order to evaluate the levels of metal pollution in the Cape Metropolitan area, South Africa. The total trace metal concentrations generally exceed the SABS (1999) maximum permissible metal contents for Pb, Zn, Ni, Cu, Cr, As, Cd, Se, Mo and Hg. The acid volatile sulphide (AVS) fraction was the main host for Pb, Zn and Cd, and to a lesser extent for arsenic, in anoxic river sediment. The organic matter fraction is host to most of the Cu, a substantial portion of Pb at all sites, and most of the Cr at one location. Metals associated with the AVS and organic matter fractions are potentially bio-available upon dredging and subsequent oxidation of river sediment. The Liesbeeck River has potential for in situ mobilisation of Pb, with a substantial portion hosted by the acid-leachable, carbonate fraction. Most of the Cr and As are associated with the residual fraction, implying a low potential for mobilisation and bio-availability in the river sediments for these elements.

In a core of sub-oxic, riparian wetland sediment, the more mobile elements such as Zn, Cd and Hg tend to occur deeper in the sediment, with peak concentrations at 7 - 9 cm depth, while the less mobile elements such as Pb, Cr and Cu have peak concentrations at 1 - 3 cm depth. The Fe-Mn oxide fraction is the dominant host for the Zn and Cd, while the organic matter fraction is the main host for Pb, Cr and Cu. Zn and Cd have the potential for seasonal bio-availability with changing redox conditions due to repeated flooding and water-logging of the wetland in the rainy season, causing a possible transfer between the oxide and sulphide mineral phases. Pb, Cr and Cu, while being strongly complexed in the organic matter, have a high potential for mobilisation with natural organic matter degradation, with some potential for immobilisation under anoxic conditions when the wetland is flooded, by the precipitation of sulphides. Metals accumulating as a sulphide have the potential for seasonal mobility during the dry season, when soil is not water-logged. Pb, Zn and Cd have substantial concentrations associated with the acid-leachable carbonate phase, and have potential for mobilisation on slight acidification, such as water with pH ≤ 5.

1. Introduction

In recent years the fluxes of many trace metals from terrestrial and atmospheric sources to the aquatic environment have increased (Forstner and Wittman, 1981). With the increase in industrial activity, and the release of pollutants into feeder rivers and direct discharges, the resulting increase in trace metal accumulation can be seen in wetland sediments downstream (Tessier and Campbell 1987).

It is often stated that sediment is the most important reservoir or sink of metals and other pollutants (Salomons and Forstner, 1984). However, some of the sediment-bound metals may remobilise either due to changes in pH, redox conditions (MacBride, 1994) or concentration and be released back to overlying waters. These may impose adverse effects on living organisms (Xiandong Li et al., 2001). Metals may adsorb onto the surfaces of plants and animals and many estuarine invertebrates process sediments as a food source (Wright & Mason, 1998). Based upon feeding rates from Poddubnaja (1961), Reynoldson (1987) estimated that 10-400g.m^{-2}yr of Pb may be ingested by worms (oligochaetes) in the Detroit River where contaminants occur in high concentrations in the sediments. In turn, many birds and fish consume these invertebrates (Wright & Mason, 1998), leading to accumulation of these contaminants and eventual toxicity.

Trace metals can have a major impact on the composition (biological species) of the biological community (Stumm and Morgan, 1996). Organisms can also influence the trace metal composition in the natural environment. For example, algae may deplete the trace element nutrients in the surface water layers, followed by regeneration of these nutrients into solution in deeper waters with microbial degradation of sinking biogenic particles (Stumm and Morgan, 1996). This mechanism may enhance the transfer of trace metals from enriched bottom waters into river and lake sediments. A consequence of large metal loads in water may result in toxic effects in algae when the toxic metal ion reaches some critical level, overflooding the system and reacting with critical enzymes (Stumm and Morgan, 1996).

The chemical forms of the metals in the sediment will influence the interaction of the metals in different environments and also their transfer from one form to another. Changes in redox and pH in the environment may be brought about by the disturbance of the sediment, by dredging river sediment, changing the pH of the overlying water column, or other properties of the water such as alkalinity, salinity etc. All these disturbances in the natural environment could potentially influence the equilibrium of metals between the solid and dissolved phases (MacBride, 1994). For example, salinity of the pore-water in contact with the sediment will influence the adsorption of metal cations onto permanent charge sites on the solid substrate, and for divalent metal cations, the fraction of metal reversibly adsorbed is lower at higher electrolyte concentrations of a monovalent salt (MacBride, 1994). This implies that increasing the salinity of the water may cause the release of divalent metals participating in ion exchange processes on the sediment surfaces.

The nature of the metal itself will also influence its interaction in nature and the form in which it exists. For example, soft Lewis acid (or Class B) metals are more toxic than borderline metals, which are more toxic than hard Lewis acid (or Class A) metals (Stumm and Morgan, 1996) and each interacts more strongly with a different type of ligand or Lewis base (Shriver and Atkins, 1999). Some of the most toxic metals are Hg, Pb, Cd, Cu, Ni, and Co (MacBride, 1994). The soft Lewis acids (or B-type) metals such as Hg, As, Se, Sn and Pb, are of particular concern due to their interaction with SH and NH groups in enzymes, which makes them particularly hazardous to the ecology and human health (Stumm and Morgan, 1996). These soft metals can also be methylated and/or released into the atmosphere as vapours (Stumm and Morgan, 1996), and the accumulation of some of these are evaluated in this study, in river bottom sediment and Riparian wetland sediment. Zn, Cr and Cu are potentially phyto-toxic and have varying degrees of mammalian toxic effects at high concentrations, while Pb, Hg and Cd are cumulative poisons in mammals and are also potentially phyto-toxic (MacBride, 1994).

The bio-available metal fractions under any particular set of circumstances could potentially affect living resources influenced by the Black River. The use of sequential extractions although more time consuming, furnishes detailed information about origin, mode of occurrence, biological and physico-chemical availability, mobilisation and transport of trace metals (Tessier et al., 1979).

1.1 The Study Area

The Black River drains the Cape Flats area in the Western Cape Province of South Africa, and forms part of the Salt River catchment area. It flows generally Westwards through Pleistocene sands and Malmesbury marine shales. It joins with the Liesbeeck River to form the Salt River before reaching the sea at Table Bay (**Fig. 1. See Appendix 1 for location map**). One of the main tributaries of the Black River, the Vygekraal River extends a considerable distance east of the Black River (**Fig. 2**), and is incorporated in this study as part of the Black River System.

The catchment area of the Black River receives about 650 mm/yr rainfall. (Day, 1995). The Black River has a very high sedimentation rate and dense vegetation, thus has to be dredged annually. The dredged sediment is removed to a hazardous waste site (pers. comm. R. Siebritz, Scientific Services, Cape Town Municipality), but also sometimes left on the banks of the river for an unknown period of time. The river collects storm-water and large quantities of litter from several industrial and residential areas upstream. Informal housing in certain areas e.g. Langa, result in raw sewage entering the river. The Black River is grossly polluted with respect to nutrients (Day, 1995), has a high concentration of bacteria and viruses, and is unsuitable for human contact (City of Cape Town Draft Interim Management Plan, 1999). Certain portions of the river are canalised. Canalisation of sections of the river has led to ecological damage, and high sediment input from the catchment area has led to siltation and flow problems (City of Cape Town Draft Interim Management Plan, 1999).

The confluence area of the Black and Liesbeeck Rivers includes three wetlands, the Raapenberg (between the Black and Liesbeeck Rivers), the Pallotti (along the banks of the Black River), and the Valkenberg (along the banks of the Liesbeeck River) wetlands. The Raapenberg and the Pallotti wetlands are virtually all that remain of the extensive wetlands that originally occurred along the Black River (City of Cape Town Draft Interim Management Plan, 1999). The Raapenberg Bird Sanctuary is a proclaimed local authority nature reserve (Provincial Notice 142/ 1986). Most of the wetlands were reclaimed for development possibly from the late 1930's to 1960, and in 1953 and 1960's the Liesbeeck and Black River Highways were constructed alongside the rivers, resulting in extensive disturbance of both river courses (City of Cape Town Draft Interim Management Plan, 1999). Aside from playing an important role in flood attenuation, the wetlands provide a range of habitats for avifauna and flora species (City of Cape Town Draft Interim Management Plan, 1999). All factors influencing the Black River are presumably the same for the riparian Raapenberg and Palotti wetland areas, which receive its silt and water from the Black River.

102 bird species have been recorded in a study area (in October/November, 1993) surrounding the Pallotti wetland on the Black River, the Valkenberg Wetland on the Liesbeeck River and the Raapenberg wetland on the confluence of the Black and Liesbeeck Rivers (City of Cape Town Draft Interim Management Plan, 1999). This represents 25% of all bird species in the southwestern Cape. The study indicated that 71 of the species are water birds of which ~26 probably breed in the area. McDowell from the Institute for Plant Conservation, University of Cape Town, conducted a flora survey in November 1993 on the wetlands in this confluence area. He identified 89 species of which 38 were indigenous and 51 were alien to the Western Cape.

Nel (1967) found an average B content of ~136 ppm in the shales of the Malmesbury Group and concluded that they are marine in origin. The highly weathered shales are consequently very rich in sodium chloride (NaCl) and the soil in this area probably originated from the shale and Table Mountain Group sandstone. The Malmesbury Shale is the underlying rock in the eastern areas of the Salt River catchment, overlain by Pleistocene sands, where the Elsieskraal, Vygekraal and Black Rivers are sourced, while the younger Table Mountain Group Sandstone lays to the west and south where the Liesbeeck River is sourced. There is a shale outcrop between the Black and adjacent Liesbeeck River, on which the Raapenberg Wetland exists (City of Cape Town Draft Interim Management Plan, 1999).

The Elsieskraal River converges with the Vygekraal River, which then joins with the Black River. The Black River converges with the Liesbeeck River to form the Salt River, which is canalised. Conductivity measurements as well as all nutrient concentrations are generally far higher in the Salt River canal sites (up to ~5.5 mg/l phosphorus, ~2.5 mg/l nitrate, ~4 mg/l nitrogen, ~6 mg/l ammonium) than the Liesbeeck River (Day, 1995). The situation has been compounded by the presence of the Athlone Waste Water Treatment Works (**Fig. 2**) which releases it's effluent into the Vygekraal River near the N2 national highway, just upstream of the Vygekraal - Elsieskraal convergence. Borchard's Quarry waste-water treatment works just East of the Vygekraal River, also releases its effluent into the Vygekraal River (R. Siebritz, Snr. Biol. Tech., Scientific Services, Cape Town Municipality, pers. comm., 2002). This will also influence the composition of the Vygekraal and Black River waters, and eventually the Black River sediments. Compared to most fluvial and marine sediments, canal sediments are relatively organic rich (e.g.~6 wt%: Singh et al., 1996) and often contain high levels of sulphur (Stephens et al., 2001).

Sediment dredging may mobilise trace metals from sediment into water, during oxidation of anoxic sediment, influencing wetlands further downstream receiving this water, potentially enriched in heavy metals. The sediments of the Black River exist under anoxic conditions there have been observed fish kills during and after the dredging process further downstream possibly associated with the release of H_2S or CH_4 during dredging (R. Siebritz, Snr. Biol. Tech., Scientific Services, Cape Town Municipality, pers. comm., 2002).

1.2 Aim of this Study

The large amount of human activity along the Black River and its tributaries, and also the sewage input from two treatment plants, must have a profound impact on the composition of the water and sediment. The regular dredging of the Black River and other disturbances in the form of chemical changes in the overlying water column will influence the partitioning of trace metals within sediment. The aim of this study is to determine the chemical partitioning of potentially toxic metals in sediments of the Black River and associated wetland, using the sequential extraction technique of Tessier et al. (1979). Information about the chemical forms of the metal in the sediment could provide an idea of the bio-available fraction of metals under certain conditions. It is also an aim to assess the possible behaviour of these trace metals as pollutants in the ecosystem.

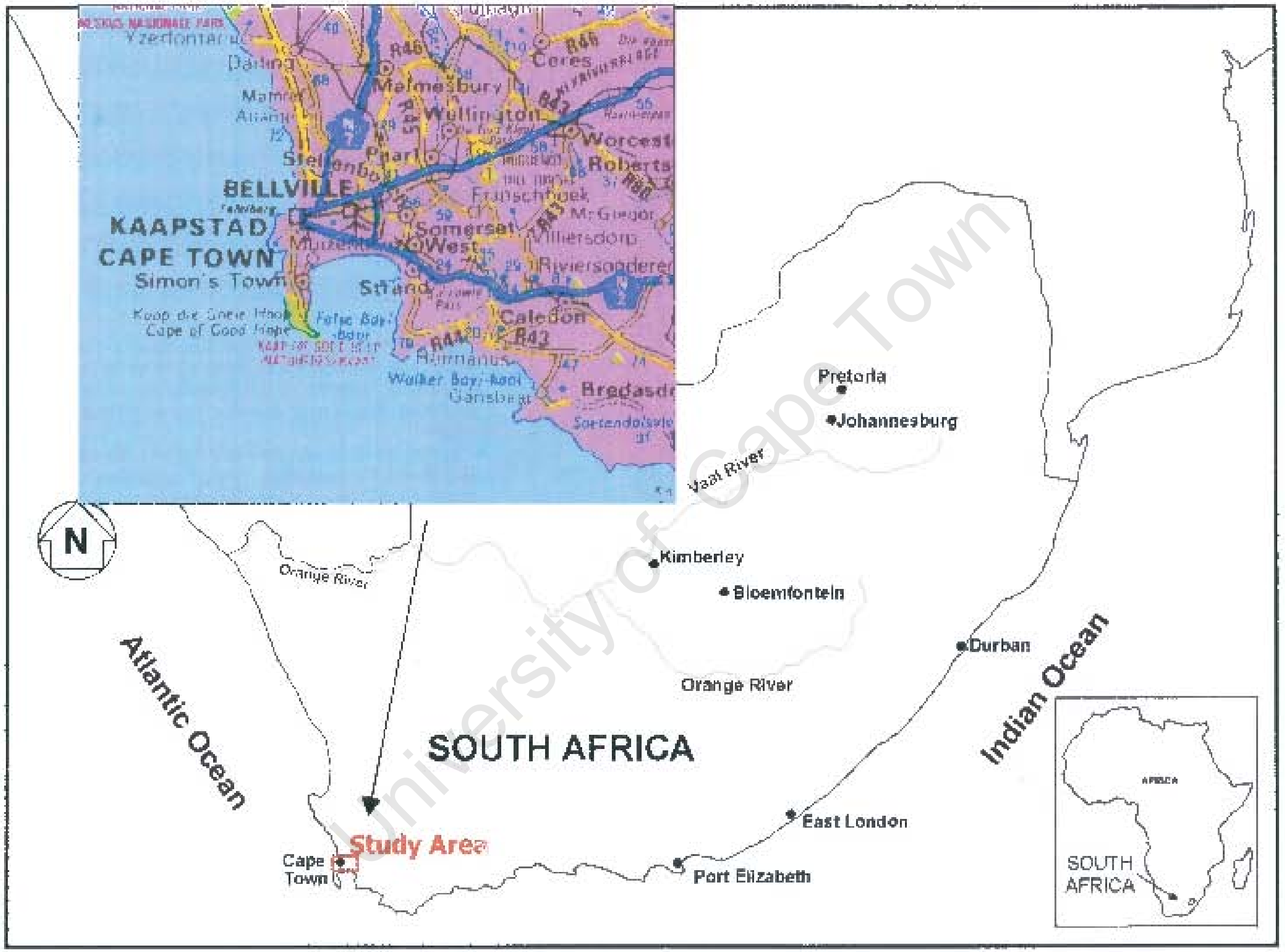

Figure 1: Location map of the study area in South Africa.

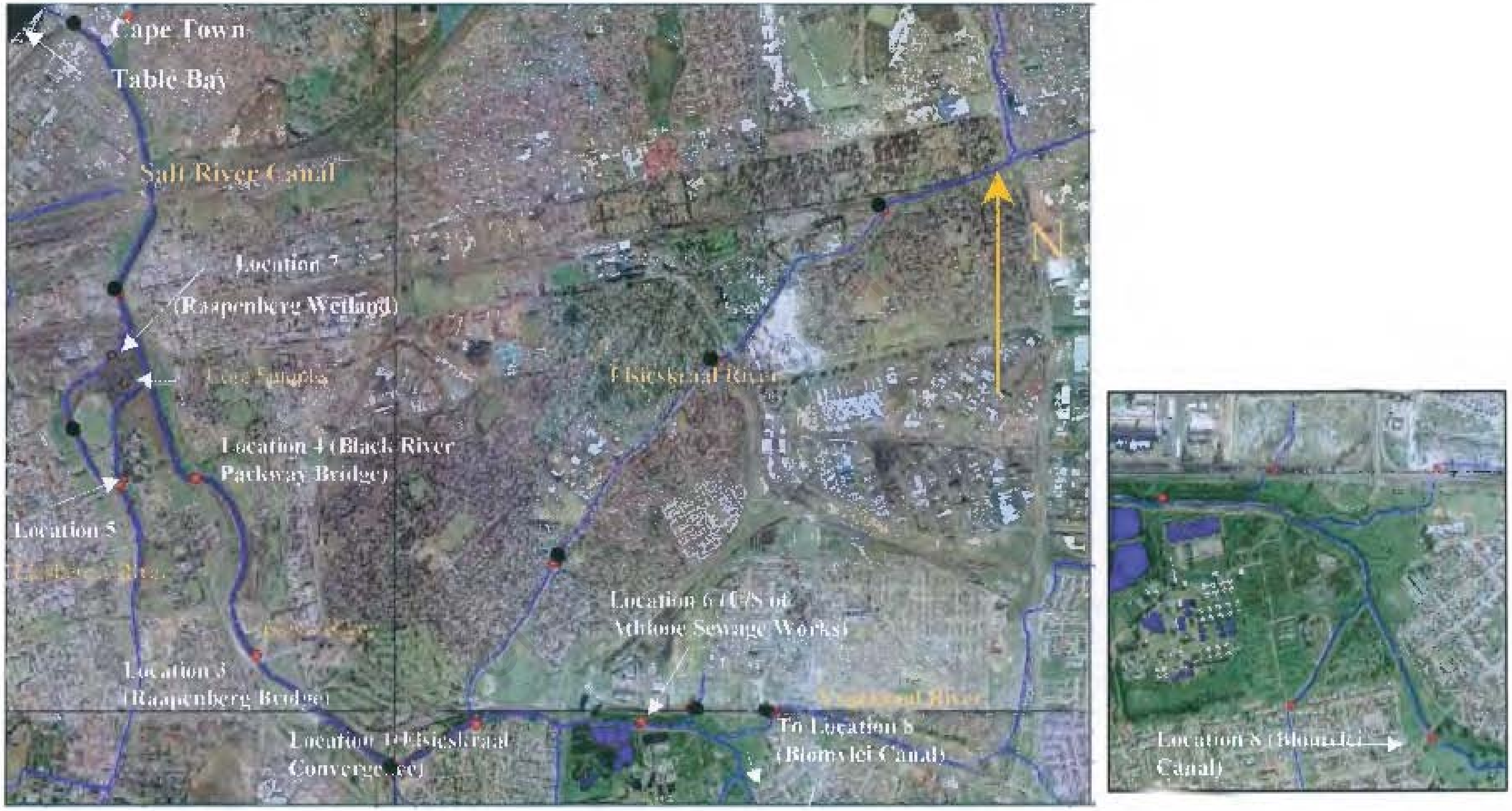

Figure 2: Aerial photograph of the Black River catchment area.

1.3 Preliminary data

Data from a preliminary study (XRF and ICP-MS water chemistry data of Chad Ulansky, GEO304F class, UCT) of the Black River water near the N2, indicates concentrations of Cl^- (>250 ppm), Ca^{2+} (~91 ppm), Mg^{2+} (~36 ppm), SO_4^{2-} (~100 ppm), considerably higher than all other fresh water bodies measured in the area. This could be taken as an indication of the level of anthropogenic input.

Eight sediment samples taken from dredged material from the Black River in the vicinity of the N2/N5 national highway interchange also indicate extremely high concentrations of potentially toxic metals e.g. maximum values of 265ppm Pb, 195ppm Sn, 140ppm Cu, 224ppm Mn, 64ppm As, 41ppm Ni, 224ppm Cr, 1259ppm Zn and 9.6ppm Co. Comparisons to the Average Shale Value which has been used as a measure of enrichment for fine grained sediments in other studies (Emmerson et al., 1997), reveals that the sediment is very slightly enriched with regard to Cu and Cr, and more severely enriched in Zn and Pb compared to the Average Shale Value of Turekian and Wedepohl, (1961). Mean concentrations of Cr, Cu, Zn and Pb for the eight samples of dredged material form the Black river, all exceed the 1999 SABS maximum permissible metal (MPM) content in soil, and the Dutch Government target values (Emmerson et al., 1997) defined as acceptable environmental quality standards. However, the total fraction of potentially toxic metals may not be all bioavailable at one time under any particular conditions of pH and redox state, depending on which phase or fraction of the sediment they reside in. A geochemistry soil report was composed, on the soil formed on shales of the Malmesbury Group on the northern slopes of Table Mountain (N. Haniff, 2002) as part of the Environmental Geochemistry class at UCT. It was found that the shales have a relatively large fraction of soluble Mn, Fe and Al i.e. 4-5ppm Mn, 3-4ppm Fe and 0-1ppm Al in the surface soil horizon, 0-1ppm Mn, 4-5ppm Fe and 3-4ppm Al in the sub-surface layer, 22cm below the surface. The soil formed on Malmesbury Shale was found to be mildly acidic and contain an accumulation of iron oxides in the sub-surface layer. This could probably have some effect on the sediment composition and adsorption characteristics (with regard to various trace metals) of the Black river sediment. The cation exchange capacity (CEC in $mmol_C/kg$) of the shale was also found to be low, 93.88mmol$_c$/kg in the 22cm thick A-horizon, in fact lower than if all the soil was composed of pure kaolinite.

Data from the Cape Town Municipality Scientific Services Division reveals that the pH of the Black River varies mainly between 7-8 at positions downstream of the Vygekraal – Black Rivers convergence, with rare occasions over the last 11 years, when the pH has varied to 6.4 or as high as 9.6. The changes in pH would have had an effect on the adsorption of heavy metals onto sediment, the complexes formed and their stabilities (See MacBride, 1994, Chapters 4&5), and subsequently on sediment and water quality.

2. Methods

2.1 Sampling

2.1.1 River Sediment Samples

On the 15th and 16th August, eight sediment samples were collected from the Black River and it's tributaries. The sampling points are as follows (**Fig. 2**):

1. Elsieskraal convergence point with the Vygekraal River, on the southern Bank, across from the convergence point.
2. Vygekraal River, downstream of the Elsieskraal convergence point. This was on the southern bank, adjacent to the walk-over golf course bridge.
3. At the Raapenberg bridge in the Vygekraal River, near the bridge pillar. Southern bank.
4. Next to the Raapenberg Wetland, in the Black River, on the southern bank. About 50m east of the walkbridge before the Maitland turnoff.
5. From the Liesbeeck River, opposite the Hartleyvale stadium, on the southern bank.
6. In the Vygekraal River, just upstream of the sewage effluent inlet.
7. Surface sediment from the Raapenberg wetland at the convergence of the Black and Liesbeeck rivers, across from the Liesbeeck canal.
8. Vygekraal river in Blom Street, far upstream of the Athlone sewage works, and downstream of Borchard's Quarry Wastewater Facility.

No sediment was found in the Salt River Canal, and there is no data available for this part of the river.

At each sampling stop, bottom sediment was scooped off the river bed, transferred from the plastic cup into two clean ziplock plastic bags, without removing pore-waters. The temperature and pH was measured for wet sediment on one bag. The other bag was flushed with nitrogen gas using a small plastic tube attached to the gas canister, and the ziplock bags were sealed with duct-tape to store. Care was taken not to bring any metal in contact with the sediment. At the laboratory, EC was measured, since no portable EC meter was available. All sediment except sample 7, which was stored at 4°C, was frozen immediately after returning to the laboratory, approximately 4 hours after sampling. See **Appendix 1** for results.

2.1.2 Riparian Wetland Samples

One 40cm core sample was taken from the Raapenberg wetland, ~20m West of the western tip of the boundary fence, of the South African Observatory, at the Liesbeeck - Black River convergence. The core was taken using PVC piping, and was sealed with rubber stoppers and plastic on either side in the field. The core was sectioned under Nitrogen in a nitrogen bag, constructed from polyethylene and duct tape. The top 10cm of the core was sectioned every 1cm using a plastic spatula, and then every ~5cm below this. Each individual section was sealed in a ziplock plastic bag and immediately frozen for future sequential extractions.

An additional 60cm long core was taken ~30cm away from the first core, for a description of the main units, grain size analyses thereof and porosity tests, the results of which can be found in **Appendix 1**.

2.2 Sequential Extraction Procedure

The sequential extraction procedure of Tessier et al. (1979) was selected for the Black River and Raapenberg Wetland samples. There have been various studies around the world all using similar ideologies and methods of analysis for heavy metal accumulation in sediments. The studies evaluated includes the Pearl River Estuary, China (Xiangdong Li et al., 2001), Nanhu Lake, China (Deming Dong et al., 2001), the Tees Estuary, England (Jones and Turki, 1997), Nordasvannet fjord, Norway (Muller, 2002), Cima Lake, Brazil (Silva et al., 2002), Massachusetts Bay, USA (Bothner et al., 2002), Sapelo Island, Georgia, USA (Koretsky et al., 2000), the Orwell and Stour Estuaries, eastern England (Wright and Mason, 1999), the Dommel and Bovenschelde Rivers, Belgium (van Ryssen et al., 1999) and the Severn Estuary, south-west Britain (Mortimer and Rae, 2000). Total digestion, partial digestion procedures and two other sequential extraction procedures were considered (Kersten and Forstner, 1986; and the BCR sequential extraction method of Ure et al., 1993) in detail.

The fairly well understood procedure of Tessier et al. (1979) described many constraints and controls on the phase being dissolved and most of the potential uncertainties of the method were also explored. Ca and Fe concentrations were measured in supernatants after different time intervals to calibrate the reaction times, thermodynamic calculations were used to predict possible reactions and X-ray diffraction was used to determine the changes in whole sediment composition after treatment with each successive reagent. Subsequent literature (Rapin et al., 1986; Kersten and Forstner, 1991) also explored the potential uncertainties of the Tessier et al. (1979) sequential extraction procedure, and therefore the limitations of the method are fairly well understood. Previous authors have attempted to compare the results of different sequential extraction procedures (Usero et al. 1998), with admittedly little success. However, there are numerous previous studies available, which have used the Tessier et al. (1979) method for sediment extraction, in similar environments, available for comparison with the results obtained in this study.

The prescribed times for each reaction were used, as they were in many other studies (Jones and Turki, 1997; Xiangdong Li et al., 2001; Mortimer and Rae, 2000; Rapin et al., 1986). Unfortunately, the time available for this project did not allow for the calibration of the process, for each site-specific sediment, to determine:

- The length of reaction time appropriate to dissolve the desired phase entirely, and if it is selective enough to not attack other phases in the sediment,
- If the reaction time is appropriate in terms of adsorption of dissolved trace metals onto the existing clay minerals, and onto edge sites of other minerals.

A certified reference material, SL-1 from the International Atomic Energy Agency (IAEA), was also sequentially reacted in order to evaluate the possible loss of sediment during the sequential extractions and overall validity of the application of the procedure. SL-1 is a well homogenised lake sediment. Certified elements include Cd, Cr, Cu, Ni and Pb (IAEA, 1979).

2.2.1 Sequential Reaction (Tessier et al., 1979)

The five sequential steps applied to an estimated 1g of dry sediment are as follows:

(a) **Fraction 1**: Metals on exchangeable sites in the sediment were leached for 1 hour with 8 ml of 1 M sodium acetate (NaOAc) at pH 8.3, with continuous agitation.

(b) **Fraction 2**: Metals associated with the carbonate phase and those specifically adsorbed, were leached for 5 hours (for the core samples) or 6 hours (for the river sediment samples) with 8 ml of 1 M sodium acetate (NaOAc) adjusted to pH 5 with concentrated, purified acetic acid (HOAc). Also with continuous agitation.

(c) **Fraction 3**: To dissolve the Fe-Mn oxides (and acid volatile sulphides) and release the associated trace metals, sediment was leached with 20 ml of 0.04 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 25% v/v HOAc at 96± 3°C for 6 hours.

(d) **Fraction 4**: Metals bound to organic matter, and resistant sulphides were leached with 5ml of 30% hydrogen peroxide (H_2O_2) at pH 2 at 85± 2°C for two hours with occasional agitation. A second aliquot of 3 ml of 30% H_2O_2 at pH 2, was added and reacted at 85± 2°C for a further 3 hours with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20% v/v nitric acid (HNO_3) was added, the sample was diluted to approximately 20 ml with distilled water and continuously agitated for 30 minutes.

(e) **Fraction 5**: Residues were ground in an agate mortar prior to digestion. The residues of the river sediment were totally digested using a 4:1 v/v mixture of hydrofluoric acid (HF) and HNO_3, then dried down and dissolved with concentrated HNO_3 twice, drying down each time. This digestion was carried out in the wet laboratory, Department of Geological Sciences, University of Cape Town. The residues of the wetland core samples were digested using a 4:1 v/v mixture of HCl and HF, which was boiled off, then the procedure was repeated with concentrated HNO_3 and then with concentrated perchloric acid ($HClO_4$). This procedure was carried out at the Department of Chemical Engineering, University of Cape Town, following the ex-Karbochem R & D laboratory method. The digested residues for both the river and wetland sediment was then diluted using 5% v/v HNO_3.

For ease of reference, Fraction 1 is referred to as the exchangeable fraction and Fraction 2 as the carbonate fraction. Fraction 3 is referred to as the oxide fraction, even though the extraction does not distinguish between acid volatile sulphides and oxides (Rapin et al., 1986) and this step may liberate metals from labile organic complexes as well (Tessier et al., 1979). Fraction 4 is referred to as the organic matter fraction, even though it may include the more resistant, well crystallised sulphides (e.g. pyrite), and Fraction5 is referred to as the residual fraction composed mainly of silicate detrital material, and may include some refractory organics and resistant sulphides (Tessier et al., 1979).

All reactions were performed in 50 ml polyethylene centrifuge vials with screw cap lids, which can withstand temperatures up to 121°C. All apparatus was acid washed in dilute nitric acid at $pH < 0.5$, and then washed in distilled water. Vials for the first three steps were sealed with parafilm under nitrogen atmosphere to minimise contact of the sample with oxygen. Reagents were also added to the vials under nitrogen atmosphere (**Photo 1, Appendix 1**). At the end of each step, the sealed vials were centrifuged at 6000 rpm for five minutes. The supernatant was removed with a pipette or a plastic dropper, and filtered through a 0.45 μm Millipore membrane syringe filter in order to remove most of the colloidal material. All supernatants were then acidified with concentrated HNO_3 to maintain $pH < 2$ and stored at ~4°C.

After the removal of the supernatants after each step, sediment residues were rinsed with ≤8 ml of distilled water to remove reagents remaining in the vial. The residue was then centrifuged, the rinse-water removed and discarded using a plastic dropper, and the centrifuge vial sealed under nitrogen atmosphere.

2.2.2 Sample Pre-treatment and Reaction Conditions

Wet sediment was reacted in the sequential extraction procedure under a nitrogen atmosphere. Previous work has shown that acceptable techniques includes freezing and that this pre-treatment caused the least change for the anoxic sediment studied

(Rapin et al., 1986). Also, previous work has shown that if oxygen is not rigorously excluded during extraction from anoxic samples, significant differences were observed between the first four fractions, due to the acid volatile sulphide concentrations (AVS) in the sample decreasing in the first two extractions (Rapin et al., 1986).

2.2.3 Sample Homogenisation

Due to wet frozen storage of sediment and extractions carried out under a nitrogen atmosphere as fast as possible to prevent fractionation, it was almost impossible to homogenise the samples. Samples were stirred with a plastic spatula, but a thorough homogenisation process, which would involve drying and sieving, was not carried out in order to avoid oxidation of samples. Thus, the samples can be considered fairly heterogeneous, for both the river sediment and the core sediment samples.

2.2.4 ICP-MS Analyses

The supernatants extracted after each sequential reaction step, were diluted 100 times in 5% HNO_3 and analysed on the quadrupole - type Ion Coupled Plasma Mass Spectrometer (ICP-MS) at the Department of Geological Sciences, University of Cape Town. While samples from the core were sectioned to 40 cm depth for sequential reaction, at 5 cm intervals, only samples to 25 cm depth were analysed on the ICP-MS due to budget constraints. All data received from the ICP-MS in mg/kg solution, were corrected for density of the reagent solutions and dilutions made prior to analyses, e.g. due to acidification of the supernatants. Blank concentrations were subtracted for each element, and concentrations in ppm, were calculated i.e. mg per kg of sediment. 40 elements were analysed in each supernatant for each sample however, only a few elements which are of potential environmental concern, in terms of elevated concentrations and toxicity, were selected for detailed analysis.

2.2.5 Duplicate Samples

Two out of eight river sediment samples were selected for duplicate sequential reactions. Four out of twelve wetland core samples were selected for duplicate sequential reactions. However, only nine core samples were analysed and only two of the duplicate samples were analysed on the ICP-MS due to financial constraints.

2.2.6 Temporal Variation during Sequential Reaction

In order to obtain an indication the variation of trace metal concentration in the supernatants, as the reaction proceeded for the second, third and fourth steps of the extraction, sub-samples were taken. Two river sediment samples were selected for monitoring of temporal variations during the sequential reactions. Approximately 200 μl was removed from each sample supernatant at different time intervals as the reactions proceeded. These two samples were exposed to oxygen during the extractions, and were duplicates of samples 1 and 7. This was in order to evaluate possible decreases in the concentration of metals in the supernatants due to the adsorption onto available solid surfaces. Due to the difficulty filtering such a small volume, the supernatant was first pipetted into a syringe, then 2 ml distilled water pipetted above, and the liquid was immediately pushed through a 0.45 μm Millipore membrane filter using a plunger into the syringe. The filtered solution was acidified with concentrated HNO_3 and stored at 4°C for future analysis. The two samples were not monitored in duplicate, and this procedure is untested, uncalibrated for error, and not a standardised method.

2.3 Sediment Porosity and Density Determination

Since wet sediment (in excess of 1g) was used in the sequential reactions, the porosity was determined for each sample to estimate the mass of water in each sample, in order to determine the dry mass of each sample reacted. Wet sediment was inserted into a syringe of known mass in order to calculate a mass per unit volume for the wet sediment. A sample of dry sediment was then inserted into the syringe in order to calculate a mass per unit volume for the dry sediment. Alternately, the wet sediment in the syringe was dried and re-weighed. The difference between the two, for each sample was taken as the mass of water in sediment, which is equal to the volume of the water for $\rho\ (H_2O) = 1.00 g/cm^3$. This allowed the calculation of the porosity for the sample (**Appendix 1**).

Porosity and density was determined in duplicate for each river sediment sample from the Black River and for each unit in the core from the Raapenberg Wetland, because of high variability between the samples from the various locations. The units in the core were determined by visually identifying grain size changes, colour, and texture changes (**Appendix 1**).

2.4 Grain Size Analysis

A portion of each river sediment sample, and of each major unit of the "description core" was oven dried in order to perform a grain size analysis. The sample was dry sieved through a 2 mm sieve in order to separate the gravel fraction, then wet sieved through a 63 μm sieve in order to separate the sand fraction from the mud fraction. The mud fraction was centrifuged to reduce the volume, ultrasonicated after adding a dispersant, and then allowed to settle to separate the clay (<2 μm) and silt (>2 μm) fractions, for a time calculated using Stoke's law (**Appendix 1**).

2.5 Organic Carbon Determination

The percent organic carbon was determined using the Walkley Black Method (**Appendix 1**). The organic carbon content was determined for each river sediment sample and each core sediment sample (taken from the same core from which the sequentially reacted samples were taken).

2.6 X-Ray Diffraction (XRD)

The clay retrieved from the grain size analyses was centrifuged to reduce the volume, and smeared onto glass slides to analyse for major mineral composition using X-ray diffraction. This was done for all river sediment samples, and each unit identified in the description core, taken ~30 cm away from the core that was used for sequential extractions. The main mineral assemblage was identified for each sample.

2.7 Whole Sediment Digestions

50 mg dry mass of each river sediment sample reacted in the sequential reaction, was digested using a 4:1 HF and HNO_3 mixture. Due to the time constraints on the project, the same was not done for the core samples, instead the concentrations from each of

the five fractions from the sequential reactions were added for a total. The whole digestion was conducted in order to compare the sum of five fractions of the sequential reactions to a total digestion of dried sediment for the river sediment. The separate sediment aliquots for the whole digestion and sequential reaction were not homogenised. All sediment was ground in an agate mortar prior to digestion.

2.8 Water Samples

Only two water samples were taken from the wetland area, and none were taken from the Black River for trace metal analysis. When the two cores were taken from the Raapenberg wetland, one for sequential reaction, and one for soil profile description, the water displaced by the core, that filled the hole, was scooped using a plastic utensil. The two pore-water samples were then filtered twice using Millipore membrane 0.45 µm filters, and acidified with nitric acid. They were then analysed on the ICP-MS in duplicate after ten times dilution.

3. Results

3.1 Selected Elemental Concentrations in Five Fractions of Black River Sediment

The concentrations (in mg/kg soil or ppm) of selected elements are shown in **Table 1**, for five fractions of Black River sediment. There is no residual fraction data available for the major elements.

3.2 Selected Elemental Concentrations in Five Fractions of Raapenberg Wetland Sediment

The concentrations (in mg/kg soil or ppm) of selected elements are shown in **Table 2**, for five fractions of Raapenberg wetland core sediment.

3.3 Organic Carbon (OC) Percent for River and Wetland Sediment

Table 3: Organic Carbon Percent, determined by the Walkley-Black method.

Wetland Core Samples (Weight percent)					
Depth (cm)	OC%	repeat1	repeat2	ave OC%	st dev
1	36.94	30.03		33.49	4.89
3	34.09			34.09	
5	13.97	17.80		15.89	2.71
7	11.86			11.86	
9	6.70			6.70	
12.5	1.72			1.72	
15	0.42	1.34		0.88	0.65
20	1.16			1.16	
25	0.80			0.80	
30	0.97			0.97	
35	1.93			1.93	
39	0.63			0.63	
River Sediment Samples (Weight Percent)					
Sample	**OC%**	**repeat1**	**repeat2**	**ave OC%**	**st. dev.**
1	1.68			1.68	
2	0.27			0.27	
3	6.70	7.19		6.95	0.35
4	4.08			4.08	
5	5.35			5.35	
6	0.23			0.23	
7	13.42	11.76	13.80	12.99	1.08
8	1.25			1.25	

Table 1. Concentrations (ppm or mg/kg soil) of Selected Elements in Five Fractions of Black River Sediment

Sample	exchangeable Cr	carbonates Cr	oxides Cr	organics Cr	residue Cr	sum Cr	total Cr	exchangeable Zn	carbonates Zn	oxides Zn	organics Zn	residue Zn	sum Zn	total Zn
U/S 8	0.00	0.85	1.41	2.03	3.57	7.86	9.18	0.00	3.31	63.15	6.57	7.72	80.7	109.4
6	0.00	0.53	0.86	0.17	2.13	3.69	3.29	0.66	5.59	15.06	0.96	6.02	28.3	46.8
1	0.19	0.84	2.40	1.81	8.59	13.82	16.64	1.00	31.37	98.34	5.28	13.96	149.9	217.3
2	0.07	0.77	1.23	0.72	2.39	5.18	6.18	0.04	4.26	36.61	1.72	5.00	47.6	59.9
3	0.00	0.45	5.97	17.40	36.35	60.17	60.81	0.09	24.90	336.35	31.57	64.50	457.4	618.2
D/S 4	0.00	1.34	10.61	42.25	22.22	76.41	70.53	2.32	12.35	196.48	25.39	38.19	274.7	480.5
Liesbeeck 5	0.00	1.19	3.18	6.05	32.18	42.60	53.99	0.00	41.05	177.13	19.01	67.59	304.8	372.6
wetland 7	7.95	0.45	0.57	5.39	31.08	45.43	34.86	5.18	13.60	51.12	9.51	72.58	152.0	190.2
	exchangeable Pb	carbonates Pb	oxides Pb	organics Pb	residue Pb	sum Pb	total Pb	exchangeable Cu	carbonates Cu	oxides Cu	organics Cu	residue Cu	sum Cu	total Cu
U/S 8	0.00	0.90	33.22	10.89	2.45	47.46	63.14	0.00	0.00	0.60	11.02	2.00	13.63	15.51
6	0.17	1.77	2.33	0.22	1.91	6.40	12.83	0.17	0.00	0.49	3.08	1.02	4.77	4.18
1	0.07	18.82	44.89	9.19	6.85	79.81	106.0	0.14	0.06	1.30	15.22	3.08	19.81	30.92
2	0.00	1.55	10.54	1.66	1.25	15.00	11.64	0.18	0.00	0.66	2.85	1.42	5.11	5.60
3	0.06	8.39	108.4	70.71	24.58	212.2	275.9	0.05	0.00	1.65	54.26	30.03	86.00	94.97
D/S 4	0.01	6.80	66.53	34.72	13.08	121.15	180.0	0.00	0.00	0.46	23.43	8.31	32.20	58.34
Liesbeeck 5	0.32	52.39	132.68	45.88	21.79	253.1	381.4	0.00	0.00	3.48	43.89	13.00	60.37	72.06
wetland 7	0.00	9.37	24.74	15.22	19.01	68.34	91.55	0.00	0.00	0.43	13.17	14.18	27.77	34.61
	exchangeable Al	carbonates Al	oxides Al	organics Al	residue	sum	total	exchangeable Se	carbonates Se	oxides Se	organics Se	residue Se	sum Se	total Se
U/S 8	2.86	16.54	326.4	240.7				0.00	0.00	0.05	0.19	0.70	0.95	0.51
6	9.75	11.97	148.6	49.59				0.06	0.00	0.00	0.00	*n.d.*	0.06	0.17
1	0.91	12.43	249.0	224.5				0.05	0.00	0.00	0.09	0.44	0.58	0.81
2	1.48	14.33	202.8	110.9				0.00	0.00	0.20	0.01	0.19	0.40	0.71
3	0.76	5.58	517.0	1530				0.07	0.00	0.26	0.54	0.51	1.38	1.26
D/S 4	0.67	17.27	918.4	1331				0.01	0.00	0.00	0.59	0.15	0.76	2.23
Liesbeeck 5	0.23	81.51	1569	2376				0.03	0.00	0.16	0.35	0.36	0.90	1.38
wetland 7	7.11	32.54	688.3	2190				3.65	0.00	0.22	0.41	0.39	4.67	1.16
	exchangeable Ca	carbonates Ca	oxides Ca	organics Ca	residue	sum	total	exchangeable Si	carbonates Si	oxides Si	organics Si	residue	sum	total
U/S 8	729	3565	18.92	45.83				0.0	37.6	164	197			
6	288	1539	0.00	24.26				25.6	12.6	37.5	41.0			
1	612	10226	540	96.45				12.4	49.3	174	189			
2	385	3114	0.0	72.44				7.4	24.0	70.7	88.0			
3	1468	9445	1322	356.4				26.4	40.0	658	475			
D/S 4	1107	2881	386	157				0.0	61.8	890	551			
Liesbeeck 5	1750	1174	293	145				1.8	137	834	535			
wetland 7	428	787	39.38	75.85				84.6	20.1	186	451			

Table 1 (continued). Concentrations (ppm or mg/kg soil) of Selected Elements in Five Fractions of Black River Sediment

Sample	exchangeable Cd	carbonates Cd	oxides Cd	organics Cd	residue Cd	sum	total	exchangeable Hg	carbonates Hg	oxides Hg	organics Hg	residue Hg	sum	total
U/S 8	0.00	0.01	0.11	0.01	0.02	0.15	0.23	0.000	0.000	0.009	0.000	0.046	0.055	0.0455
6	0.02	0.01	0.03	0.00	0.00	0.06	0.06	0.000	0.000	0.027	0.078	0.178	0.283	0.2439
1	0.00	0.01	0.11	0.00	0.01	0.14	0.33	0.029	0.000	0.152	0.101	0.816	1.099	1.0752
2	0.00	0.02	0.04	0.00	0.00	0.05	0.05	0.006	0.000	0.136	0.059	0.601	0.804	0.7859
3	0.00	0.01	0.63	0.07	0.07	0.77	1.26	0.000	0.000	0.091	0.107	0.513	0.711	0.8776
D/S 4	0.01	0.01	0.67	0.36	0.02	1.06	1.04	0.000	0.000	0.191	0.059	0.349	0.599	0.4474
Liesbeeck 5	0.00	0.03	0.34	0.02	0.04	0.44	0.58	0.000	0.000	0.071	0.083	0.218	0.372	0.3538
wetland 7	0.26	0.02	0.21	0.00	0.00	0.49	0.47	1.275	0.000	0.066	0.004	0.148	1.493	0.1537

	exchangeable Ni	carbonates Ni	oxides Ni	organics Ni	residue Ni	sum Ni	total Ni	exchangeable As	carbonates As	oxides As	organics As	residue As	sum As	total As
U/S 8	0.00	0.18	0.31	0.31	0.56	1.36	2.33	0.04	0.14	0.96	0.26	0.52	1.92	1.32
6	0.00	0.00	0.12	0.09	0.16	0.38	0.53	0.02	0.01	0.15	0.05	0.17	0.39	0.46
1	0.00	0.58	2.01	0.48	1.47	4.54	6.14	0.04	0.16	0.73	0.38	1.65	2.96	3.37
2	0.00	0.58	0.70	0.36	0.61	2.26	1.91	0.03	0.03	0.27	0.08	0.33	0.73	1.41
3	0.00	4.08	6.79	3.52	11.63	26.01	31.43	0.10	0.21	1.84	1.09	4.85	8.10	10.53
D/S 4	0.00	1.00	3.46	3.86	6.48	14.80	19.97	0.14	0.43	1.98	0.99	2.05	5.59	9.78
Liesbeeck 5	0.00	0.11	1.28	1.16	4.41	6.96	12.75	0.05	0.65	1.83	1.05	12.37	15.95	15.66
wetland 7	0.00	0.06	1.10	1.02	8.69	10.87	10.73	0.25	0.73	1.30	0.98	9.35	12.61	12.89

	exchangeable Co	carbonates Co	oxides Co	organics Co	residue Co	sum Co	total Co	exchangeable Fe	carbonates Fe	oxides Fe	organics Fe	residue	sum	total
U/S 8	0.00	0.03	0.13	0.17	0.22	0.56	0.81	0.00	353	435	307			
6	0.00	0.02	0.04	0.04	0.07	0.17	0.23	0.80	51.2	106	44.2			
1	0.01	0.24	0.34	0.21	0.53	1.33	1.63	3.14	312	728	118			
2	0.00	0.04	0.09	0.13	0.26	0.52	0.44	0.00	200	275	61.4			
3	0.01	0.28	0.67	0.76	2.90	4.62	5.15	2.37	798	1911	1054			
D/S 4	0.00	0.21	0.89	1.84	2.12	5.06	5.25	0.00	554	2068	2588			
Liesbeeck 5	0.03	0.48	0.96	0.61	2.29	4.37	4.94	0.00	439	3120	641			
wetland 7	0.00	0.41	0.58	0.47	2.95	4.41	4.66	0.00	183	1974	841			

Note that no residual fraction data is available for the major elements. Zero values imply concentrations below the detection limit of the ICP-MS or within the concentration range of the blank samples. U/S 8 is the most upstream sample, with samples in order from top to bottom towards the most downstream sample, D/S 4. Liesbeeck 5 is the river bottom sediment from the Liesbeeck River, while wetland 7 is the scooped sediment sample from the Raapenberg Wetland. **Total** elemental concentrations are the results of whole digested analyses, of a separate whole aliquot of sediment, while the **Sum** is the addition of the concentrations for the five fractions extracted and analysed individually.

Table2. Concentrations (ppm or mg/kg soil) of Selected Elements in Five Fractions of Raapenberg Wetland Core.

Depth (cm)	exchangeable Cr	carbonates Cr	oxides Cr	organics Cr	residue Cr	sum Cr	exchangeable Zn	carbonates Zn	oxides Zn	organics Zn	residue Zn	sum Zn
1	0.62	0.00	6.85	68.99	63.25	139.72	1.98	28.87	160.10	35.24	112.25	338.42
3	0.20	0.72	17.75	182.38	74.21	275.26	3.15	31.44	104.71	28.33	93.16	260.79
5	0.23	0.00	6.06	27.14	54.24	87.67	8.19	71.82	298.40	73.86	159.28	611.54
7	0.17	0.00	6.00	27.33	54.67	88.16	5.22	59.70	344.63	86.81	136.13	632.49
9	0.15	0.00	0.00	11.95	26.12	38.23	7.35	66.92	305.46	51.86	94.09	525.68
12.5	0.13	0.00	2.53	3.65	14.12	20.43	3.79	51.76	194.18	17.89	5.67	273.29
15	0.15	0.48	4.08	7.74	21.56	34.01	3.96	65.66	251.35	24.74	96.20	441.90
20	0.30	0.55	2.70	3.81	16.35	23.70	0.00	5.53	83.67	13.64	85.36	188.20
25	0.25	0.74	4.72	2.44	15.29	23.44	0.00	6.83	90.22	11.59	82.21	190.84
SL-1	0.50	0.00	6.63	2.60	86.56	96.29	2.33	19.05	61.44	12.76	152.36	247.94

Depth (cm)	exchangeable Cu	carbonates Cu	oxides Cu	organics Cu	residue Cu	sum Cu	exchangeable Pb	carbonates Pb	oxides Pb	organics Pb	residue Pb	sum Pb
1	0.41	0.00	1.59	82.35	57.90	142.25	0.67	32.37	119.43	93.07	68.48	314.02
3	0.00	0.00	1.59	83.79	72.67	158.05	1.04	48.58	148.98	198.51	50.95	448.06
5	0.00	0.00	3.29	57.52	42.72	103.53	2.12	25.41	102.80	117.45	39.10	286.89
7	0.00	0.00	4.02	61.35	29.15	94.52	1.43	16.22	83.79	116.10	40.01	257.54
9	0.09	0.00	4.05	30.73	12.66	47.53	1.39	17.91	73.70	49.37	25.51	167.87
12.5	0.13	0.00	3.82	7.92	4.17	16.04	0.14	4.83	50.46	19.15	8.94	83.52
15	0.00	0.15	4.36	9.79	6.61	20.90	0.16	5.86	55.15	25.60	14.25	101.02
20	0.00	0.14	3.81	7.35	8.46	19.75	0.06	5.03	66.13	23.34	17.48	112.04
25	0.00	0.22	5.46	6.28	5.11	17.06	0.13	8.39	51.96	14.62	12.58	87.67
SL-1	0.58	0.03	1.35	4.80	22.83	29.58	0.01	0.71	14.25	5.22	13.31	33.49

Depth (cm)	exchangeable As	carbonates As	oxides As	organics As	residue As	sum As	exchangeable Ca	carbonates Ca	oxides Ca	organics Ca	residue Ca	sum Ca
1	0.08	1.01	7.07	2.42	15.87	26.45	5483	2556	746	166	0	8952
3	0.08	1.34	5.47	2.29	0.00	9.18	3352	1292	747	219	373	5984
5	0.10	0.53	3.51	4.06	13.14	21.34	4050	1574	1416	514	0	7555
7	0.10	0.68	3.93	4.94	20.53	30.17	4857	1846	1735	568	0	9006
9	0.00	0.21	2.08	2.53	15.11	19.93	3156	998	777	200	0	5131
12.5	0.00	0.02	1.59	2.34	6.62	10.56	1269	389	256	98	0	2012
15	0.01	0.09	1.30	3.64	19.98	25.02	1184	546	357	75	1457	3619
20	0.01	0.06	0.99	2.98	4.07	8.11	1106	511	221	80	1492	3410
25	0.01	0.04	0.58	1.48	19.83	21.95	638	296	179	157	2401	3671
SL1	0.00	0.09	4.18	3.24	30.81	38.32	2836	279	116	127	1423	4782

Table2 (continued). Concentrations (ppm or mg/kg soil) of Selected Elements in Five Fractions of Raapenberg Wetland Core.

Depth (cm)	exchangeable Mo	carbonates Mo	oxides Mo	organics Mo	residue Mo	sum Mo	exchangeable Cd	carbonates Cd	oxides Cd	organics Cd	residue Cd	sum Cd
1	0.30	0.00	0.56	3.52	0.00	4.38	0.02	0.02	0.46	0.09	0.05	0.63
3	0.18	0.00	0.59	8.16	0.00	8.93	0.00	0.05	0.31	0.09	0.00	0.45
5	0.15	0.00	0.30	1.20	1.15	2.79	0.02	0.14	1.03	0.19	0.00	1.38
7	0.13	0.00	0.29	1.44	0.00	1.86	0.01	0.12	1.36	0.27	0.00	1.75
9	0.12	0.00	0.23	0.72	0.00	1.07	0.02	0.17	0.67	0.09	0.00	0.96
12.5	0.03	0.00	0.10	0.27	0.00	0.40	0.03	0.14	0.36	0.02	0.00	0.55
15	0.02	0.00	0.05	0.32	0.00	0.39	0.02	0.13	0.63	0.04	0.00	0.82
20	0.01	0.00	0.01	0.25	0.00	0.27	0.01	0.05	0.11	0.01	0.00	0.18
25	0.01	0.00	0.01	0.18	1.67	1.87	0.00	0.03	0.09	0.01	0.00	0.13
SL-1	0.00	0.00	0.14	0.00	0.00	0.15	0.05	0.10	0.01	0.01	0.00	0.18

Depth (cm)	exchangeable Co	carbonates Co	oxides Co	organics Co	residue Co	sum Co	exchangeable Ni	carbonates Ni	oxides Ni	organics Ni	residue Ni	sum Ni
1	0.20	0.88	1.21	1.06	5.17	8.53	0.43	0.00	2.46	2.74	44.00	49.63
3	0.16	0.54	1.45	1.16	6.02	9.33	0.12	0.00	2.10	4.38	34.03	40.63
5	0.22	0.81	3.76	1.42	7.08	13.27	0.21	0.00	6.09	7.83	82.67	96.80
7	0.16	0.70	4.47	1.84	7.24	14.42	0.19	0.32	3.94	6.44	32.23	43.12
9	0.17	0.83	3.79	0.84	3.45	9.08	0.16	0.48	3.78	1.39	19.20	25.01
12.5	0.09	0.53	2.05	0.23	2.47	5.38	0.14	0.28	1.34	0.00	31.41	33.17
15	0.10	0.64	2.36	0.30	2.41	5.80	0.05	0.34	2.63	0.00	16.66	19.68
20	0.02	0.14	1.80	0.29	2.70	4.95	0.02	0.07	0.85	0.00	14.81	15.75
25	0.01	0.10	1.23	0.21	2.42	3.97	0.05	0.32	0.84	0.00	13.14	14.36
SL-1	0.48	0.91	6.28	1.78	8.07	17.52	0.05	0.00	1.42	0.03	51.62	53.11

Depth (cm)	exchangeable Se	carbonates Se	oxides Se	organics Se	residue Se	sum Se	exchangeable Fe	carbonates Fe	oxides Fe	organics Fe	residue Fe	sum Fe
1	0.26	0.00	0.12	1.56	0.00	1.95	128	1618	7845	3238	18398	31227
3	0.05	0.24	0.40	1.45	0.00	2.13	97	347	4730	2576	21261	29012
5	0.05	0.27	0.63	3.83	0.00	4.78	26	255	6005	2492	25693	34471
7	0.00	0.35	0.65	3.77	0.00	4.77	13	137	5744	2971	27026	35891
9	0.00	0.52	0.33	2.78	0.00	3.64	6	92	4428	1094	19835	25455
12.5	0.00	0.06	0.40	0.88	0.00	1.33	4	36	5490	787	16837	23154
15	0.24	0.05	1.02	1.06	0.00	2.37	0	25	5279	1591	17876	24771
20	0.11	0.00	0.88	0.63	0.00	1.63	0	6	4566	765	19791	25128
25	0.03	0.13	0.24	0.18	0.00	0.58	0	0	2566	543	15804	18914
SL-1	0.00	0.23	0.30	0.50	0.00	1.03	9	349	16599	3297	48206	68460

Table 2 (continued). Concentrations (ppm or mg/kg soil) of Selected Elements in Five Fractions of Raapenberg Wetland Core.

Depth (cm)	exchangeable Hg	carbonates Hg	oxides Hg	organics Hg	residue Hg	sum Hg
1	0.58	0.00	0.00	0.00	0.17	
3	0.22	0.38	0.07	0.08	4.26	
5	0.28	0.43	0.00	0.00	0.00	
7	0.23	0.38	0.00	0.00	0.00	
9	0.16	0.21	1.09	0.00	0.00	
12.5	0.05	0.05	0.21	0.03	0.00	
15	0.00	0.00	0.04	0.00	0.08	
20	0.00	0.00	0.00	0.46	0.00	
25	0.00	0.00	0.00	0.28	0.00	

SL-1 is the certified reference material, a lake sediment, from the International Atomic Energy Agency.

3.4 Combined Sampling Heterogeneity and Procedural Error in River Sediment

Two samples were sequentially reacted in duplicate. The results allow an estimation of the combined procedural error and sample heterogeneity, since samples were not completely homogenised.

Table 4: Average Combined Sampling Heterogeneity and Procedural Precisional Error, P, at the 95% confidence limit.

Concentration Ranges	**P ((s/X)*200%)**	**(s/X)*100%**	**n**
error on values < 0.1ppm	273.94	136.97	8
0.1ppm <error on values <2ppm	142.53	71.27	21
2ppm <error on values <10ppm	131.25	65.63	9
10ppm <error on values <100ppm	68.17	34.09	13
100ppm <error on values	62.32	31.16	7

Calculated from duplicates for selected elements (Pb, Zn, Cu, Cr, Ca, Al, Ni, Fe, As) for various concentration ranges (for four fractions). P = two standard deviations (2σ) as a percent of the mean (X). The third column gives one standard deviation as a percent of the mean.

Calculated standard deviations for each element in **Appendix 2**.

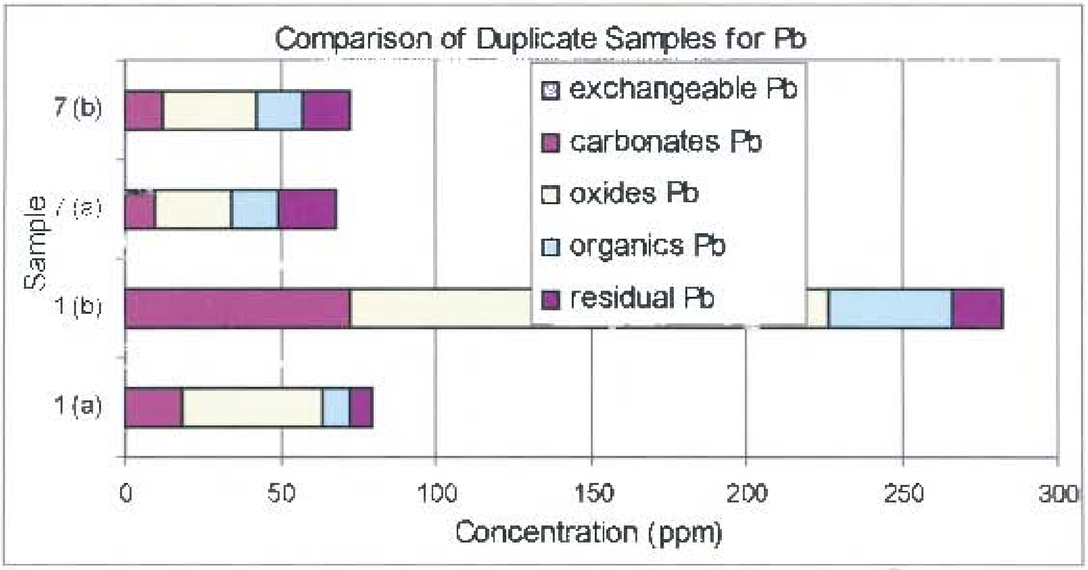

Figure 3: Pb in five fractions of river sediment. Sample 1 is sand from the most upstream region of the sampling area, while Sample 7 is an organic-rich, muddy sediment from the wetland area

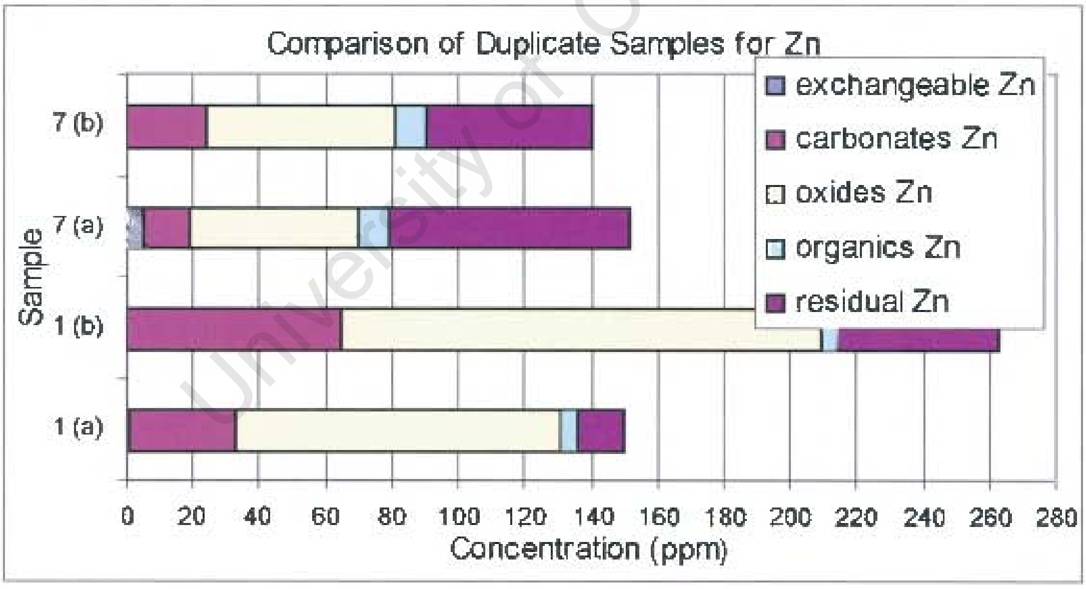

Figure 4: Zn in five fractions of river sediment. Sample 1 is sand from the most upstream region of the sampling area, while sample 7 is an organic-rich, muddy sediment from the wetland area.

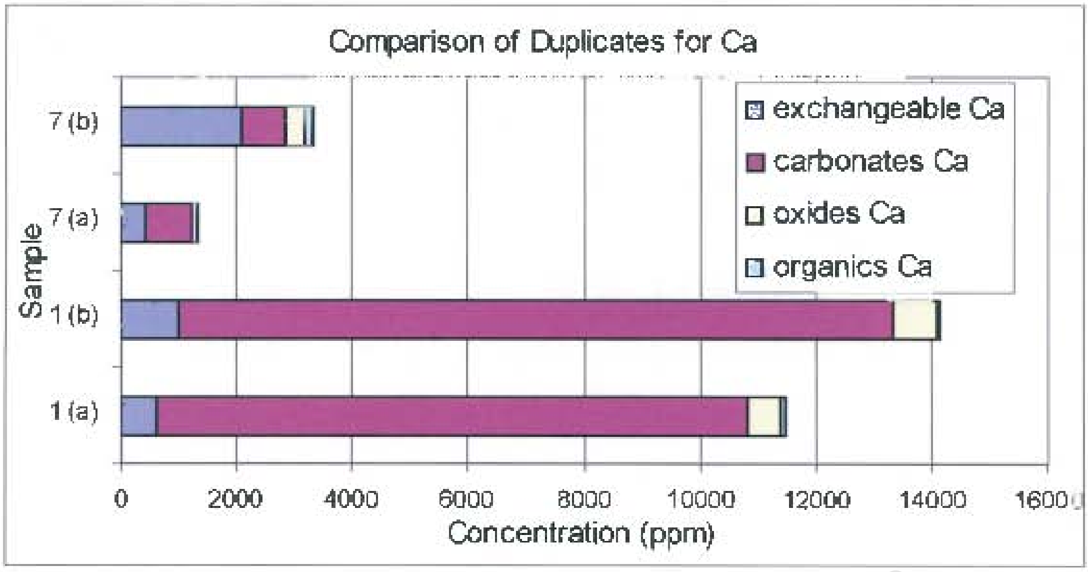

Figure 5: Ca in four fractions of river sediment. Sample 1 is sand from the most upstream region of the sampling area, while Sample 7 is an organic-rich, muddy sediment from the wetland area.

3.5 Analytical Error for River Sediment Supernatant Analyses

Three samples were analysed in triplicate on one run on the ICP-MS, at the beginning, middle and end of the run. Three different reagent types were chosen for the triplicates. An estimation of the precision of the ICP-MS can be obtained from these data, but the error will also include pipetting and diluting errors, which are unavoidable. The standard deviations of the individual results from the triplicate mean, were calculated as a percent of the mean (**Table 5**). This was taken as an estimate of the error on the entire dataset.

Table 5. Analytical Error for Aquatic Sediment Supernatant Analyses on the ICP-MS.

Analytical Error of triplicate ICP-MS samples

Precision or Scatter of samples at the 95% Confidence Limit. (Beginning, middle and end of run)

%P (200*(st.dev./mean	Li	Be	B	Na	Mg	Al	Si	K	Ca
NIST-1640 (%Bias)	3.90	27.95	4.40	19.24	8.38	13.81	9.27	21.93	-10.04
TRIP:C1 (%P)	-		194.56		15.45	21.39	129.77	127.56	18.79
TRIP:S3 (%P)	-	244.55	346.41	19.03	2.84	5.42	15.90	41.39	25.21
TRIP:FM4 (%P)	57.39	-	88.62	96.51	41.61	45.14	58.89	47.48	52.50
average %P	57.39	244.55	209.86	57.77	19.97	23.98	68.19	72.14	32.17
%P (200*(st.dev./mean	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	As
NIST-1640 (% Bias)	-4.67	4.02	23.15	2.67	1.41	6.84	24.38		1.46
TRIP:C1 (%P)	141.71	9.12	8.02	108.70	9.42	-	10.18	23.02	45.29
TRIP:S3 (%P)	6.92	2.81	3.08	11.90	3.02	1.29	2.58	4.08	9.05
TRIP:FM4 (%P)	59.33	43.52	37.90	66.17	39.70	31.11	43.89	48.34	51.44
average %P	69.32	18.48	16.33	62.25	17.38	16.20	18.88	25.15	35.26
%P (200*(st.dev./mean	Se	Rb	Sr	Mo	Ag	Cd	Sb	W	Hg
NIST-1640 (%Bias)	7.85	2.74	6.70	-0.53	-7.58	-2.29	-2.27		
TRIP:C1 (%P)	-	50.38	6.72	-		11.68	270.14	-	-
TRIP:S3 (%P)	17.69	2.31	3.88	2.68	40.18	21.78	4.61	8.82	
TRIP:FM4 (%P)	223.21	39.93	43.88	59.10	-	44.06	79.56	142.46	218.29
average %P	120.45	30.87	18.16	30.89	-	25.84	118.10	75.64	218.29
%P (200*(st.dev./mean	Tl	Pb							
NIST-1640 (%Bias)		6.31							
TRIP:C1 (%P)	-	9.43							
TRIP:S3 (%P)	49.52	2.92							
TRIP:FM4 (%P)	43.35	41.61							
average %P	46.43	17.99							

There is generally a higher error on the lowest concentration samples due to low concentrations of some elements in the sample, close to the blank concentrations. The relativley high blank concentrations also influences the low concentration samples to a larger extent than the high concentration samples.

Percent Bias

The NIST-1640 is the water standard used to quantify the bias of the quadrupole ICP-MS. The value for each element for the NIST-1640 standard is the percent bias of the analysis for each element. Positive values indicate a tendency towards higher than accurate values, and negative values indicate a tendency towards lower than accurate values. The % Bias is given as a percentage difference between the true or accepted value and the measured value. All other values are the Precision (%P), which equals 200*(σ/mean).

3.6 Sample Heterogeneity and Procedural Error for Wetland Core Samples

Four samples (sections or slices from the core) were sequentially reacted in duplicate. The supernatants of two of the four duplicates were analysed by the ICP-MS. The results allow an estimation of the combined procedural error and sample heterogeneity, since samples were not completely homogenised.

Table 6: Average Combined Sampling Heterogeneity and Procedural Precisional Error, P at the 95% confidence limit for Wetland Core samples.

Concentration Ranges	**P=(s/X)*200%**	**(s/X)*100**	**n**
error for values < 0.1ppm	119.23	59.62	12
0.1ppm < error for values < 2ppm	82.72	41.36	31
2ppm < error for values < 10ppm	43.91	21.96	15
10ppm< error for values < 100ppm	25.27	12.64	12
100ppm < error for values < 1000ppm	25.30	12.65	11
error for values >1000ppm	55.51	27.76	6

Calculated from duplicates for selected elements (Cr, Zn, Pb, Ni, Co, Cu, As, Ca, Fe, Cd, Mo, Se) for various concentration ranges. P = <u>two</u> standard deviations (2s) as a percent of the mean (X). Includes data from fractions 1 to 4 (excludes the residual fraction). The third column gives one standard deviation as a percent of the mean. Calculated standard deviations for each element in **Appendix 2**.

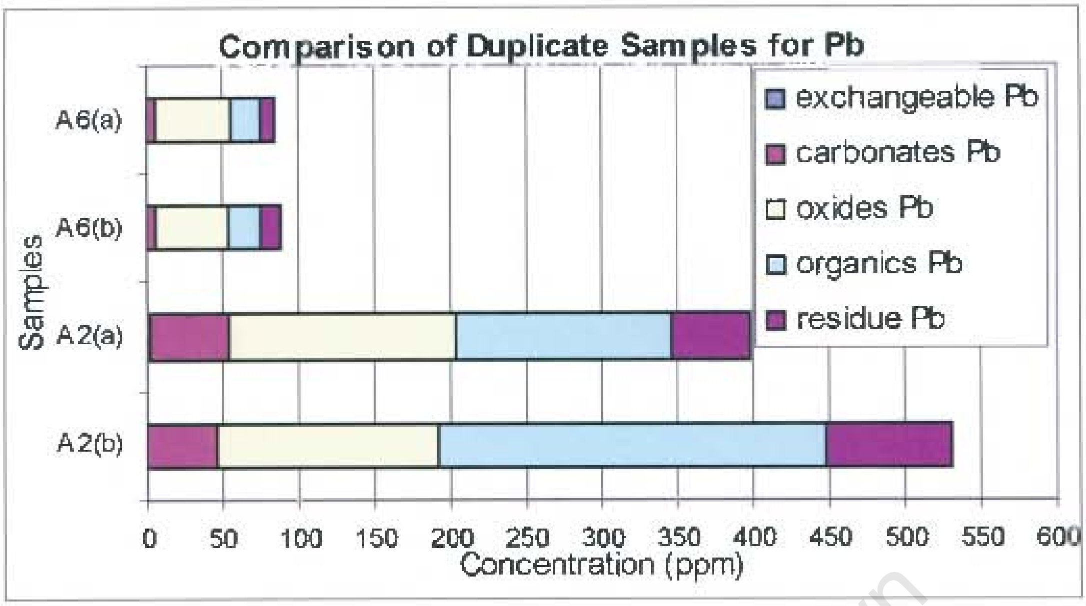

Figure 6: Pb in five fractions of wetland sediment. Sample A2(a) is an organic-rich, muddy sediment from 2-3cm depth in the core, and is the duplicate of sample A2(b). Sample A6(a) is an organic-poor, silty-sand from 10-12.5cm depth in the core and is the duplicate of sample A6(b).

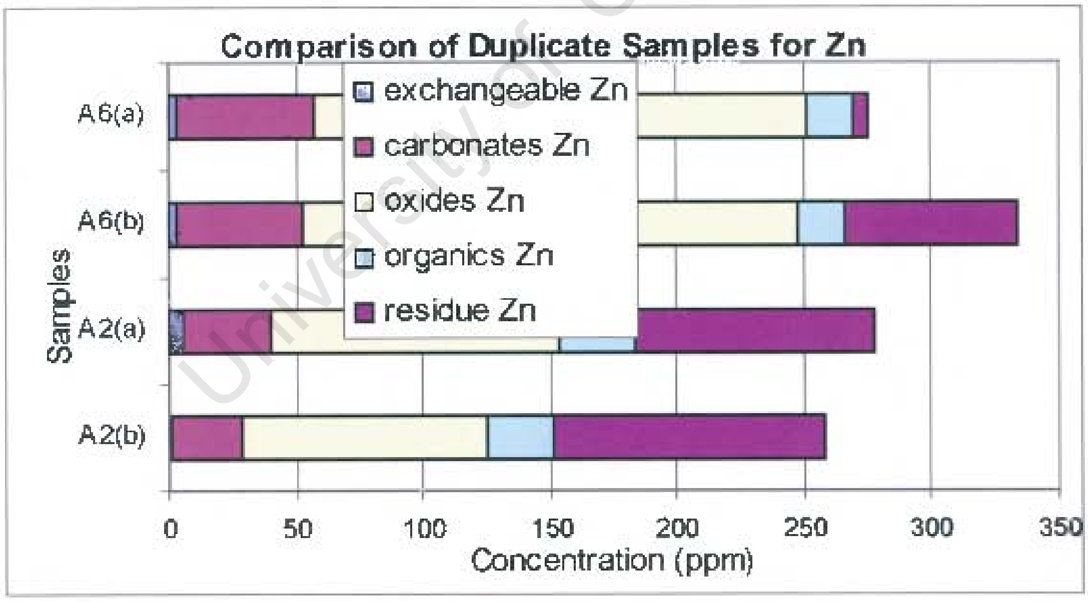

Figure 7: Zn in five fractions of wetland sediment. Sample A2(a) is an organic-rich, muddy sediment from 2-3cm depth in the core, and is the duplicate of sample A2(b). Sample A6(a) is an organic-poor, silty-sand from 10-12.5cm depth in the core and is the duplicate of sample A6(b).

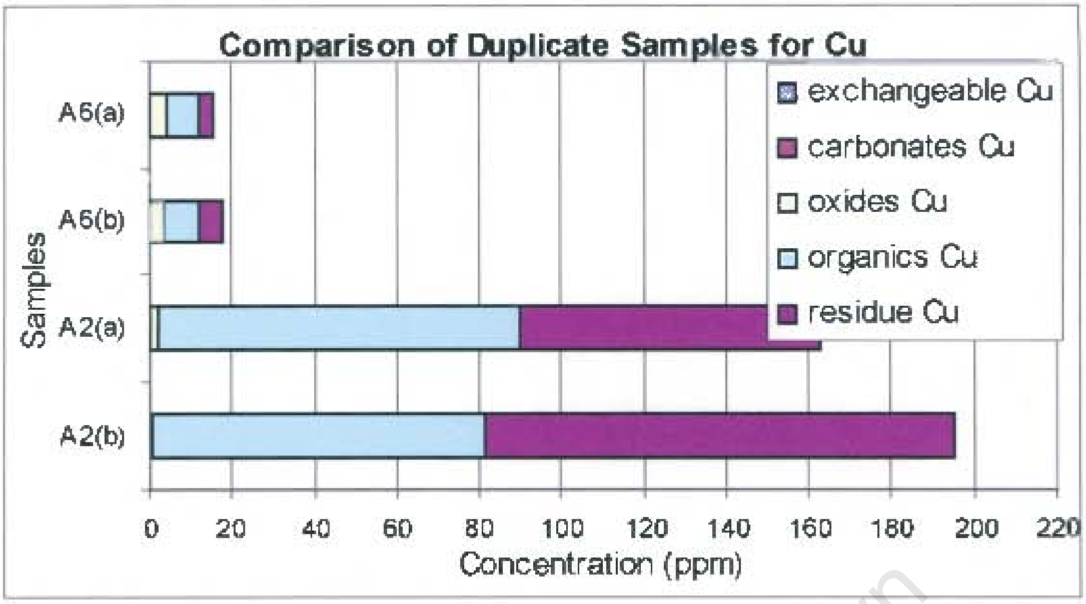

Figure 8: Cu in five fractions of wetland sediment. Sample A2(a) is an organic-rich, muddy sediment from 2-3cm depth in the core, and is the duplicate of sample A2(b). Sample A6(a) is an organic-poor, silty-sand from 10-12.5cm depth in the core and is the duplicate of sample A6(b).

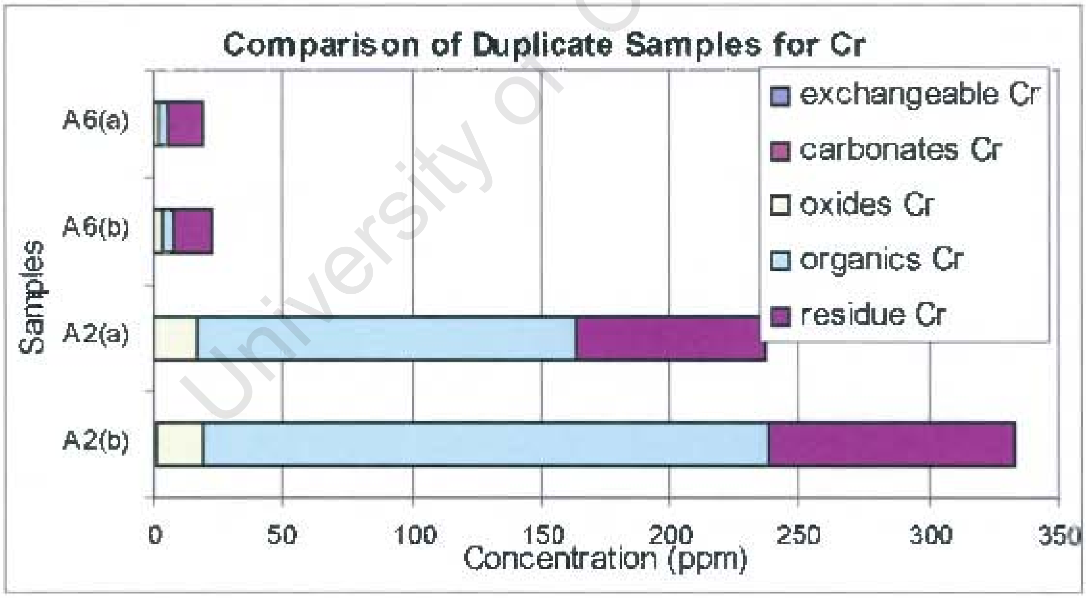

Figure 9: Cr in five fractions of wetland sediment. Sample A2(a) is an organic-rich, muddy sediment from 2-3cm depth in the core, and is the duplicate of sample A2(b). Sample A6(a) is an organic-poor, silty-sand from 10-12.5cm depth in the core and is the duplicate of sample A6(b).

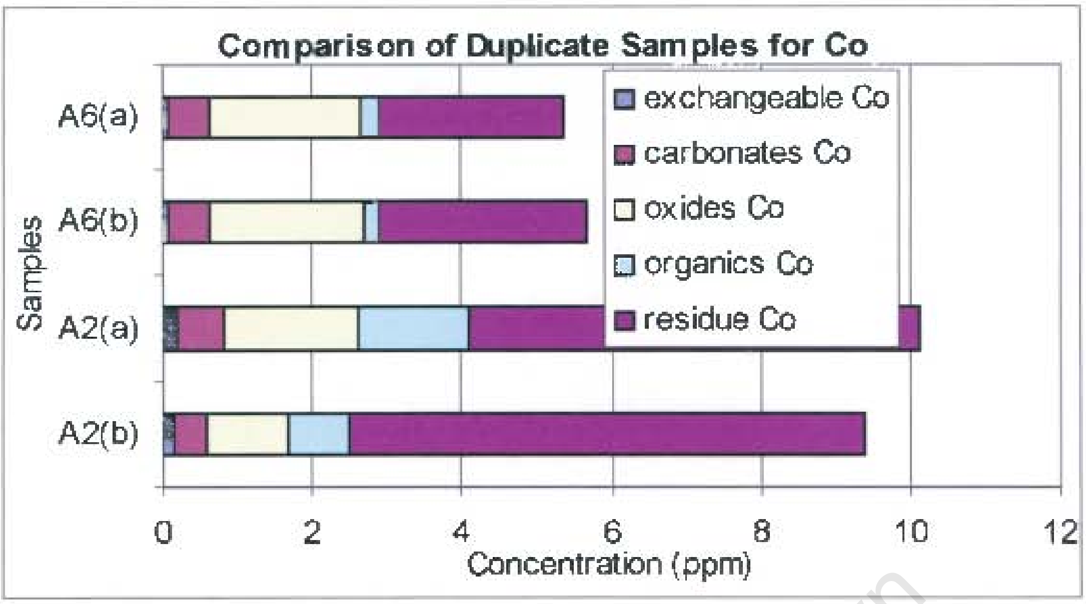

Figure 10: Co in five fractions of wetland sediment. Sample A2(a) is an organic-rich, muddy sediment from 2-3cm depth in the core, and is the duplicate of sample A2(b). Sample A6(a) is an organic-poor, silty-sand from 10-12.5cm depth in the core and is the duplicate of sample A6(b).

3.7 Analytical Error for Wetland Core Supernatant Analyses

Two samples were analysed in triplicate on one run on the ICP-MS, at the beginning, middle and end of the run. Two reagent types were chosen for the triplicates. An estimation of the precision of the ICP-MS can be obtained from these data, but the error will also include pipetting and diluting errors. The standard deviations of the individual results from the triplicate mean, were calculated as a percent of the mean for each element. This was taken as an estimate of the error for the precision of the ICP-MS to analyse each element for a specific matrix. Results can be found in **Table 7**, where, for each element, the standard deviation as a percent of the mean, is averaged.

Table 7. Analytical Error for Wetland Core Sample Supernatant Analyses on the ICP-MS.

Analytical error of Triplicate ICP-MS Samples

Precision, P or Scatter of values at the 95% Cofidence Limit (Samples at the beginning, middle and end of run)

%P=200*(st.dev./mean)	Li	Be	B	Na	Mg	Al	Si	K	Ca
NIST-1640(%Bias)	6.29	10.41	2.02	8.09	1.82	31.26	7.99	6.86	3.34
TRIPA2FM(%P)	4.78	280.0	26.75	47.71	7.14	9.70	5.78	59.92	41.35
TRIPB1S(%P)	6.76	346.4	346.41	8.97	2.79	7.79	11.84	256.54	85.31
Average %P	5.77	313.21	186.58	28.34	4.96	8.75	8.81	158.23	63.33
%P=200*(st.dev./mean)	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu
NIST-1640(%Bias)			-3.32	-0.36	0.51	33.99	5.54	-0.89	8.64
TRIPA2FM(%P)	346.41	4.59	39.21	5.58	7.36	6.30	87.72	3.39	5.08
TRIPB1S(%P)	18.95	2.19	39.37	19.34	1.34	4.95		2.79	4.29
Average %P	182.68	3.39	39.29	12.46	4.35	5.62		3.09	4.69
%P=200*(st.dev./mean)	Zn	Ga	As	Se	Rb	Sr	Y	Zr	Mo
NIST-1640(%Bias)	28.55		-0.24	4.33	3.25	3.24			0.15
TRIPA2FM(%P)	7.92	7.64	11.71	266.89	4.10	6.06	6.17	19.26	4.83
TRIPB1S(%P)	3.00	0.72	7.05	84.18	2.08	1.95	4.21	3.48	2.48
Average %P	5.46	4.18	9.38	175.53	3.09	4.01	5.19	11.37	3.66
%P=200*(st.dev./mean)	Ag	Cd	Sb	Cs	Ba	La	Ce	Nd	W
NIST-1640(%Bias)	3.90	-1.70	-0.38		-1.75				
TRIPA2FM(%P)		15.12	4.74	15.87	3.42	4.86	5.70	7.10	292.85
TRIPB1S(%P)		28.65	2.96	7.49	1.72	3.21	2.98	5.45	191.93
Average %P		21.89	3.85	11.68	2.57	4.04	4.34	6.27	242.39
%P=200*(st.dev./mean)	Hg	Tl	Pb	Th	U				
NIST-1640(%Bias)			8.64						
TRIPA2FM(%P)	202.87	24.28	2.28	48.53	3.56				
TRIPB1S(%P)	346.41	30.85	3.21	4.85	4.77				
Average %P	137.32	13.78	1.37	13.35	2.08				

The NIST-1640 is the water standard used to quantify the bias of the quadrupole ICP-MS. The value for each element for the NIST-1640 standard is the percent bias of the analysis for each element. Positive values indicate a tendency towards higher than accurate values, and negative values indicate a tendency towards lower than accurate values. The % Bias is given as a percentage difference between the true or accepted value, and the measured value. All other values are the Precision (%P), which equals 200*(σ/mean).

3.8 Temporal Variation during Sequential Reaction

Measurements were conducted for the second, third and fourth extraction steps. The data is used as an approximate indication and confirmation that

(a) the reaction times applied to the sediment were appropriate in dissolving the desired phases, and that,

(b) the soluble metal concentration in the supernatant did not decrease substantially due to adsorption onto the solid phase, just before, or while simultaneously extracting the supernatant.

The two samples chosen for the monitoring of temporal variations are sample 9 and sample 10. These samples are duplicates of two river samples. Sample 9 is a sand sample from the Elsieskraal convergence point with the Vygekraal River, and corresponds to location 1 on the map. Sample 10 is an organic-rich, muddy river sediment from the Raapenberg Wetland and correspond to location 7 on the map. Graphs of 'temporal variation' samples are available in **Appendix 6**.

3.9 Grain Size Analysis

3.9.1 River Sediment

The particle/grain sizes are defined as follows:
Clay < 2 μm diameter
2 μm < Silt < 63 μm diameter
63 μm < Sand < 2 mm diameter
Gravel > 2 mm diameter

Table 8: Grain Size Distribution for River Sediment (Weight percent)

Sample Number	**Gravel fraction %**	**Sand %**	**Silt %**	**Clay %**
1	3.4	90	5.5	1.1
2	1.5	>98.3	0.1	<0.1
3	6.2	56	33.2	4.7
4	31.2	52.6	16.2	<0.1
5	4.3	43.5	46.2	6
6	0.0	99.4	~0.55	<0.1
7	14.6	39.7	39.1	6.6
8	1	88	5	6

3.9.2 Wetland Core Samples

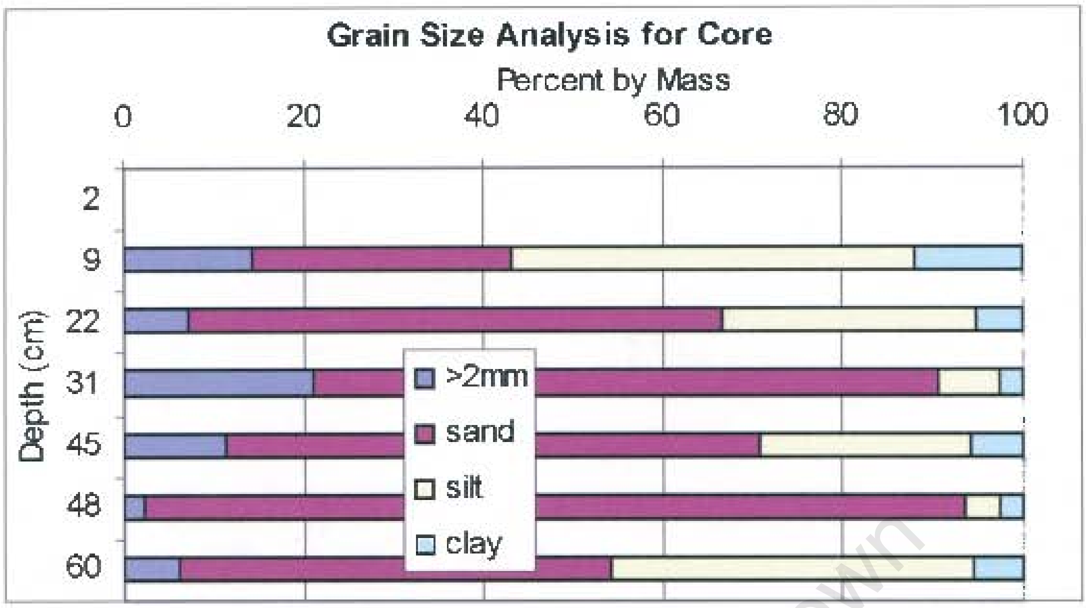

Figure 11: Variation in the grain size distribution with depth for major zones logged in the core. The depth axis is not to scale. The depth represents the base of the zone that was homogenised for the grain size analysis.

3.10 X-Ray Diffraction (XRD)

The separate clay fraction from each river sediment sample yielded the following results on the XRD (OM = organic matter):

Table 9: Mineralogy of the clay size fraction of river sediment samples.

Sample	Minerals
1	Illite/mica-smectite, kaolinite.
2	Illite/mica-smectite, kaolinite.
3	Mainly kaolinite, lesser illite.
4	Mainly kaolinite, lesser illite/mica-smectite.
5	Kaolonite, mica, smectite, possible gibbsite.
6	Illite, kaolinite.
7	Kaolinite, illite/mica-smectite.
8	Kaolinite, calcite, lesser illite.

OM feature or 'hump' in all XRD scans.

Table 10: Mineralogy of clay size fraction of the wetland core sediment samples.

Depth in core (cm)	**Minerals**
2 – 9	Kaolinite, illite/mica, goethite.
9 – 22	Kaolinite, illite/mica-smectite, goethite, gibbsite.
22 – 31	Kaolinite, illite/mica, goethite.
31 – 45	Mainly kaolinite, illite, mica-smectite, goethite, gibbsite, possible calcite.
45 – 48	Kaolinite, illite, mica-smectite, gibbsite.
48 – 60	Kaolinite, lesser illite, K-feldspar, Goethite, possible white mica

There was one unidentified peak at 2.38 angstroms in 3 of the six slides. OM feature occurred in all but one (48 – 60 cm sample) XRD scan. XRD raw data is available in **Appendix 3**.

3.11 Whole Sediment Digestion for River Sediment

Graphs summarising results of whole sediment digestions, and the procedural and analytical error for the aquatic sediment samples are available in **Appendix 4**. Whole sediment digestion was not performed on the wetland core samples due to time constraints.

3.12 Porewater (PW) Trace Metal Concentrations

Table 11: Trace Metal Concentration (ppb or µg/l) in porewater displaced by the two cores ~30cm apart taken from the Raapenberg Wetland.

Element	PW1 (ppb)	PW2 (ppb)	mean	st dev
Cr	9.74	8.98	9.36	0.540
Mn	609.0	689.0	649.0	56.50
Fe	18999	17879	18439	792
Ni	75.4	121.0	98.19	32.19
Co	8.17	8.61	8.39	0.312
Cu	21.44	25.66	23.55	2.98
Zn	111.4	153.6	132.5	29.90
As	18.17	18.85	18.51	0.485
Se	17.94	18.77	18.36	0.590
Mo	2.64	2.77	2.71	0.093
Ag	0.06	0.05	0.05	0.009
Cd	0.11	0.15	0.13	0.024
Hg	0.43	0.33	0.38	0.069
Tl	0.06	0.07	0.07	0.009
Pb	64.26	68.68	66.47	3.12

PW1 is from the core used for the sequential reaction and PW2 is from the core taken for sediment description. PW1 and PW2 had pH values of 6.56, 6.45 and Electrical Conductivity (EC) values of 4.25 mS/cm, 4.34 mS/cm, respectively (at 20°C). Analytical error and sampling heterogeneity for pore-water samples can be found in **Appendix 5**.

4. Discussion of Results

4.1 Pollution Levels for Various Elements

4.1.1 River Sediment

For the river sediment, a separate aliquot of each sediment sample was subjected to a whole digestion procedure to evaluate the total metal concentration of the sediment. This aliquot of sediment was subjected to much lower losses of sediment due to the whole digestion procedure applied to it, than the aliquot subjected to the sequential extraction procedure. Therefore, for the river sediment where whole digestion data are available, these data will be used for comparison to the Government guidelines (**Table 9**) and critical limits, rather than the sum of the concentrations from the five fractions of the sequential extraction procedure. Error on data is reported at the 95% confidence limit, in percent precision (%P), calculated from duplicate samples. The %P value calculated from the sand-rich duplicate samples will be applied to other sandy samples, the %P value from the silty, moderately organic rich duplicate samples will be applied to similar samples, and the %P from the highly organic rich duplicate samples will be applied to similar samples. In this way, the highly variable river sediment sample characteristics are accounted for, which is important since clay and humus rich samples tend to accumulate more trace metals and sometimes have different critical limits (USEPA website). In the case of guideline comparisons for river sediment, using whole digested sediment data, the %P is for the digestion procedure and the analytical process combined, and excludes sample heterogeneity.

Table 12: 1999 South African Bureau of Standards (SABS) Maximum Permissible Metal (MPM) and Inorganic Content in Soil (due to phyto- and zoo-toxicity effects).

Element	Maximum Permissible Metal and Inorganic Content in Soil (mg/kg or ppm)
Cadmium, Cd	2
Cobalt, Co	20
Chromium, Cr	80
Copper, Cu	100
Mercury, Hg	0.5
Molybdenum, Mo	2.3
Nickel, Ni	15
Lead, Pb	56
Zinc, Zn	185
Arsenic, As	2
Selenium, Se	2

Zinc (Zn)

Zinc is a particularly serious problem in the Black River study area probably due to its association with sewage sludge from the two sewage treatment facilities discharging into the Black River. This association is mainly due to household products such as shampoo, sunblock, creams etc. (ATSDR Report, 2002). Sediment at locations 1, 2, 6 and 8 on the map were sandy in nature and concentrations of most heavy metals were lower than for the silty samples. However, Zn at 217 ppm (P=1.1%) at location 1 (**Fig. 19**) exceeds the SABS maximum permissible metal (MPM) in soil of 185 ppm and all European country critical limits, up to 200 ppm (USEPA website). The silty samples including the Liesbeeck sediment far exceed the MPM for Zn (**Table 12**), with the highest at 618 ppm (P=5.8%) at location 3, up to three times the SA and some European limits (USEPA website).

Lead (Pb)

The anthropogenic Pb present could possibly be sourced from household water, due to old Pb pipes or from waste not properly disposed of, however, a much more likely and dominant source is probably atmospheric deposition from automobile exhaust emissions (ATSDR Report, 2002). All sand samples (2, 6, 8) show low values below the SABS MPM limit, except for location 1 at the mouth of the Elsieskraal River (**Fig. 17**), which contains ~106 ppm Pb (P=10.2%). The Pb in the silty samples far exceeds the SABS MPM limit of ~56 ppm (**Table 12**), with the Raapenberg Bridge sample at ~276 ppm (P=8.1%), second only to the Liesbeeck River at ~381 ppm (P=8.1%).

Chromium (Cr) and Nickel (Ni)

Cr, also potentially sourced from the brake emissions of automobiles, and Ni, have values lower than the SABS MPM limit in sand sediment samples. The silty samples have values of Cr lower than the SABS limits with the most elevated values at location 3 and 4 (**Fig. 21**). Ni content in sediment exceeds the SABS MPM content of 15 ppm at location 3 with ~31 ppm (P=5.4%) and at location 4 with ~20 ppm (P=5.4%) (**Table 1**).

Copper (Cu)

The Cu in all samples is less than the SABS MPM content, but is high at location 3 with ~95 ppm (P=7%), ~72 ppm (P=7%) in the Liesbeeck River, and ~58 ppm (P=7%) at location 4 (**Fig. 23**). These 3 locations exceed the critical limits for most European countries (USEPA website).

Mercury (Hg), Cadmium (Cd) and Arsenic (As)

Hg concentrations in most samples slightly exceed the 1999 SABS MPM content of 0.5 ppm, with a high at location 1 of 1.1 ppm (no error estimate available), 0.88±0.38 ppm (or P=86.4%) at location 3, and relatively lower values in the two most upstream samples at locations 8 and 6, but where no error estimates are available (**Fig. 26**). The wetland sample also has a lower concentration with 0.15±0.054 ppm (or P=70.0%).

Cd concentrations are lower than the SABS MPM contents but approach about half the limit at location 3 with 1.26±0.11 ppm (or P=17.5%) and at location 4 with 1.04 ppm (P=17.5%).

Arsenic exceeds the SABS MPM content of 2 ppm (**Table 12**) for most locations except the upstream sandy samples (**Fig. 25**). The highest values found are location 3 with 10.5 ppm (P=69.4%), location 4 with 9.8 ppm (P=69.4%), the Liesbeeck River with the highest 15.7 ppm (P=69.4%), and the wetland sample with 12.9 ppm (P=1.4%).

4.1.2 Wetland Core Samples

The top 1cm of the core that was sequentially extracted, was predominantly root-mass and contained very little sediment (**Appendix 1**), other than some mud adhering to the roots. In this top 1 cm, Arsenic and Cu were at their maximum total concentrations (sum of the five fractions), and so were the Ca and Fe concentrations (**Table 2**). For most elements the concentration was highest in the top 10cm of the core. In this top root zone, where the organic carbon content is also substantial (**Fig. 15**), the peak concentrations often exceed the SABS MPM contents (**Table 12**), and/or some European critical limits (USEPA website). Pb, Zn, Cr, Ni, Cu, As, Mo, Se (up to 448 ppm, 632 ppm, 275 ppm, 96.8 ppm, 158 ppm, 30.2 ppm, 8.93 ppm, 4.78 ppm respectively, for five fractions added) exceeds the SABS (1999) limits. Error estimates for each fraction are available in **Appendix 2**. Hg (up to 5.00 ppm, **Table 2**) also exceeds the SABS limits however, the error on the Hg results, which are discussed elsewhere in detail, prevents major conclusions to be drawn from this, and further work is required here. While Cd does not exceed the SABS limit of 2 ppm, it does approach them at certain depths (up to 1.75 ppm), and exceeds most European critical limits (USEPA website).

4.2 The Extraction Procedure: Reagent Selectivity, Fraction Definition and Metal Recovery Efficiency

The method of Tessier et al. (1979) was selected for this study, and is one of the most thoroughly researched and widely used sequential extraction methods to evaluate the possible chemical associations of metals in sediment (Xiangdong Li et al., 2001). The Tessier et al. (1979) method was used on oxic to suboxic salt marsh sediment (Mortimer and Rae, 2000), on organic rich clayey-silt estuary sediment (Jones and Turki, 1997), and on estuary sediment cores (Xiangdong Li et al., 2001). The application of this study to the sub-oxic wetland core is very similar to these previous studies. The basis of leaching of certain metals is that a particular reagent is phase specific, however, it is common for studies to point out that the various extractants used are not as selective as expected (Kersten and Forstner, 1991).

In the first stage of extraction, or exchangeable fraction the exchangeable metals are released from ion exchange adsorption sites. While the 1M NaOAc (pH 8.2) has been shown to release a lesser amount of the exchangeable fraction of metals compared to the 1M $MgCl_2$ (Tessier et al., 1979), the NaOAc reagent was chosen.

The second stage of the extraction dissolves Ca and Mg carbonate or $CaMg(CO_3)_2$ and also possibly specifically adsorbed trace metals due to the strong pH dependence of desorption of metals off the solid substrate (Tessier et al., 1979). This fraction would represent the acid soluble fraction of metals in the sediment. Divalent salts such as ferrous and manganese carbonates may also dissolve (Tessier et al., 1979).

The largest concentration of Ca was released in the extraction step that was intended to dissolve the carbonates (**Fig. 12**). In comparison, the concentration of Ca released in subsequent steps was far lower, indicating that most, if not all of the carbonate was dissolved. Only in the Liesbeeck sediment sample, did the Ca in the exchangeable fraction exceed that in the carbonate fraction, but the Liesbeeck sample diverges in many other ways, and the sediment is sourced in a different area (Table Mountain Group sandstones), so differences are expected. In the wetland core samples, the largest portion of Ca was released in the exchangeable fraction of the sediment (**Table 2**), and not the carbonate fraction. It is assumed that most of the Ca is associated with exchangeable sites, since the original calibration of this method indicated only 2-3% dissolution of carbonates in the first step (Tessier et al., 1979).

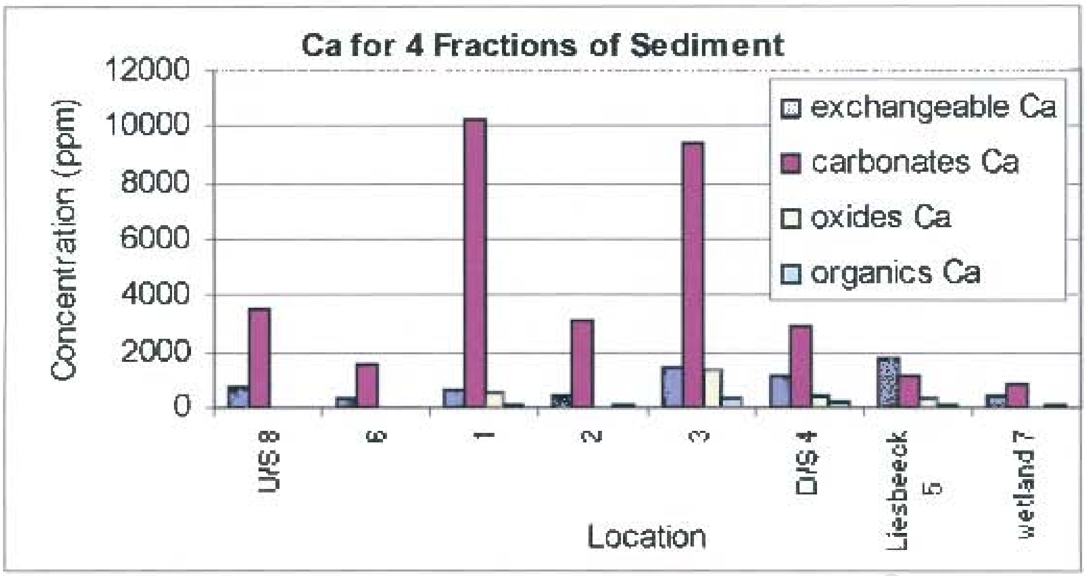

Figure 12: Ca in four fractions of sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5.

The third stage is to dissolve the reducible Fe/Mn oxides in the sediment, with the Mn oxides more easily leached than the Fe oxides, and the organic carbon content of the samples were shown to be undiminished (Tessier et al., 1979). Rapin et al. (1986) showed that under a N_2 atmosphere the acid volatile sulphide, or amorphous sulphide concentrations were maintained (87 – 100%) in the first two extractions, but that it decreased to ≤5% of the initial concentrations after the third extraction phase. So, the stage meant to dissolve the Fe/Mn oxides, also releases the metals associated with the AVS in the sediment (Rapin et al., 1986). This means that for anoxic sediment such as the river sediment, where presumably H_2S or CH_4 bubbles were observed exiting on sampling, that the third extractions stage actually represents the metals associated with the AVS or Fe-monosulphides (FeS). The possible liberation of metals from labile organic complexes could also not be excluded (Tessier et al., 1979). Fe was released predominantly in the third extraction step **(Fig. 13)**. The appreciable amount of Fe in the carbonate fraction was previously explained by the dissolution of divalent salts e.g. $FeCO_3$ (Tessier et al., 1979). The large amounts of Fe associated with the fourth, organic fraction for location 4, could reflect an association with the organic fraction or pyrite (FeS_2), since the original method determined that increasing the leaching time, did not affect the Fe concentration in the leachates (Tessier et al., 1979). However, while all other samples showed that most Fe was liberated in the third extraction step, and the sediments are all comprised of similar minerals (**Table 9**), location 4 has the largest coarse faction >2 mm (**Table 8**), so it is possible that not all the AVS and oxide had dissolved completely in the third extraction step.

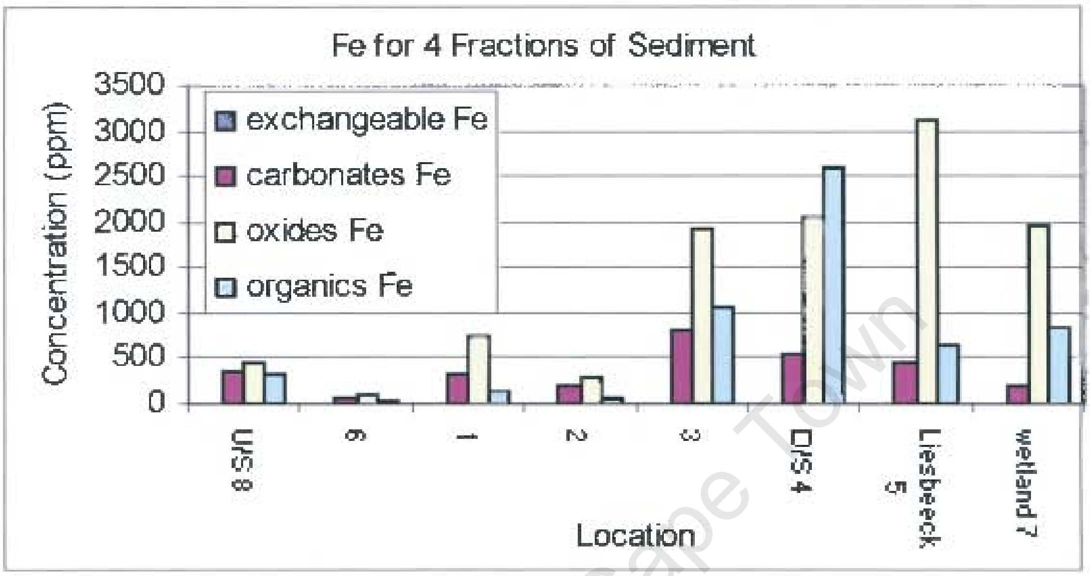

Figure 13: Fe in four fractions of sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5.

The fourth stage attacks all oxidisable phases such as organic matter and well-crystallised sulphide phases e.g. pyrite, but the oxidation of organic matter is incomplete, while only a slight attack on the silicate residual phase occurred with this treatment (Tessier et al., 1979). The choice of H_2O_2 represents a compromise between complete oxidation and alteration of silicate material (Tessier et al., 1979). The procedure applied to the certified reference material SL-1, indicates a good recovery for some of the certified metals evaluated in this study. The sum of metals recovered in five fractions agreed to within the 95% confidence limit, or very close to it (**Table 13**).

Table 13: Certified Values for Metals in Reference Material, SL-1 from the International Atomic Energy Agency (1979) *vs* the Sum of Five fractions from Sequentially Reacted Reference Material, SL-1, in this study.

Element	Accepted Values (ppm)	Degree of Confidence for accepted value	Sum of Five Fractions (ppm)
Cr	104 ± 9	R	96
Zn	223 ± 10	H	248
Ni	44.9 ± 8	R	53.1
Cu	30.0 ± 5	R	29.6
Co	19.8 ± 1.5	H	17.5
Pb	37.7 ± 7.4	R	33.5
As	27.5 ± 2.9	H	38.3
Cd	0.26 ± 0.05	R	0.18
Hg	0.13	Value not certified.	1.52
Mo	1.3	Value not certified.	0.15
Se	2.9	Value not certified.	1.03

H is a certified value with a high degree of confidence. R is a certified value with a reasonable degree of confidence. All certified values are shown with the 95% confidence limits.

The sum of recovered concentrations for five fractions of the sequential extraction procedure were within the 95% confidence limit of the certified values for Cr, Cu and Pb, slight differences for Zn (6.41%), Co (-4.26%), Ni (0.40%), and larger differences for As (26.05%), Cd (-14.29%). Hg, Mo and Se values are not certified and show phenomenal differences of 1069%, -88.51% and –64.45% respectively (**Table 13**). Positive differences represent an over-estimation of the concentration, while negative differences represent an under-estimation. The relatively good recovery verifies the overall accuracy of the sequential extraction procedure.

4.3 Metal behaviour: Stability and Mobility

4.3.1 Spatial Metal Distribution

The Raapenberg Bridge area, and Black River Parkway bridge area (locations 3 and 4 respectively) have the among the highest concentrations of Pb, Zn, Ni, Cu and As and the Liesbeeck River (location 5) with regard to Pb, As and Zn. These areas have an accumulation of silt and organic matter, indicating slower flow and lower gradient, hence more deposition of fine material, than further upstream. There is a good correlation between the silt content (**Table 8**) and organic matter (OM) percentage (**Fig. 14**) in the six Black River sediment samples (**Fig. 15**). Generally the deposition of more clay with its high surface area entails the deposition of both more organic matter and trace metals (Muller, 2002). The OM probably originates in part, from the sewage particles settling at these depositional locations, thereby increasing the nutrient load, i.e. nitrates, phosphates etc. that enhances plant and algal growth.

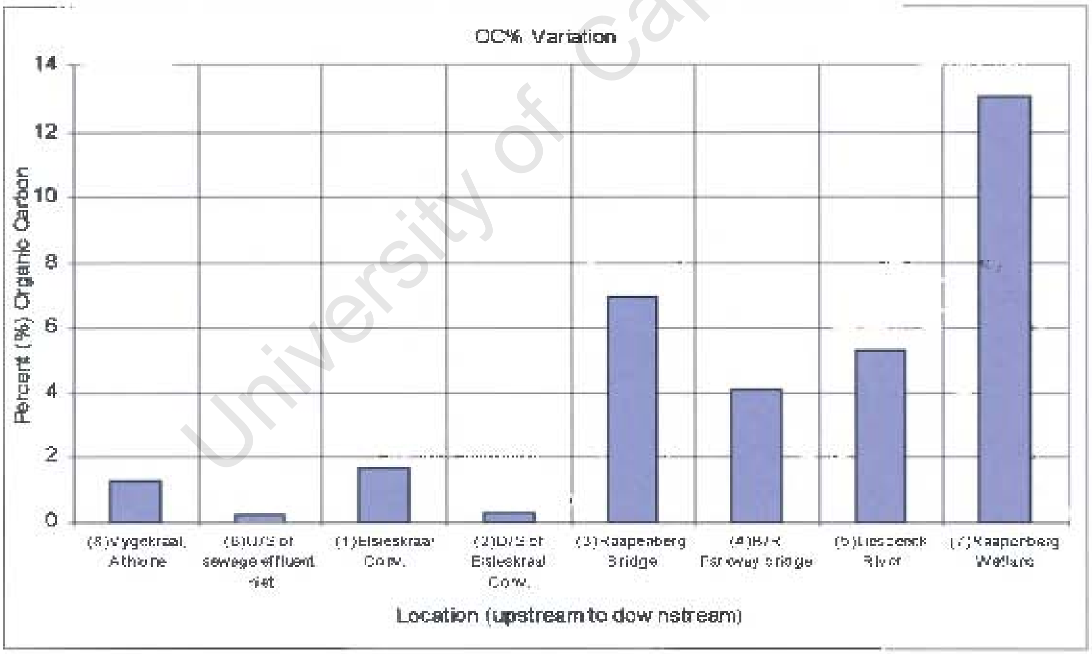

Figure 14: Organic carbon weight percent in river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. One triplicate and two duplicate samples gave one standard deviation from the mean of 7.0% ±0.35%, 13.0% ±1.1%, respectively.

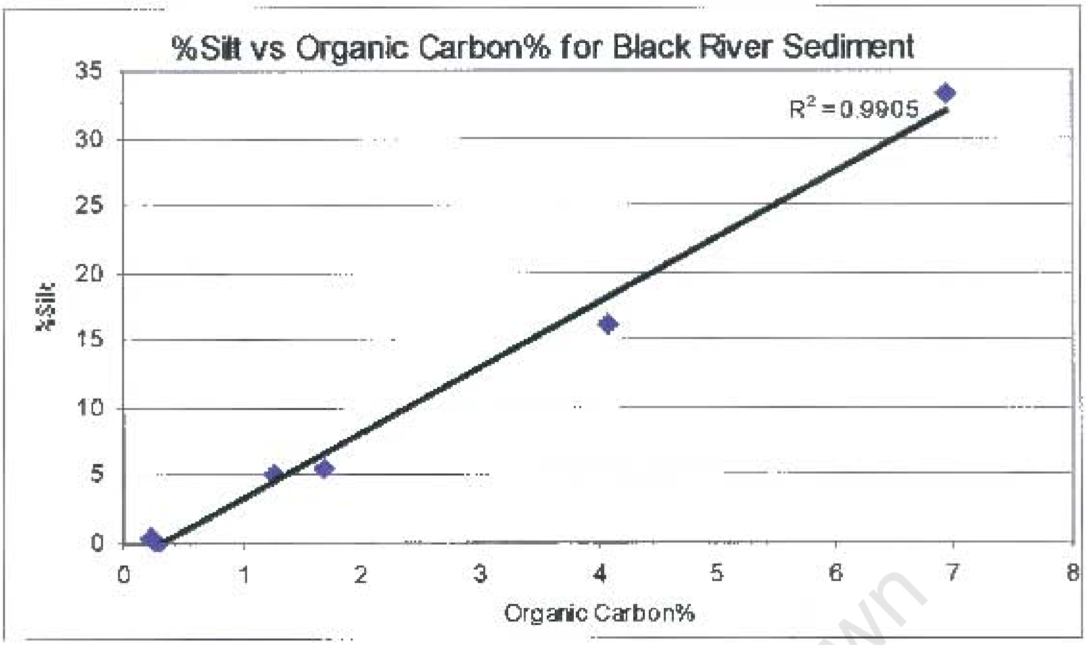

Fig. 15: Correlation between Silt Content and Organic Matter for 6 Black River sediment samples. Correlation coefficient = R^2.

Unfortunately, locations 3 and 4 which are associated with silt deposition and the resultant elevated trace metal concentrations are the same locations where dredging of sediment occurs, by the local Municipality in order to keep the water flow efficient. Location 1, at the mouth of the Elsieskraal River also shows some elevated concentrations for trace metals evaluated, even though it is sandy in nature.

Concentrations of all selected trace elements in the core decreases with depth, since the more recent, shallower sediment, probably reflects a recent increase in industrial activity and anthropogenic input, as has been shown in studies where sediments have been dated (Silva and Rezende, 2002; Bothner et al., 2002). Atmospheric deposition, in part from exhaust fumes from recently built (1930's - 1960's) highways alongside the Raapenberg wetland, and increased urbanisation and population, must certainly have contributed to this trace metal accumulation. This is consistent with findings at other locations, for example, the enrichment of Pb, Zn and Cu in the top 15 cm of the Pearl River Estuary, China, with metals maintaining fairly constant concentrations below 35 cm depth, and these were taken to reflect background concentrations (Xiangdong Li et al., 2001). Another influence on the distribution of heavy metals is the grain size variations with depth or location. The greatest concentration of heavy metals have been found in the intervals of finer sediments, attributed to the greater surface area of the smaller particles (Silva and Rezende, 2001). This may justify further work to greater depth to include the deeper mud layers in the wetland core **(Appendix 1)**.

Elements such as Cd and Zn which are rated as medium and high mobility metals, respectively, in acidic, oxidising environments, and Hg which has a dominant soluble species, $Hg(OH)_2^0$, above a pH of 4 (MacBride, 1994), tend to have moved lower in the depth profile of the Raapenberg Wetland core with peak concentrations at 7 - 9 cm. Elements such as Cu, Cr and Pb which are very tightly bound to organic matter, and are considered quite immobile in this form (MacBride, 1994), have peak concentrations at 1-3 cm, much shallower in the depth profile. This correlates with the top-most organic rich layer in the core **(Fig. 16)**.

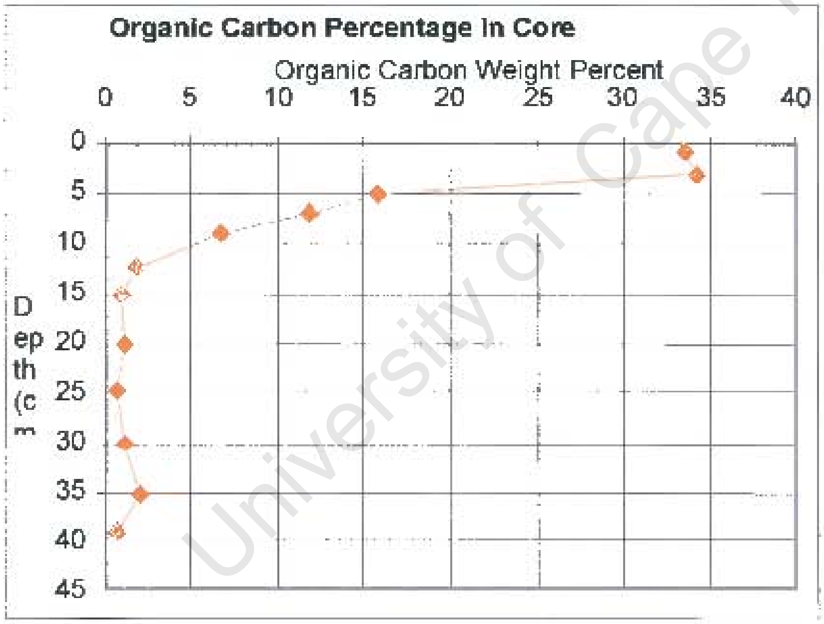

Figure 16: Organic carbon percent in wetland sediment from core sample. Three duplicate samples gave 1 standard deviation from the mean of 33.5% ±4.9%, 15.9% ±2.7% and 0.88% ±0.65%.

4.3.2 Controlling Processes on Solubility and Bio-availability

Each trace metal is bound to dominantly one or two phases of the sediment depending on its basic chemistry. In order to become mobile, it will have to begin with desorption or dissolution followed by diffusion and advection away from the area of maximum concentration, and may undergo re-adsorption or precipitation which can then immobilise the element (MacBride, 1994). These processes are influenced by pH and redox conditions (MacBride, 1994), which will probably change seasonally with rains and subsequent water-logging of the wetland. Discharges into the river altering the pH of the water column may also influence mobility of metals. Dredging of the Black River will probably be accompanied by a decrease in pH as the sulphides oxidise in the dredged piles of sediment:

$$FeS_2 + 7.5\ O_2 + H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+ \qquad (1)$$

(Stephens et al., 2001).

Acidification in an environment by any mechanism, possibly by equation (1), may make metals available by the dissolution of an oxide phase that may host trace metals:

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \qquad (2)$$

(MacBride, 1994).

Acidification in the environment may also cause the dissolution of carbonate minerals, which are buffering reactions:

$$H^+ + CaCO_3 \rightarrow HCO_3^- + Ca^{2+} \qquad (3)$$

(MacBride, 1994).

This reaction may also release trace metals that have co-precipitated with the dissolving mineral phase, in this case, carbonate or that have adsorbed to the phase, similar to the Fe-sulphide and gibbsite ($Al(OH)_3$) dissolution reactions in equations (1) and (2), respectively.

Redox Reactions in Sediment:

Redox stratification occurs in sediment with depth due to the sequential utilisation of terminal electron acceptors in the microbial degradation of organic matter (Koretsky et al., 2000). The organic matter decays progressively, and decreases in content with increasing depth (**Fig. 16**). Microbial activity changes from aerobic to anaerobic when the dissolved oxygen diminishes to trace levels (about 10^{-6} M) (MacBride, 1994), which occurs with depth as it becomes more difficult for oxygen to diffuse into the sediment. The sequential depletion of electron acceptors with depth is accompanied by the build-up of reduced inorganic by-products, and the depletion occurs in the order:

(a) O_2 (aerobic) respiration of organic matter,

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{4}$$

(b) Mn^{4+} respiration to form Mn^{2+} in the suboxic zone,

$$2MnO_2 + CH_2O + 3H^+ \rightarrow 2Mn^{2+} + HCO_3^- + 2H_2O \tag{5}$$

(c) Fe^{3+} respiration to form Fe^{2+} in the suboxic zone,

$$4FeOOH + CH_2O + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 6H_2O \tag{6}$$

(d) Sulphate reduction to form H_2S (sulphide) in the sulphidic zone,

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^- \tag{7}$$

(e) Methanogenesis in the methanogenic zone (Koretsky, 2000).

$$2CH_2O \rightarrow CH_4 + CO_2 \tag{8}$$

(all species are aqueous except for mineral phases which are solids)

Most reduction reactions consume H^+ ions, causing a rise in the pH towards 7 (MacBride, 1994). Step (a) occurs in the oxic zone of the soil, and metals bound to organic matter are potentially available by this reaction. Steps (b) and (c) can occur during early diagenesis, releasing soluble Fe^{2+} and Mn^{2+} species and metals associated with the oxide phases to porewaters, and possibly the overlying water column (Jones and Turki, 1997). With the onset of sulphate reduction, probably within a few centimetres of the sediment-water interface of a river or lake sediment, any remaining Fe^{3+} and Mn^{4+} species will be rapidly converted to monosulphides and eventually pyrite (Jones and Turki, 1997). When aqueous sulphide reacts with aqueous iron (or directly with oxyhydroxides such as goethite and gibbsite) to form solid FeS (monosulphides), any trace metals that are released by these processes may complex strong ligands (e.g. organic matter), coprecipitate with Fe-sulphides, or adsorb to the surface of existing pyrite and AVS minerals (Cooper and Morse, 1998).

Temporary bio-availability of metals released from the dissolution of oxyhydroxides may occur after the start of oxyhydroxide dissolution but before the onset of sulphate reduction. Certain fractions or phases in the sediment may also be available to different organisms in the environment. For example, previous studies have shown that trace metal levels in benthic organisms correlate better with the trace metal concentration in sediments when normalised to the Fe- hydrous oxide and/or organic content of the sediments (Tessier and Campbell, 1986).

High concentrations of dissolved Fe and Mn in porewaters sampled from the cores taken from the Raapenberg wetland (**Table 11**), confirms reduction of Fe and Mn oxides in the Raapenberg sediments, and demonstrates the potential for diagenetic mobilisation of oxide bound metals. A similar conclusion from high dissolved Mn concentrations in Tees Estuary water, was reached by Jones and Turki, (1997). In an anaerobic environment continued sulphate reduction will result in a sulphide dominated environment, where higher concentrations of aqueous sulphide inhibit metal-ligand formation, favour the formation of metal-sulphide minerals, and allow rapid pyrite formation to sequester trace metals within pyrite via the reaction of FeS with aqueous H_2S (Cooper and Morse, 1998). When sulphidisation of Fe minerals is complete, pyrite will be the dominant host for metals, and as long as conditions remain reducing, these metals will be unavailable for reaction or uptake by biota (Jones and Turki, 1997). Key factors in predicting the trace metal reactivity in an aquatic environment are the potential for sulphide minerals to trap free metals and the potential for the sulphide minerals to be destroyed via oxidative dissolution (equation (1)) at a later date (Cooper and Morse, 1998).

Metals associated with the OM in the oxic zone will be progressively released as a result of microbial oxidation of the organic substrate. With increasing depth, these organic-associated metals will be progressively released due to further degradation of organic matter. Also, sulphide ions (S^{2-}) in aqueous solution have been known to assist the dismutation of certain organometallic compounds:

$$2(CH_3)M+ + S^{2-} \rightarrow [(CH_3)_4M + (CH_3)_2MS \quad (M = Sn, Pb) \qquad (9)$$

(Harrison and de Mora, 1996).

With diagenesis and the onset of reducing conditions some of the metals released from OM microbial degradation, will probably be fixed as pyrite, but if the sediment is agitated and mixed with oxygenated water, oxidative degradation of organic matter (Jones and Turki, 1997) and dissolution of the solid sulphide minerals could potentially mobilise all metals associated with these phases. A leachability study by Stephen et al. (2001) on dredged sediment, showed the redistribution of metals from various phases during drying and oxidation. They found significant metal loads in run-off and percolating water. Sulphides are only sparingly soluble in water (MacBride, 1994) but dredging of river sediment and subsequent oxidation of sulphides will change the sulphide/sulphate ratio (Stephen et al., 2001), changing the solubility.

Of course, the precipitation of oxides could scavenge some of the metals released (Rapin et al., 1986). Tessier et al., (1979) illustrated the strong scavenging efficiency of Fe-Mn oxides for trace metals in oxic sediment. This would especially be the case if the metals are strongly sorbing metals, or hard Lewis acids that bond well with the O^{2-} ligand. In the wetland core samples (**Table 10**), the main mineral phases are the Fe-oxide, goethite and gibbsite (instead of sulphide) because the core was under sub-oxic conditions at the time of sampling. There is probably also amorphous Mn –oxide present since the parent material is quite rich in Mn (Soil Report, 2002, N. Haniff).

4.4 Metal Partitioning

4.4.1 Lead (Pb)

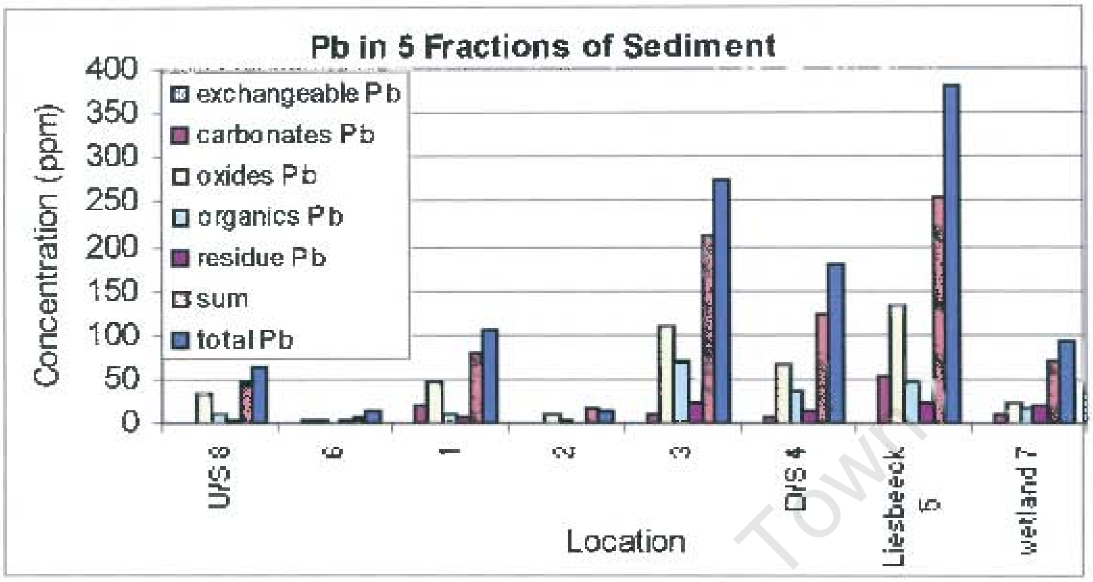

Figure 17: Pb concentration in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

One of the highest concentration metals in this study, Pb, a chalcophile is predominantly associated with the AVS or oxide fraction in the anoxic river sediment, and to a slightly lesser extent the organic fraction, with the exception of the Liesbeeck sample, which has the carbonate fraction as the second most dominant (**Fig. 17**). A dominant association with the Fe-Mn oxide (or AVS) fraction was also found in the Tees Estuary, north-east England (Jones and Turki, 1997) and western sediments in the Pearl River Estuary, China (Xiangdong Li, 2001). Pb in nature predominantly exists as the Pb^{2+} ion (MacBride, 1994), which is a borderline soft Lewis acid (Shriver and Atkins, 1999). This means that it would form more complexes where covalent bonding is important (Shriver and Atkins, 1999) with soft bases such as the S^{2-} sulphide, and R^- organic ligands, rendering it fairly immobile in nature, and Pb is immobile even under oxic conditions if the pH is raised (MacBride, 1994). Transport processes and acidic solutions could still leach trace metals during oxidation. This implies that the Pb locked in the AVS fraction of in situ river sediment should not be considered a biohazard, unless disturbed e.g. by dredging, changing pH of overlying waters.

The borderline soft metal, Pb (Shriver and Atkins, 1999), will most easily bond with organic ligands and other borderline ligands, then the soft ligands, and then with hard ligands to some extent e.g. O^{2-}. So, it is possible that when the sulphide and organics have scavenged as much Pb that they can (in this case up to 108 ppm and 71ppm in the Black River, respectively), being the preferred phases, the remainder binds with the harder ligands such as the carbonate (CO_3^{2-}) ion (8 ppm in the same Black River sample). The carbonate fraction may then become particularly loaded where the metal concentrations are exceptionally high, as in the Liesbeeck sediment sample (**Fig. 17**). This will mean that where concentrations are higher, a larger portion of the metal reserve is likely to be more easily bio-available e.g. a larger portion will be found in the easily acid-leachable carbonate fraction.

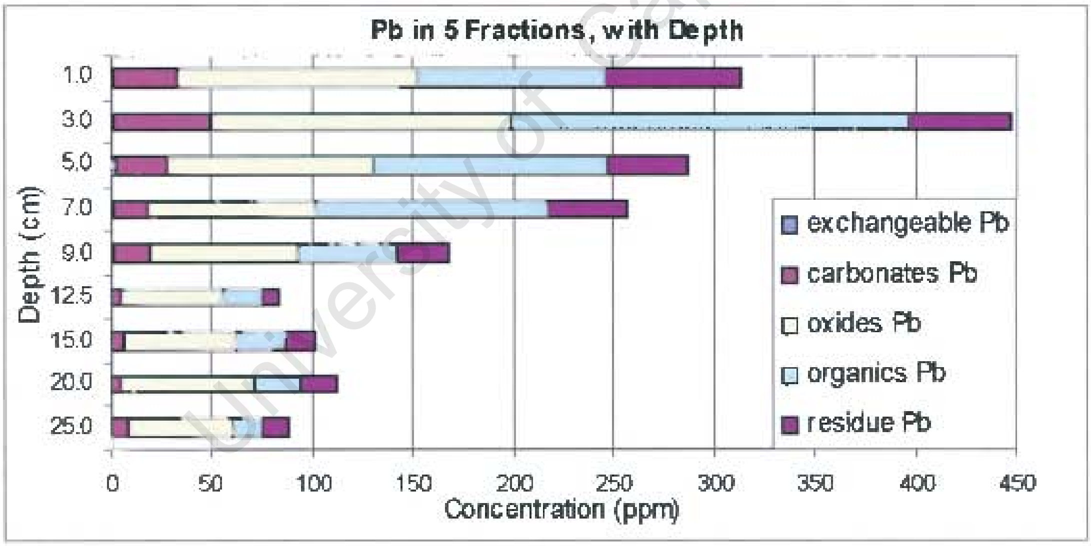

Figure 18: Pb concentrations in five fractions of Raapenberg wetland sediment. Samples are in order of depth in the core and concentrations are for dry weight of sample. The depth axis is not to scale and the label represents the base of the unit.

In the top 7 cm of the 25 cm of the sub-oxic wetland core samples, the dominant fraction with regard to Pb is the organics fraction, while with increasing depth, the dominant fraction becomes the oxide (reducible) fraction (**Fig. 18**). Xiangdong Li, (2001) found from Pb isotope results in the Pearl River Estuary (China), that the most of the anthropogenic Pb may be accumulated by Fe-Mn oxides and organic matter. Pb^{2+} undergoes strong complexation with organic matter and tends to bioaccumulate in this layer (here, up to 448 ppm Pb), but generally this type of Pb accumulation has shown very little leaching over many years and appears to be unavailable to plant tops (MacBride, 1994). The concentration of Pb also decreases with depth in the older sediment, as does the organic carbon content (**Fig. 16**). As OM decays, Pb (and other trace metals released), may then becomes hosted by the Fe/Mn oxides to some extent and some potentially released. With burial and possible flooding of the wetland, the Pb is likely to form PbS, which is very insoluble in reduced soils (MacBride, 1994).

If the top 1cm of root-rich sediment is excluded, then the top 1cm of the most recent sediment, just below the root-mass, contains up to ~50 ppm (P=22.6%) acid-leachable Pb (**Fig. 18**). This is substantial considering that even rainwater is potentially sufficiently acidic to leach this during the rainy season, on equilibration with this sediment. This fraction of Pb is of concern since it is the most easily bio-available.

4.4.2 Zinc (Zn)

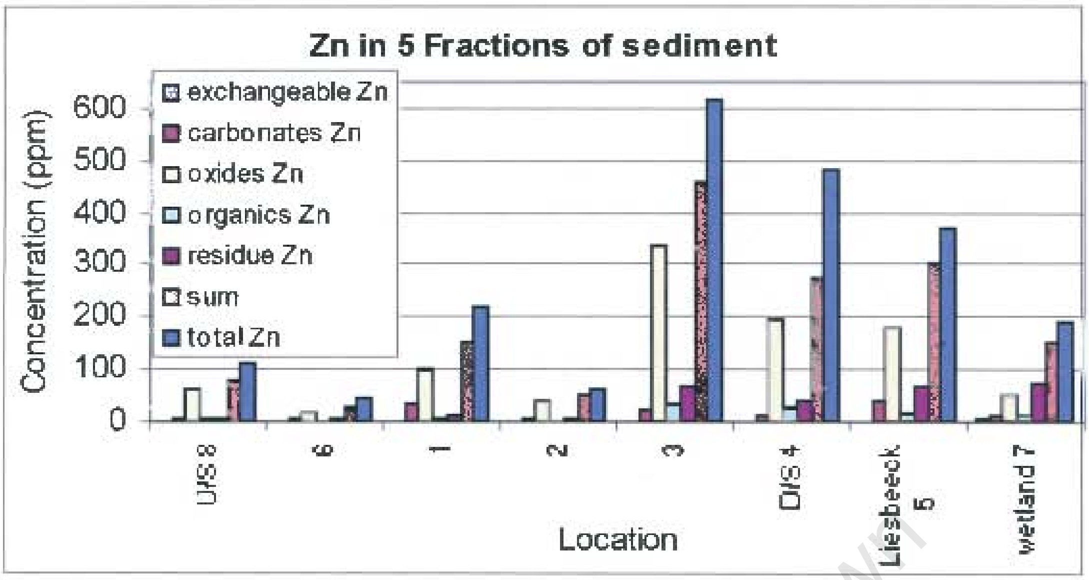

Figure 19: Zn in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

Zn, a borderline hard metal and chalcophile, is predominantly associated with the AVS and Fe/Mn oxide fractions, respectively, in both the river (up to 336 ppm) and wetland (up to 345 ppm) sediments **(Figures 19 and 20)**. In the river sediment another dominant fraction is the residual fraction. The wetland core samples also show that a substantial portion of the Zn partitions into the carbonate fraction (up to ~72 ppm), even more so than into the organic fraction. Zn tends to form oxides, hydroxides, hydroxycarbonates at pH 6 or higher where there are high levels of Zn in the soil (MacBride, 1994). And, the borderline hard acid will prefer bonding, based on the ion charge ratio, to hard or borderline ligands, such as OH^-, O_2^-, CO_3^{2-} (Shriver and Atkins, 1999), unlike the soft organic ligand R^-.

Zn, being a chalcophile is probably associated with the extremely insoluble ZnS (MacBride, 1994) in the anoxic river samples. As is the case with Pb, on oxidation of dredged material, the Zn may be available while the sulphides dissolve to re-precipitate as oxides. In acidic environments, Zn^{2+} is one of the most soluble and most mobile of the trace metal cations (MacBride, 1994), as may be the case in the dredged piles of sediment from the Black River.

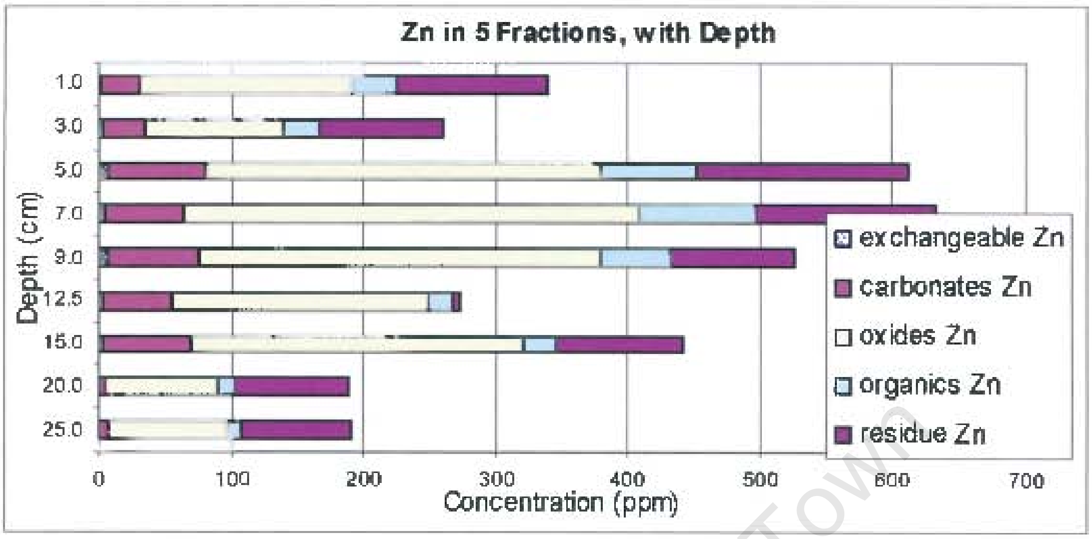

Figure 20: Zn concentrations in five fractions of Raapenberg wetland sediment. Samples are in order of depth in the core and concentrations are for dry weight of sample. The depth axis is not to scale and the label represents the base of the unit.

On flooding the wetland in the rainy season, the release of Zn from dissolving Fe/Mn oxides may initially increase availability, but be ultimately restricted by the formation of ZnS (MacBride, 1994). Neutral pH, such as the currently exists at the wetland, is essential to reduce the mobility of Zn (MacBride, 1994). For metal cations such as Zn^{2+} and Cd^{2+} however, there is less tendency to form soluble organic complexes such as Cu^{2+} and Fe^{3+}, and so conditions promoting adsorption and precipitation such as increasing pH tends to reduce availability (MacBride, 1994). Only in alkaline environments, similar to Pb, Zn-organic complexes become soluble or the formation of Zn-hydroxy anions can increase mobility.

4.4.3 Chromium (Cr)

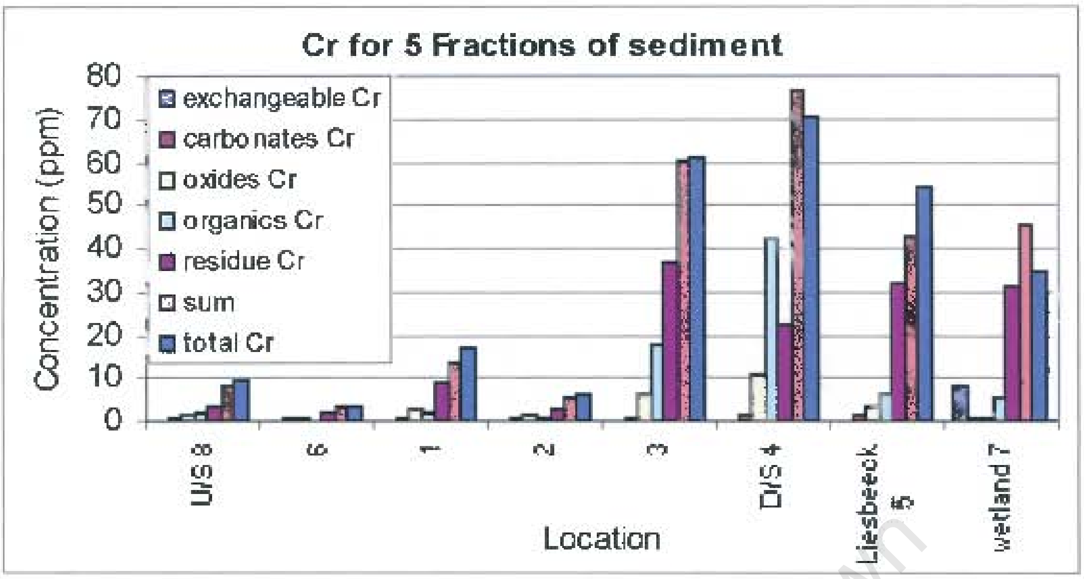

Figure 21: Cr in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

For most river sediment samples, the most dominant phase for Cr is the residual fraction, which is the least available fraction of the sediment **(Fig. 21)**. At only two locations, with the highest Cr contents (the Raapenberg and Black River Parkway bridges, locations 3 and 4 respectively) does a significant portion of Cr associate with the organic fraction. Cr is usually present as the very immobile Cr^{3+} form in soils and complexes very strongly with organic matter (MacBride, 1994). In the wetland samples most of the Cr is associated with the organic fraction **(Fig. 22)**, with the highest concentration in the topmost layer of soil, below the root-mass. As this decays, the Cr would probably chemisorb on Fe-oxides and clays in the soil, as is the strong tendency for Cr^{3+} (MacBride, 1994). At high pH, Cr substitutes for Fe in the mineral structure and precipitates as $Cr(OH)_3$, and is very immobile and unavailable to plants (MacBride, 1994). Only at very high pH could the Cr become oxidised to CrO_4^{2-}, a very toxic form of Cr, which is promoted by Mn-oxides (MacBride, 1994). This should probably be investigated considering the high Cr content (~201ppm) in the wetland top-soil.

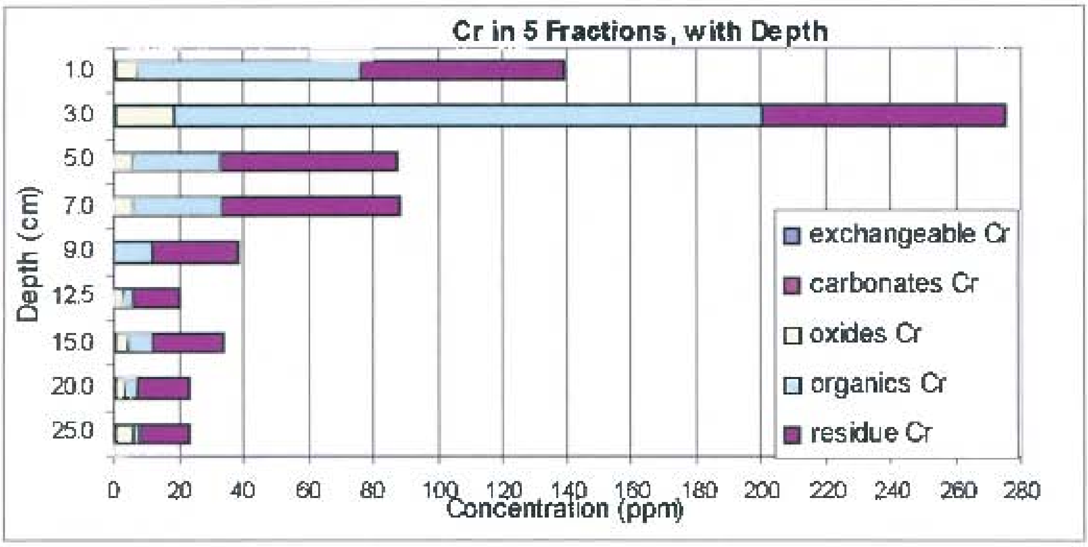

Figure 22: Cr concentrations in four fractions of Raapenberg wetland sediment. Samples are in order of depth in the core and concentrations are for dry weight of sample. The depth axis is not to scale and the label represents the base of the unit.

4.4.4 Copper (Cu)

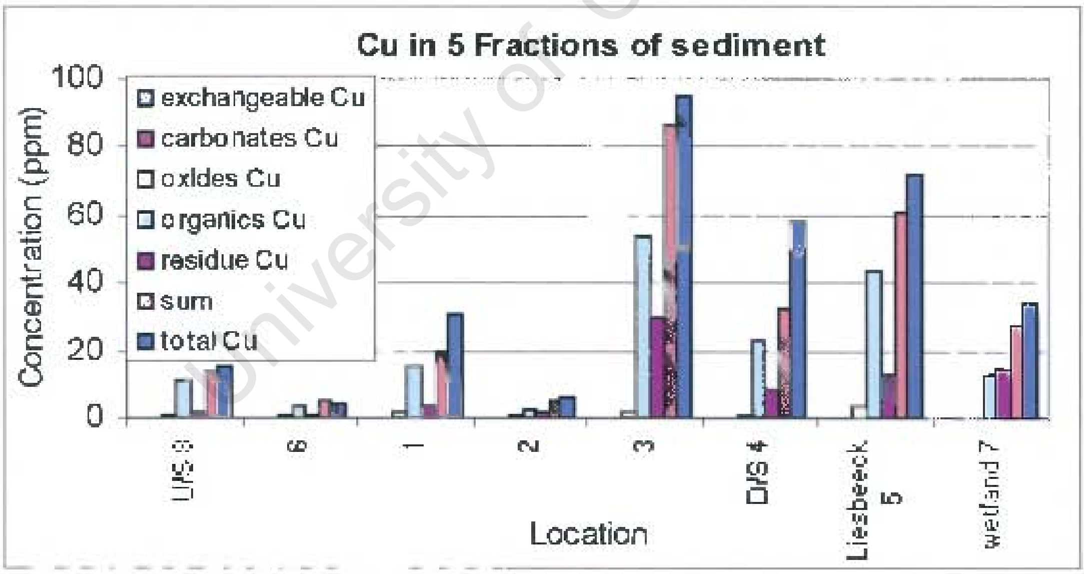

Figure 23: Cu in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

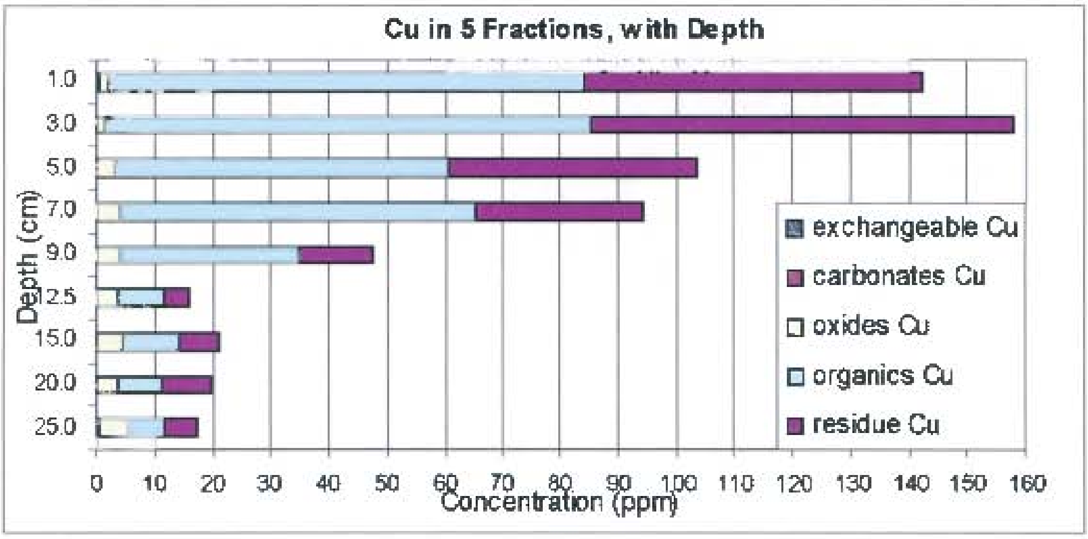

Figure 24: Cu concentrations in five fractions of Raapenberg wetland sediment. Samples are in order of depth in the core and concentrations are for dry weight of sample. The depth axis is not to scale and the label represents the base of the unit.

In both the wetland core samples and the river sediment the organic fraction is by far the dominant host of Cu (up to 54 ppm and 83 ppm, respectively). The residual and oxide/AVS fractions host smaller portions of the Cu (**Figures 23 and 24**). One would think that river sediment will release the fraction of Cu hosted by the AVS fraction and the oxidisable (organic) fraction if the material is dredged, especially with a decrease in the pH as the river sediment dries and oxidises.

As the organic matter decays with depth in the wetland, there is to some extent a transfer into the Fe-oxide fraction, which increases slightly with depth (**Fig. 24**). Cu, like Fe, migrates to the roots of plants in the form of non-adsorbing organic complexes, and usually factors that decrease solubility of free metal cations in the soil solution, will not affect the uptake of these complexes by plants (MacBride, 1994).

The Cu^{2+} ion is more tightly bound to organic matter than any other divalent transition metal (MacBride, 1994), probably since Cu^{2+} is a very soft acid while the R- ligand is a soft base (Shriver and Atkins, 1999). Consequently, Cu is rated as a low mobility element in near neutral, humus-rich soils (MacBride, 1994). The recent wetland sediment has accumulated far more Cu than the river sediment. The largest potential problem in the wetland is Cu accumulation as CuS due to episodes of reduction after bioaccumulation in humus (MacBride, 1994), and could happen with subsequent burial and reduction of Cu-rich humus when the wetland is flooded. This mechanism could also be seen as not a problem but a solution to stabilising the free metal and soluble organic complex concentrations, which are available to plants, since CuS is extremely insoluble. A complication of this mechanism is that there is probably a large seasonal variation in available concentrations of Cu due to the successive flooding and drying events in the wetland causing changes in redox conditions.

4.4.5 Arsenic (As) and Mercury (Hg)

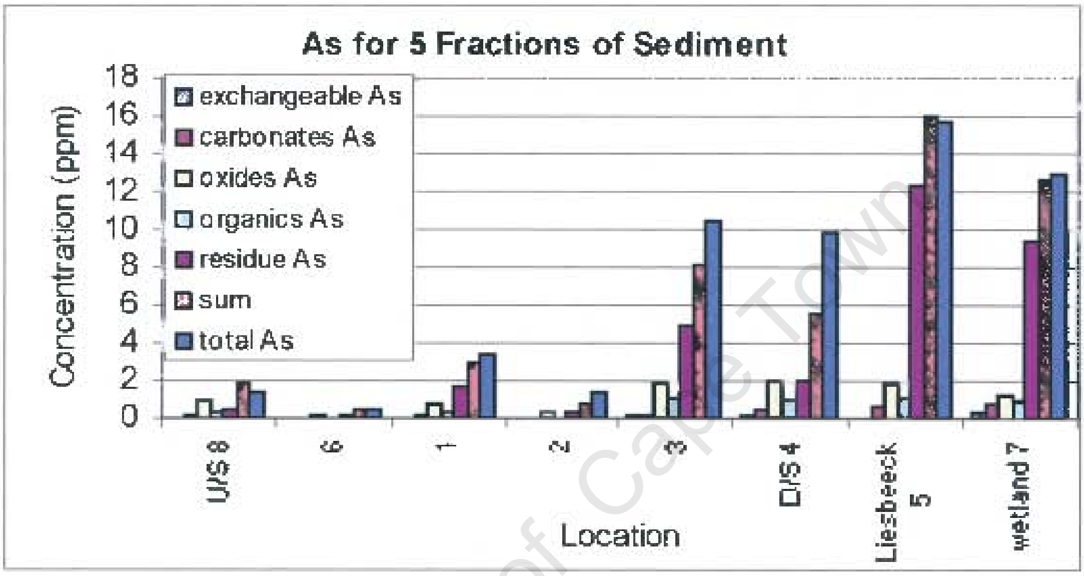

Figure 25: Arsenic, As in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

Hg, Arsenic and Se are the soft metals (or B-type metals) that can be released into the atmosphere as inorganic vapours from the burning of coal (Stumm and Morgan, 1996). Most of the arsenic in the river sediment is associated with the residual fraction and to a much lesser extent, the AVS and organic fractions (**Fig. 25**). While the residual is the least available fraction, work by Stephens et al., (2001), showed that between 2 and 5 weeks of drying and oxidising canal sediment, the arsenic shifted from predominantly the residual fraction to mainly the oxidisable fraction, which they thought was related to the bacterially mediated reaction of As_2S_3 precipitation. This is an unexpected outcome, however, the oxidisable fraction could possibly be converted to arsenate AsO_4^{3-}, the oxidised state, by soil microbes and Mn oxides

(MacBride, 1994). This may be favourable in acidic dredged piles of sediment since AsO_4^{3-} adsorbs effectively in an acidic environment, in soils with high clay or oxide content (MacBride, 1994).

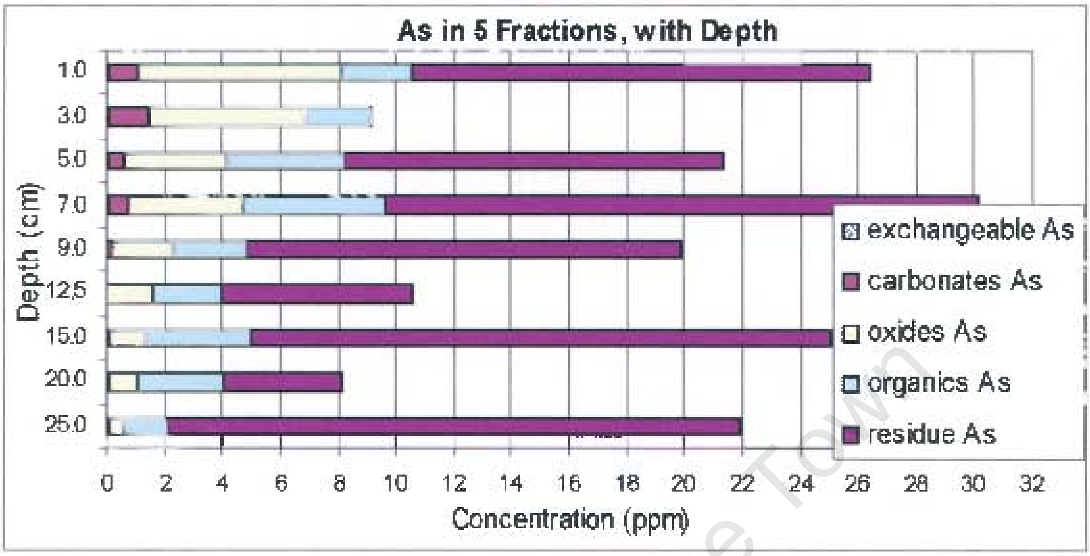

Figure 26: Arsenic, As concentrations in five fractions of Raapenberg wetland sediment. Samples are in order of depth in the core and concentrations are for dry weight of sample. The depth axis is not to scale and the label represents the base of the unit.

As_2S_3 precipitation could also occur in the wetland sediment due to flooding, bringing about reducing conditions, resulting in arsenic accumulation. In the wetland, the arsenic is dominantly associated with the residual fraction, and to a lesser extent with the oxide and organic fractions, and to a lesser extent in the carbonate (acid-leachable) fraction in the more recent sediment (**Fig. 26**). Arsenic shows an increased association with the organic fraction with depth. In this case the organic fraction at greater depth may actually be indicating a crystalline sulphide phase since the organic carbon percent decreases to a minimum in the lower half of the core. The greatest danger at the current circum-neutral pH in the wetland (**Appendix 1**), on soil originating on Malmesbury marine shale, which is rich in sodium chloride (Soil Report, 1992, N. Haniff), is that arsenic may be mobile in the soluble Na arsenate form (MacBride, 1994).

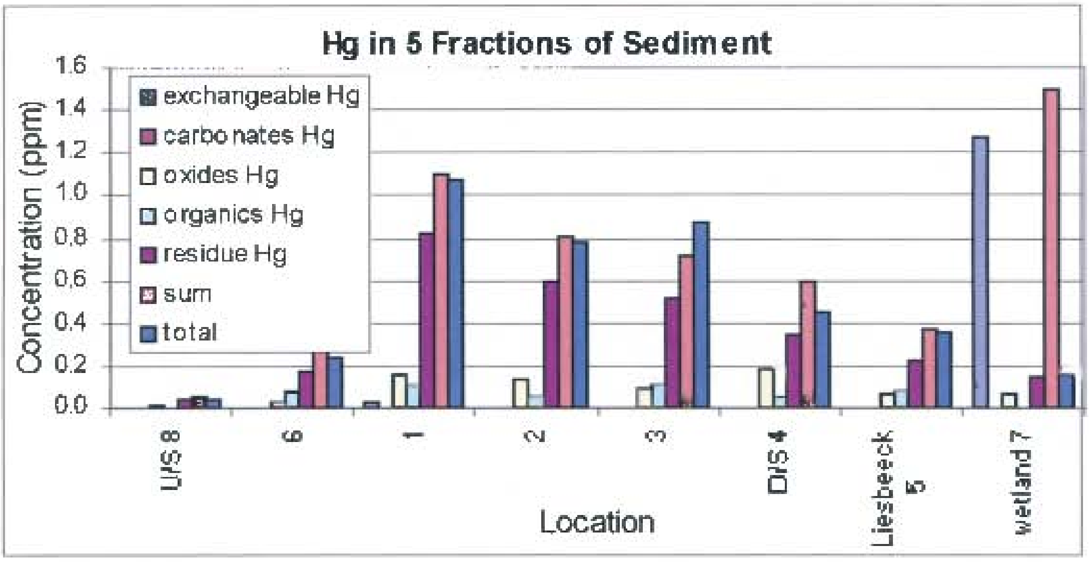

Figure 27: Hg in five fractions of river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. The Sum is the addition of five fractions and the Total is the whole sediment digested independently.

Most of the Hg in the Black River river samples is associated with the residual fraction and to a much lesser extent, the AVS and organic fractions. Hg is a soft Lewis acid (Shriver and Atkins, 1999) and should be hosted by the sulphide and organic fractions, and it is uncertain why the association is strongest with the residual fraction. It is possible that extraction techniques used here did not liberate the Hg effectively since, the dominant soluble form, $Hg(OH)_2^{\circ}$ exists *above* pH4 (MacBride, 1994). It is also possible that the Hg exists in the river sediment as the extremely insoluble HgS and this was not effectively dissolved. The highest Hg concentration is at the mouth of the Elsieskraal River (**Fig. 27**, location 1), and decreases gradually away from this location. This trend is seen both for the whole digested sediment, and the sum of the five fractions of the sediment, which were processed and analysed separately. Results agree to within a maximum of 20.8% of each other (excluding the anomalous wetland sample 7). Further work is thus warranted on this basis, using alternate methods of analysis, on the Hg levels in the Elsieskraal River sediment, and water.

The Hg concentrations in the wetland core approach a maximum at 9 cm depth (**Table 2**), and generally appears to be hosted by the exchangeable and carbonate fractions at shallower depth, and by the oxide and organic fractions deeper in the core. However, there is no clear or smooth trend seen, and further work is required, either by a different extraction technique selected just for Hg, or another means of analysing leachates which has a better precision for Hg than the ICP-MS. The organic fraction shown at greater depth, is possibly a well crystallised phase e.g. pyrite, which hosts the Hg, but it is difficult to evaluate.

Hg is a 'sulphur seeking', soft Lewis acid, and can form insoluble HgS under reducing conditions (Stumm and Morgan, 1996). However, this may not be entirely favourable if the wetland is flooded, since volatile organomercury can also form under these conditions (MacBride, 1994). Also of significance is that the wetland soil originates from NaCl-rich Malmesbury marine shale (Soil Report 2002, N. Haniff), and Hg (and to a lesser extent Cd and Zn) is particularly prone to chloride induced mobilisation, forming metal-chloride pairs which are soluble (MacBride, 1994).

4.4.6 Cadmium (Cd)

The highest concentrations of Cd in the river sediment, like all other data, are at locations 3, 4 and 5 which are the Raapenberg bridge location, the Black River Parkway bridge, and in the Liesbeeck River, in order of high to low concentrations (1.26 ppm, 1.06 ppm and 0.58 ppm, respectively). The main host of Cd is the AVS fraction with a lesser organic fraction association (**Table 1**). Cd, another chalcophile, should be associated with the AVS fraction. While no Cd concentrations measured in this study exceed the SABS (1999) MPM content of 2 ppm, concentrations >0.5 ppm is considered evidence of soil pollution (MacBride, 1994). The likely sources in this case are the sewage effluent released into the Black River and the proximity to the N2 and other highways. Cd^{2+} is even more mobile than Zn, has a very high toxicity to animals and humans, and has a medium to high mobility in acidic oxidising solutions (MacBride, 1994). This is an element of fair concern in the piles of dredged sediment, which often lays on the banks of the Black river and alongside the Raapenberg wetland, before disposal elsewhere.

In the wetland core samples the Cd is hosted mainly by the oxides, likely goethite, gibbsite and amorpous Mn oxides, and to a lesser extent by the carbonate and then the organic fraction, with maximum concentrations at 5-7 cm depth (**Table 2**) of up to 1.75 ppm. This is very close to the SABS (1999) MPM content. The wetland is currently at circum-neutral pH, so the mobility of Cd is low. If the wetland is continuously waterlogged in the rainy season, the precipitation of CdS under the reducing conditions, will result in also low Cd mobility (MacBride, 1994). If the sediment is well drained, though, it may allow the uptake of hazardous levels of Cd by plants (MacBride, 1994), as is probably the case in this wetland in the dry season.

4.5 Temporal Variation during Sequential Extraction Procedure

Two river samples were used to monitor variations in concentration of elements with reaction time. This was done in order to evaluate whether adsorption and desorption are influencing the concentrations in the supernatants, and if this influences at all the times at which the reaction is stopped. Adsorption will be reflected by a decrease in concentration. Unfortunately, no time is available to evaluate the exact reaction time for each sediment type, so the prescribed time for this method of extraction was applied. The variations in concentration therefore also reflects the various phases being dissolved, and logically, the start of the next phase being dissolved, should be accompanied by a sharp increase in concentration. A description of the variation in concentrations of various elements with time, for four steps of the sequential reactions and graphs of these variations is shown in **Appendix 6**.

4.6 Confidence in Data

4.6.1 Sampling Heterogeneity and Procedural Error

The certified reference material SL-1 showed fairly good reproducible concentrations through the sequential extraction procedure for all certified trace elements of concern, Cr, Zn, Ni, Cu, Co, Pb, As and Cd (**Table 13**). Therefore the precisional error, %P can be attributed mainly to sample heterogeneity since the overall procedural error is most likely minimal in comparison. The duplicate values of the two river samples and duplicates of the two wetland core samples are used to estimate the error on all the results obtained for each set of samples. *The average error was evaluated for the first four fractions only*. There is a larger variation in the precision for lower concentration than higher concentration samples (Ramsey, 2000). The Precision (%P), calculated as (σ/mean)*200, was chosen to represent the percent scatter on the total dataset, at the 95% confidence limit. Note that this will give *twice* the error as is represented by the standard deviation, as it represents the scatter both above and below the mean, combined. The higher the precision, the lower the scatter on 95% of the samples, the lower the percentage shown in **Tables 1 & 3**. The precision or scatter was averaged for elements of concern, for various concentration ranges. The precision for each element, is available in **Appendix 2**. The sum of the five fractions, compared with the total concentrations of whole digested sediment, also have the problem of sample heterogeneity, since the wet sediment was not homogenised completely. These differences seen graphically in sections 3.4 and 3.6 are thus a reflection of sample heterogeneity and minor procedural error. The only way to estimate the procedural error will be to use the standard material SL-1that was sequentially reacted.

The River Sediment Samples:
The sampling heterogeneity was evaluated for Pb, Zn, Cu, Cr, Ca, Al, Ni, Fe and As. While the precision data are available for each element in **Appendix 2**, the mean of the data is discussed here to explain an overall perspective of the error. It is believed the sampling heterogeneity to be the dominant source of low precision, and the procedural error to be minimal in comparison, due to the lack of a homogenising process and the nature of the river bottom sediment. The scatter on values <0.1 ppm is

extremely low (**Table 4,** P=274%), and the standard deviation on duplicate samples not homogenised, is 137% in excess of the mean. This was taken by the author to imply the invalidity of the results with values <0.1 ppm, due to the high level of sample heterogeneity. Values in this low concentration range are not the focus in this study. Nor are the values in the 0.1 ppm to 2 ppm range, with the exceptions of Hg, As and Cd and Se, which are discussed briefly. The values in the range of 0.1 to 2 ppm also have a very low precision, with an average standard deviation as a percent of the mean of 71% (**Table 4**) and a scatter or precisional error of 143%. While this is extremely low precision due to sample heterogeneity, the values can be taken as only a rough indication of the actual concentration.

Generally, river sediment values have a very large scatter, with values between 2 and 10 ppm showing an average scatter of ~131%, values between 10 and 100 ppm an average scatter of ~68% and values greater than 100 ppm a scatter of ~62% at the 95% confidence limit (**Table 4**). This translates in simple terms, to values between 2 and 10 ppm being a rough indication of concentrations in the bottom sediments, with a quantifiable error. Values in the two higher ranges are taken as fair indications of the concentrations in the system as a whole, with acceptable standard deviations of ~34% and ~31% of the mean respectively. This does not account for the overall heterogeneity in the entire Black River, but merely in the actual samples taken. The 7 river samples taken from the river bottom sediment are probably not representative of the entire Black River System, which is probably much more heterogeneous on a larger scale.

There is considerable variation between the precision on different elements due predominantly to sample heterogeneity, the reason depending to a large extent on the mode of deposition and particle size of the fraction with which the element is associated. So the precision will vary not only from element to element, but for each sediment type as well. For example, Pb shows a lower precision than the average for one sediment, as has been seen in other studies. This has been attributed to the relatively large (>8μm) lead-rich particles originating from the combustion of gasoline (Tessier et al., 1979).

The Wetland Core Samples:

The wetland core combined sample heterogeneity and procedural error was evaluated for each element in two duplicates out of nine samples sectioned from the core. More supernatants were available (both duplicates and samples), but due to financial constraints, only the data presented here was analysed on the ICP-MS. However, in order to obtain an overall perspective of the heterogeneity and error on the wetland core results, the %P was averaged for Cr, Zn, Pb, Ni, Co, Cu, As, Ca, Fe, Cd, Mo and Se for various concentration ranges (**Table 6**).

The wetland core samples have a much better precision than the river sediment, which is expected, due to the differences in deposition between the two environments and the compactness of the sediment. Firstly, heterogeneity and error estimates given in this study in no way approximates the heterogeneity in the wetland as a whole, and to estimate this, several cores will have to be analysed for trace metal concentrations. These are estimates for variations within the samples taken, and within one single core. The values < 0.1 ppm have a low precision, with a scatter of ~119%. The standard deviation is ~60% of the mean for these elements combined, which means that these values are only a rough indication of actual values in the samples taken. Values between 0.1 and 2 ppm have an overall precision of ~83%. This is a very high scatter, with the average standard deviation ~41% of the mean. While this is a high scatter, it may be appropriate as a rough indication of the actual value within the core. This would be applicable to elements such as Arsenic, Cd, Mo, Se etc., that have concentrations sometimes close to the SABS (1999) MPM content. The other categories chosen all have fairly acceptable scatter or precision at the 95% confidence level, ranging from ~44% precision or ~22% standard deviation to ~25% scatter/precision or ~13% standard deviation, scatter decreasing with increasing concentration (**Table 6**). Only above concentrations of 1000 ppm does the scatter increase to ~57% or standard deviation 28% of the mean. The concentrations that are the focus of this study, are mainly in the concentration range with the lowest scatter, i.e. the highest confidence. This is encouraging in applying the results obtained from the core samples in this study, since it allows a comparison with other studies, and governmental guidelines with a fairly high level of confidence.

4.6.2 Analytical Error

For each analytical run on the ICP-MS, 2 or 3 samples (~5%) were analysed in triplicate at the beginning, middle and end of the run. *The analytical error was evaluated for the first four fractions only*. The variation in the data obtained, was used to calculate the scatter or precision of the ICP-MS with regard to each element analysed. The average error was calculated for each element for the 2 or 3 triplicate analyses. About every 10 samples, the external sea-water standard, NIST-1640 was run, and the averaged value of these runs was used to calculate the percent bias of the ICP-MS, of the measured value from the accepted/certified value. All error includes possible pipetting errors, since the samples had to be diluted 100 times before analysis.

River Sediment Analytical Error:

Of the main elements discussed here, the triplicate analyses of the samples show an average analytical precision of <20% for Mn, Fe, Co, Cu, Zn and Pb (**Table 5**), which translates to a standard deviation <10% of the mean. Ni and Cr had lower precisions, at ~62% and ~69% respectively at the 95% confidence limit, with standard deviations at ~31% and ~36% respectively. The lower concentration elements had much lower precision, as expected, with Cd, Mo, As showing low, but still acceptable scatters of ~26%, ~30% and ~35% respectively, at the 95% confidence limit. These values for precision are for the purposes of this study, sufficient to reach conclusive statements about these concentrations for these elements. However, Se and Hg have precisions of ~120% and ~218% respectively, which translates to no similarity about a mean value, if all the data are scattered outside the 95% limits from the mean. While no conclusions at any acceptable confidence level may be reached with regard to Se and Hg, the data could possibly be used as a proxy for further testing with alternate analytical techniques. The percent bias of the analyses was fairly low for almost all elements, generally under 10% for all elements discussed. Fe and Zn were the highest with a positive bias of ~23% and ~24%, respectively.

Wetland Core Samples Analytical Error:

Analyses of the wetland core samples run on the ICP-MS were also much more precise than for the river samples. Pb, Co, Mn, Mo, Cu, Zn all had a precision (%P) in the triplicate runs of ≤ 5% (**Table** 7). The high precision for these elements allows conclusions to be drawn with a high level of confidence. Fe and As also showed a good precision of 6% and 9% respectively, while Cr and Cd had acceptable precisions of 12% and 22% respectively. Hg still had a low precision, with 137% scatter on the triplicate analyses, which translates to ~69% standard deviation as a percent of the mean. While this is poor, it may provide a rough indication of concentrations in the wetland, as a proxy for further study.

The percent bias of the analyses for each element is very low for most elements discussed, generally < 5%. For Ni, Cu, and Pb there is a 5 - 10% positive bias on the analyses, while on Fe and Zn, a high positive bias of 34% and 29%, respectively. Fe and Zn, therefore on two separate runs, for the river and core sediment, indicated high positively biased readings on the ICP-MS. This may have been due to samples with relatively high Fe and Zn concentrations contaminating the ICP-MS vacuum chamber with these elements, and it not being totally flushed out, before the next sample was analysed.

5. Conclusion

The River Sediment:

The anoxic river sediment is enriched in Pb, Zn, Ni, Cu, As, Hg, Cr, Cd, for some of these toxic elements, far beyond the recommended (1999) SABS permitted levels. The main association for many metals is with the third stage of extraction, targeted for Fe-Mn oxides, but which has been shown to extract the AVS fraction for anoxic sediments (Rapin et al., 1986). Particularly Pb and Zn, the most highly concentrated trace metals, and Cd are hosted by the AVS fraction. The dominant sulphide association implies a very low level of mobility within in situ river sediment, but an increase in the bioavailability on dredging due to the rapid oxidation (Stephens et al., 2000) of the AVS fraction on exposure to oxygen. Only the Liesbeeck River sample, with the highest Pb concentration, showed a large fraction of the Pb to be hosted by the carbonate fraction implying potential in situ availability, on acidification of the overlying water column.

Most of the Cu, some Pb and minor arsenic is hosted by the organic fraction of the sediment. For Cu, Pb and arsenic, this fraction represents tightly complexed metals, however is potentially available on oxidation of the sediment and/or through the natural degradation of organic matter. The release of this fraction of metals will occur both in in situ river sediment under anoxic conditions, where the metal released will most likely be sequestered by AVS minerals and eventually locked in pyrite (Cooper and Morse, 1998), and also in dredged sediment, where part of the metal could be scavenged by the oxide minerals, or possibly become soluble or shift to a more bio-available fraction.

Cr, Hg, Ni, Co and most of the arsenic, are also enriched in the river sediment, but are primarily hosted by the residual fraction at most locations, which is the least bio-available fraction. This implies a low potential for bio-availability both in situ and on dredging of sediment. The only location that showed a strong association of Cr with the oxidisable, organic fraction is at the Black River Parkway area (location 4), which becomes potentially available on dredging.

Second to the residual fraction, the AVS and organic fractions host a large proportion of the remaining pool of metals, particularly at locations 3 and 4 where overall concentrations were almost always the highest. Oxidation of the anoxic river sediment on dredging will result in the precipitation of Fe-Mn oxides (MacBride, 1994), which are very effective in scavenging trace metals out of proportion to their own concentration (Tessier et al., 1979). Elements such as As which have strong adsorption to Fe-Mn oxides and clays, particularly at low pH conditions that are likely to exist in dredged, oxidising piles of sediment will be associated with these Fe-Mn oxides. Further work is required to establish the main complex formation for Hg, to determine the availability on dredging, since the chemistry of Hg is much more complex than for other metals (MacBride, 1994).

Samples are relatively heterogeneous because they were not completely homogenised. This produced a high degree of scatter in the data, or low precision of data for the duplicates at the 95% confidence limit. The analytical precision was within acceptable limits. The analytical bias was also within acceptable limits. Further work is required for Hg concentrations in sediment and water of the Elsieskraal River, with a method of analysis with a higher precision for Hg, than the ICP-MS.

The Wetland Core:

The Wetland Core samples, also showed values higher than SABS (1999) MPM contents for several potentially toxic trace metals. Pb, Zn, Cr, Ni, Cu, As, Se, Mo and Hg significantly exceed the SABS (1999) MPM limits at their peak concentrations with depth, while the elevated Cd levels approach the SABS (1999) MPM limits. All metal concentrations are greater in the top 10 cm of the core than the lower 15 cm, because the shallower sediment is more recent reflecting increased industrial anthropogenic and urbanisation input. The more mobile elements showed peak concentrations at greater depth than the less mobile elements, indicating a downward movement of elements through the profile, and possibly eventual fixation of these metals as sulphides at greater depth, reducing mobility and availability.

Zn, As and Co are hosted primarily by the Fe-Mn oxide fraction. These metals probably have a large seasonal fluctuation in bio-availability due to repeated flooding of the wetland in the rainy season, most likely producing anoxic conditions in the soil. This seasonal fluctuation also applies to metals which may exist as sulphides in the deeper part of the soil profile, which may mobilise during the dry season due to oxidation. This should be investigated by further sampling of the wetland. Arsenic availability in recent sediment is a potential hazard in this salt-richy soil, due to its mobility at neutral to high pH (*MacBride, 1994*). There is also some association of arsenic with the carbonate fraction at shallower depth, indicating potential for bio-availability with a decrease to pH~5. This also applies to Pb and Zn which have substantial portions associated with the carbonate fraction (up to 48 ppm and 71 ppm, respectively. Pb, Cr and Cu, the more immobile elements (*MacBride, 1994*) in humus-rich soil, show a predominant organic fraction association, with a minor portion of the metal being hosted by the oxide fraction. Pb is strongly associated with both the oxide and organic fractions. These metals have definite potential for bio-availability as the organic matter in shallow sediment is progressively oxidised.

With subsequent deposition and burial of shallow sediment and/or flooding during the rainy season, bringing about reducing conditions in the wetland, it is likely that metals will precipitate as metal sulphides. This will both accumulate metals and reduce bioavailability due to the sparingly soluble nature of sulphides (*Stumm and Morgan, 1996*). With drying of the wetland in the summer, the sulphides could oxidise and precipitate oxides once again, producing temporary seasonal availability as the metals transfer from one phase to the next. Changes in redox conditions probably play a strong role in the potential of seasonal toxicity of trace metals. Lower pH conditions, for example pH ≤ ~5 could make bioavailable metal associated with the carbonate fraction. In this case, free Pb and Zn could increase to toxic levels. Severe increases in alkalinity in the wetland could also produce soluble organic metal complexes (MacBride, 1994), and have a toxic effect on plants and wildlife. It is thus important to monitor these basic chemical indices in this urban natural environment, to ensure that no major anthropogenic influences bring about such sudden changes. It is therefore recommended that strict monitoring of pH, alkalinity and salinity occur for the Black river catchment area and in the Raapenberg wetland.

The precision on the trace metal data, as indicated by the duplicate samples is primarily determined by the sample heterogeneity and to a lesser extent by the procedural error. There is a higher precision in the wetland core samples than for the river sediment samples, due to much greater homogeneity in the compacted wetland sediment, and allows conclusions to be made with a higher level of confidence. The analytical precision was very high for all elements. Only Hg has a low precision (high scatter) and requires further work due to elevated levels, using an alternate method of analysis. The results for the core samples have an overall high precision and small bias, which lends substantial validity to the conclusions reached.

The sequential extraction procedure performed on the sediment could be used in the future to establish relationships to organisms feeding on sediment as has been done in other studies (Langston, 1982) and those exposed to the dissolved trace metal fraction associated with the sediment. Much more work will be required in the future on the biological and water aspects, to obtain a holistic view of the impacts on all rivers and to determine an accurate summation of their interaction with each other.

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Appendix 1

TableA: Electrical Conductivity (EC), Temperature, and pH for Aquatic Sediment samples measured in the field.

Sample No	T °C	pH	EC µS/cm	Water level (cm)	Dissolved oxygen (mg/l)	Comment
1	12	6.88	-	~75	6.41	Dry sample.
2	17	7.10	-	~50	6.88	Dry sample.
3	15	6.94	5.87mS/cm	~100	4.84	Bubbled gas.
4	15	7.14	823	~200	3.61	
5	13.5	6.93	380	~150	6.13	Bubbled gas.
6	12.7	7.08	351	~20	-	
7	22	6.69	-	~20	-	
8	18	7.17	583	~10	-	

Table B: Electrical Conductivity (EC) and pH on porewater samples corresponding to the two cores taken at the Raapenberg Wetland.

Unfiltered Porewater Sample	pH	EC at 20°C
Porewater 1 (Core for sequential reaction)	6.56	4.20 mS/cm
Porewater 2 (Core for Description)	6.45	4.33 mS/cm

2. Porosity and Density Measurements

Each sediment sample was evaluated for porosity and density using syringes and mass measurements. The 'wet density' test was conducted twice due to the possible presence of free water.

$$\text{Porosity} = \frac{\text{Volume}_{\text{void}}}{\text{Vol}_{\text{void}} + \text{V}_{\text{sediment}}}$$

Table C: Porosity and Density data for Aquatic Sediment Samples

Sample Number	Dry density (g/cm3)	Porosity
1	1.42	0.38
2	1.63	0.33
3	0.82	0.51
4	1.05	0.63
5	0.71	0.76
6	1.58	0.46
7	0.69	0.67
8	1.43	0.45

Table D: Porosity and Density data for Wetland Core

Sample depth in core (cm)	Dry density (composite) (g/cm^3)	Porosity (composite)
0-2cm	0.21	0.79
2-9cm	0.42	0.75
9-22cm	1.39	0.57
22-31cm	1.62	0.54
31-45cm	1.45	0.53
45-48cm	1.79	0.52
48-60cm	1.63	0.53

3. Grain Size Analysis

3.1 The Grain size analysis was conducted for all 8 samples and is as follows:
A combination of dry and wet sieving was used to determine the grain size.

Clay < 2μm diameter
2μm < Silt < 63 μm diameter
63μm < Sand < 2mm diameter
Coarse sand > 2mm diameter

Small dry weighed samples were dry sifted to separate the fractions of soil greater and less than 2mm. The finer fraction was then wet-sieved through 63μm sieve, to separate the sand from the silt/mud fraction. The finer fraction was than diluted with distilled water in a beaker, and ~100ml of 0.16 mmol/l Sodium hexametaphosphate (dispersant) was added to each sample, then ultra-sonicated to disperse the clay/silt effectively. The settling times were calculated using Stoke's Law, and solutions were left to settle, in order to separate the clay and silt, for the exact times calculated using Stoke's Law (See below). A grain-size diameter of 2μm was used in calculations in order to separate the clay from the silt. After the settling time, the supernatants were decanted and centrifuged at 6000rpm for 5minutes to concentrate the clay for XRD analysis. When dried the residual silt fraction was weighed.

<u>Specimen Calculation of Stoke's Law Settling Time Samples.</u>

$$\text{SETTLING TIME } t = \frac{18\eta h}{g(d_P - d_l)\,D^2} = \frac{18\,(1.002\ \text{exp}(-2)\ g/cm.s)\,(4.3cm)}{(981cm/s^2)\,(2.65 - 1g/cm_3)\,(2\ \text{exp}(-4)cm)^2}$$

$$= 11978.3s \sim 3hrs\ 20mins$$

Key: η = vicosity
h = height of water in beaker
g = gravity
$d_P - d_l$ = difference in density between particle and liquid (taken as $1g/cm^3$)
D = particle diameter; used 2μm to separate silt from clay.
Units can be seen in calculation.

4. Sequential Reaction

4.1 The Tessier et al. (1979) method of sequential reaction was conducted for the 8 sediment samples, under nitrogen gas atmosphere for the first three steps (See **Photo 1**).

4.2 Reagents were prepared as the method required, and reaction times were adhered to. The amount of samples in the batch (12) leads to reaction time errors, however, to merely obtain an idea of potentially bioavailable fractions of metal, the compliance was sufficient.

Photo 1: Centrifuge vials in nitrogen bag, made of plastic and duct tape. The bag was filled through a plastic tube inlet, attached to a nitrogen gas canister.

5. Core Description

*Depth reflects the base of the unit, and starts at 0cm.

*Depth (cm)	Description	Basal contact
1	Massive, fine root-mass. Minor mud. Dark brown.	Distinct
8	Abundant root-mass. Dark brown. Clayey with nodules/pebbles to ~15mm. Some coarse roots ~3mm diameter.	Sharp
9	Transition from dark brown clay to fine sand.	Gradational
17	Silty med-brown, sand with reddish brown nodules ~5mm diameter.	Gradational
21	Silty, med-brown fine sand. Minor reddish nodules.	Distinct
28	Med-coarse sand. Med-light brown.	Distinct
31	Silt. Med-brown.	Distinct, sharp
35	Predominantly fine mud. Med-dark brown. Coarsening downwards.	Irregular, Gradational
40	Med-coarse sand.	Irregular
45	Light yellow-brown mud. Fining downwards.	Sharp
48	Med-coarse sand. Light brown.	Distinct
59.5	Fine mud. Med. Yellow-brown. Massive.	Broken

6. Organic Carbon Determination: Walkley Black Method

The Walkley-Black (1935) method was used to determine the organic carbon content of all sediment samples. Reagents were used in the same concentrations as specified in the method. Sediment was air dried or oven dried at ~40°C and then ground with an agate mortar and pestle. 10cm^3 of 0.167M Potassium dichromate ($K_2Cr_2O_7$) solution was added to ground samples. Flasks were swirled and then 20ml of Conc. H_2SO_4 was added rapidly. The flasks were then swirled rapidly for a time of 1minute. The flasks were cooled for 30 minutes, then 150ml distilled water and 10ml Ortho-Phosphoric acid was added. 3 drops indicator (Barium diphenylamine sulphonate: 0.4g dissolved in 100ml distilled water) was added and then the solution was titrated with ~0.4998M Iron (II) Ammonium Sulphate till the colour changed to a distinct green.

The reaction for the oxidation of organic matter in the sample:

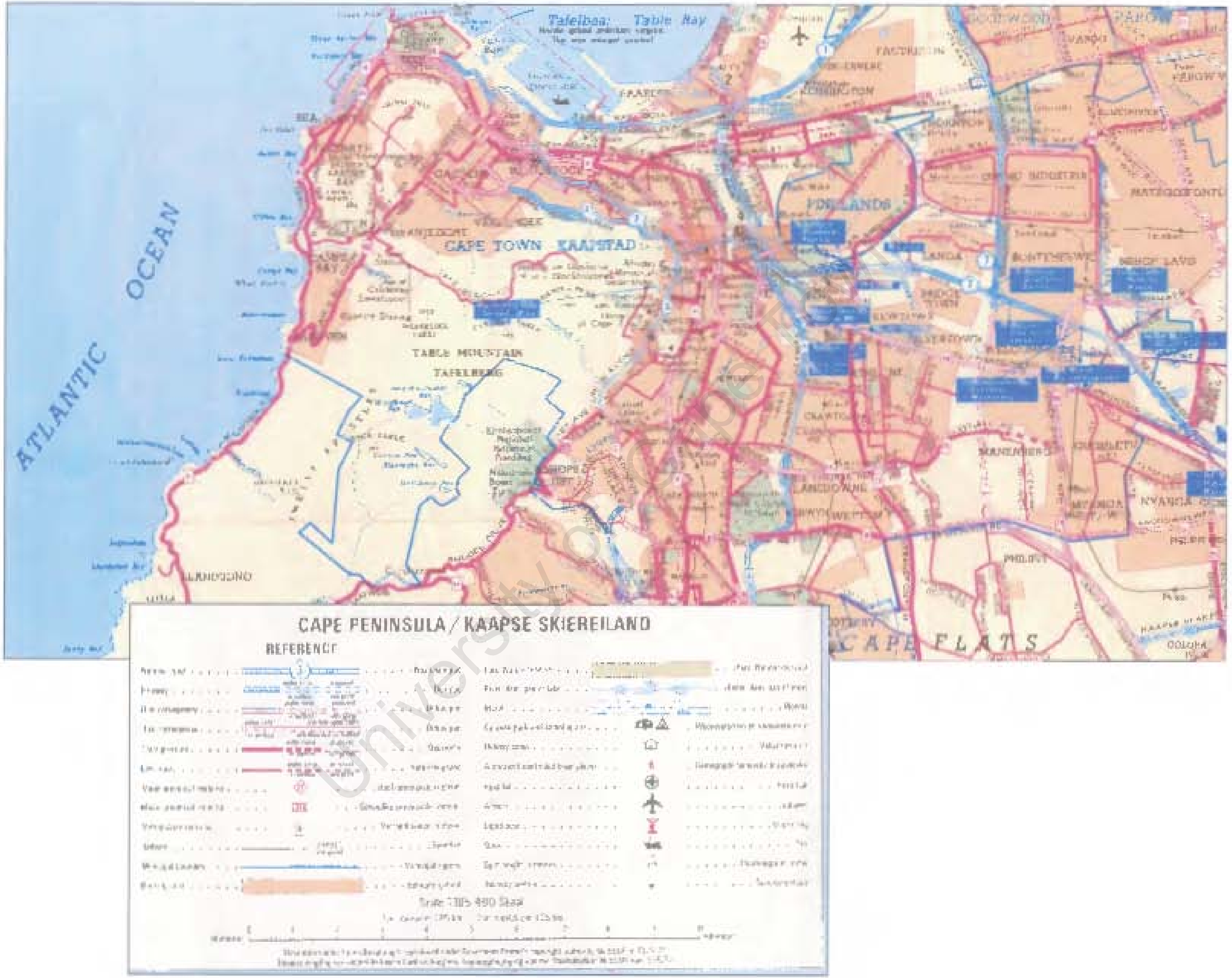
$2Cr_2O_7^{2-} + 3C + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O$ Schollenberger (1927)

0.5 g sample was used for organic-poor samples, and 0.2 g or 0.1 g was used for organic-rich samples. The blank solution titrated was used to standardize the concentration (M) of the $Fe(NH_4)_2(SO_4)_2$ using the formula:

$$M = \frac{10cm^3\ K_2Cr_2O_7 * 0.167 * 6}{cm^3\ Fe(NH_4)_2(SO_4)_2}$$

The titrated volume was used to calculate the organic carbon content using the formula:

$$\frac{[cm^3\ Fe(NH_4)_2(SO_4)_2\ blank - cm^3\ Fe(NH_4)_2(SO_4)_2\ sample] * M * 0.3 * 1.3}{soil\ mass\ (g)}$$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REFERENCE
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Tafelbaai Table Bay
CAPE TOWN KAAPSTAD
TABLE MOUNTAIN
TAFELBERG
PINELANDS
LANGA
CRAWFORD
LANSDOWNE
MANENBERG
NYANGA
PHILIPPI
CAPE FLATS
LLANDUDNO
GOODWOOD
PAROW

Appendix 2

Table A: Error (%P) at the 95% Confidence Limit for River Sediment Samples

Means and %P of Duplicate Samples for River Sediment (Samples 1 & 7)

mg/kg soil %P=(σ/X)*200	exchangeable Pb	carbonates Pb	oxides Pb	organics Pb	exchangeable Zn	carbonates Zn	oxides Zn	organics Zn
mean: 1	0.04	45.66	99.46	24.55	0.53	48.06	121.57	5.26
%P: 1	211.58	166.27	155.20	176.97	252.71	98.24	54.04	0.80
mean: 7	0.03	10.73	27.46	15.02	2.66	18.81	53.89	9.67
%P: 7	282.84	35.73	28.05	3.73	266.96	78.32	14.56	4.82

	exchangeable Cu	carbonates Cu	oxides Cu	organics Cu	exchangeable Cr	carbonates Cr	oxides Cr	organics Cr
mean: 1	0.07	0.03	2.08	15.88	0.12	0.44	3.15	1.19
%P: 1	282.84	282.84	106.85	11.73	186.16	262.84	67.67	147.46
mean: 7	0.00	0.00	0.63	15.59	3.98	0.23	0.28	6.05
%P: 7	-	-	91.07	43.79	282.84	282.84	282.84	30.83

	exchangeable Ni	carbonates Ni	oxides Ni	organics Ni	exchangeable Fe	carbonates Fe	oxides Fe	organics Fe
mean: 1	0.078	0.348	1.056	0.415	1.84	300.23	1040.21	134.33
%P: 1	282.84	189.50	256.28	43.95	198.61	10.89	84.84	33.74
mean: 7	0.058	0.029	0.819	0.636	7.55	166.13	2377.92	878.20
%P: 7	282.84	282.84	95.87	172.61	282.84	29.14	48.10	12.11

	exchangeable Ca	carbonates Ca	oxides Ca	organics Ca	exchangeable Al	carbonates Al	oxides Al	organics Al
mean: 1	808.58	11269.56	658.48	82.95	0.77	17.01	430.64	263.46
%P: 1	68.62	26.20	50.82	46.06	48.55	76.12	119.29	41.80
mean: 7	1248.33	782.52	192.69	97.35	3.64	35.75	851.51	2440.43
%P: 7	185.92	1.62	225.04	62.46	268.83	25.37	54.22	29.06

	exchangeable As	carbonates As	oxides As	organics As
mean: 1	0.022	0.209	0.868	0.342
%P: 1	282.84	71.82	45.66	30.92
mean: 7	0.126	0.705	1.351	1.104
%P: 7	282.84	8.26	10.75	31.68

Table B: Error (%P) at the 95% Confidence Limit for Wetland Core Sediment Samples.

Means and %P of Duplicate Samples for Wetland Core Sediment (Samples A2 & A6)
A6 (Depth 10-12.5cm) Muddy, organic rich
A2 (Depth 2-3cm)Sandy sample

mg/kg soil %P=(σ/mean)*200	exchangeable Cr	carbonates Cr	oxides Cr	organics Cr	exchangeable Zn	carbonates Zn	oxides Zn	organics Zn
mean: A2	0.197	0.717	17.75	182.38	3.15	31.44	104.71	28.33
%P: A2	193.25	-	12.51	56.60	228.80	28.44	23.08	22.81
mean: A6	0.129	0.000	2.53	3.65	3.79	51.76	194.18	17.89
%P: A6	105.37	-	43.95	54.21	9.67	11.96	1.09	3.84
	exchangeable Ni	carbonates Ni	oxides Ni	organics Ni	exchangeable Co	carbonates Co	oxides Co	organics Co
mean: A2	0.117	0.000	2.097	4.381	0.16	0.54	1.45	1.16
%P: A2	282.84	-	55.18	20.70	33.10	48.17	68.52	84.65
mean: A6	0.145	0.277	1.338	0.000	0.09	0.53	2.05	0.23
%P: A6	15.04	33.17	13.80	-	17.62	4.53	2.55	1.76
	exchangeable Cu	carbonates Cu	oxides Cu	organics Cu	exchangeable Pb	carbonates Pb	oxides Pb	organics Pb
mean: A2	0.00	0.00	1.59	83.79	1.04	48.58	148.98	198.51
%P: A2			94.82	12.77	94.91	22.61	3.36	80.70
mean: A6	0.13	0.00	3.82	7.92	0.14	4.83	50.46	19.15
%P: A6	48.30		9.41	9.42	13.13	7.04	3.31	7.54
	exchangeable As	carbonates As	oxides As	organics As	exchangeable Ca	carbonates Ca	oxides Ca	organics Ca
mean: A2	0.08	1.34	5.47	2.29	3351.61	1291.80	747.46	219.46
%P: A2	168.00	128.29	113.39	68.81	66.00	50.26	1.64	46.44
mean: A6	0.00	0.02	1.59	2.34	1269.18	389.31	255.90	97.67
%P: A6		282.84	21.03	10.37	26.21	7.99	30.38	41.08
	exchangeable Fe	carbonates Fe	oxides Fe	organics Fe	exchangeable Se	carbonates Se	oxides Se	organics Se
mean: A2	97.43	347.38	4729.91	2576.07	0.05	0.24	0.40	1.45
%P: A2	96.64	16.62	78.34	102.47	282.84	219.71	10.62	143.19
mean: A6	3.62	35.72	5489.86	787.49	0.00	0.06	0.40	0.88
%P: A6	8.92	39.76	9.75	10.38		282.84	27.00	39.72
	exchangeable Mo	carbonates Mo	oxides Mo	organics Mo	exchangeable Cd	carbonates Cd	oxides Cd	organics Cd
mean: A2	0.18	0.00	0.59	8.16	0.00	0.05	0.31	0.09
%P: A2	142.50		144.65	16.26	232.52	17.90	28.50	57.84
mean: A6	0.03	0.00	0.10	0.27	0.03	0.14	0.36	0.02
%P: A6	18.62		35.77	15.41	7.76	20.81	1.28	26.20
	exchangeable Hg	carbonates Hg	oxides Hg	organics Hg				
mean: A2	0.22	0.38	0.07	0.08				
%P: A2	226.52	259.73	282.84	282.84				
mean: A6	0.05	0.05	0.21	0.03				
%P: A6	131.93	268.39	210.81	282.84				

Appendix 3

Raw Data for XRD scans on clay concentrated from River sediment and Wetland Core sediment.

Sample Index:

Scan Name	**Sample Name**
claysmear8	Smear of sample U/S 8
claysmear6	Smear of sample 6
claysmear1	Smear of sample 1
claysuspen2	Suspension of sample 2
claysmear3	Smear of sample 3
claysmear4	Smear of sample D/S 4
claysmear5	Smear of sample Liesbeeck5
claysmear7	Smear of sample wetland7
P2(core sample)	From 2 to 9 cm depth in the wetland core
P3(core sample)	From 9 to 22 cm depth in the wetland core
P4(core sample)	From 22 to 31 cm depth in the wetland core
P5(core sample)	From 31 to 45 cm depth in the wetland core
P6(core sample)	From 45 to 48 cm depth in the wetland core
P7(core sample)	From 48 to 60 cm depth in the wetland core

U/S 8 is the most upstream sample from the Blomvlei Canal, with samples in order from top to bottom towards the most downstream sample, D/S 4.
Sample 1 is from the Elsieskraal convergence point with the Vygekraal River.
Sample 2 is from the Vygekraal River, downstream of the Elsieskraal convergence point.
Sample 3 is from the Raapenberg bridge area in the Vygekraal River.
Sample D/S 4 is from the Black River next to the Raapenberg Wetland.
Liesbeeck 5 is the river bottom sediment from the Liesbeeck River.
Wetland 7 is the scooped sediment sample from the Raapenberg Wetland.

All core samples are from the Raapenberg Wetland core.

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Graph: claysmea.6

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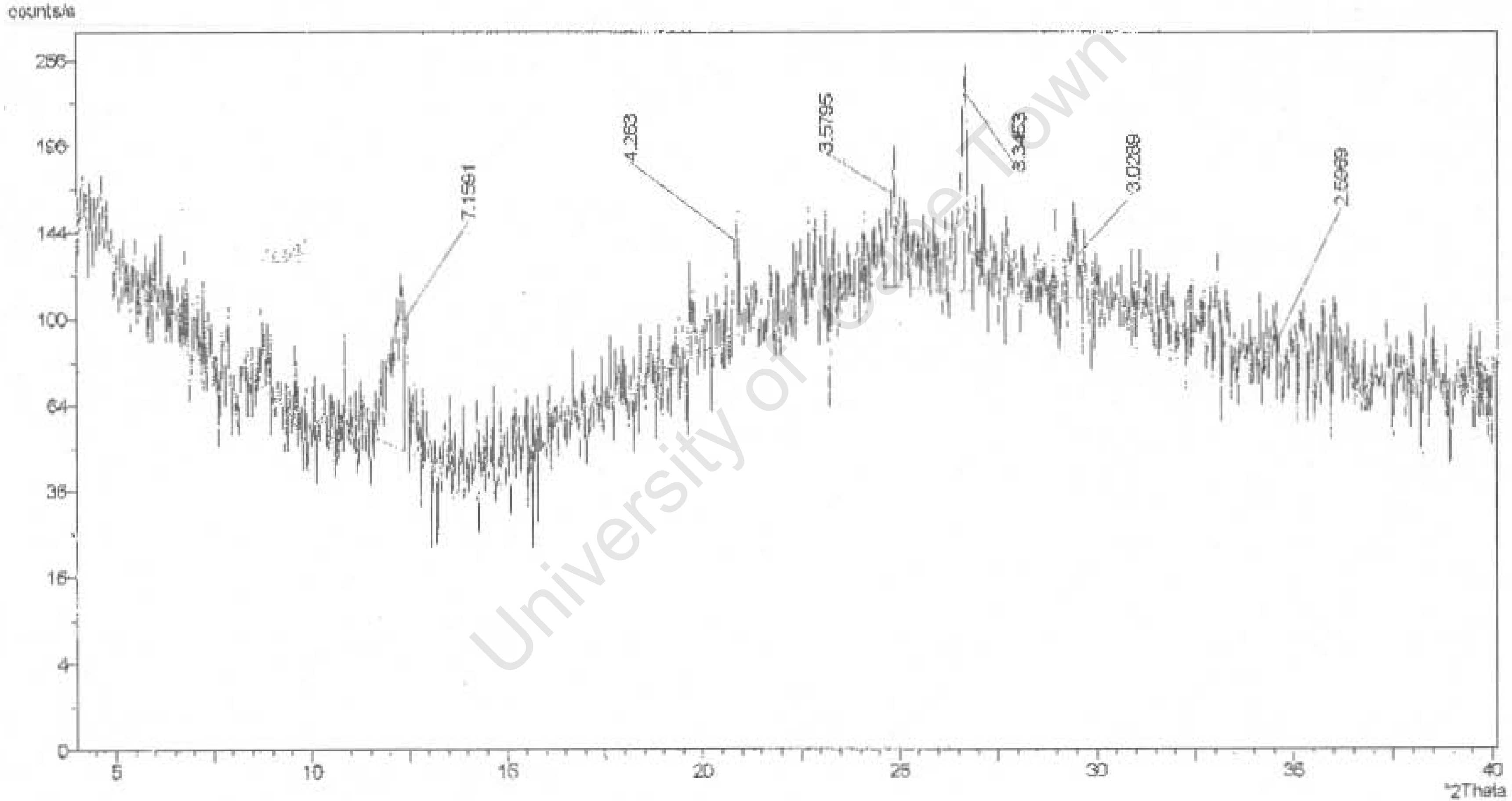

Philips Analytical

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Graph: claysmear6

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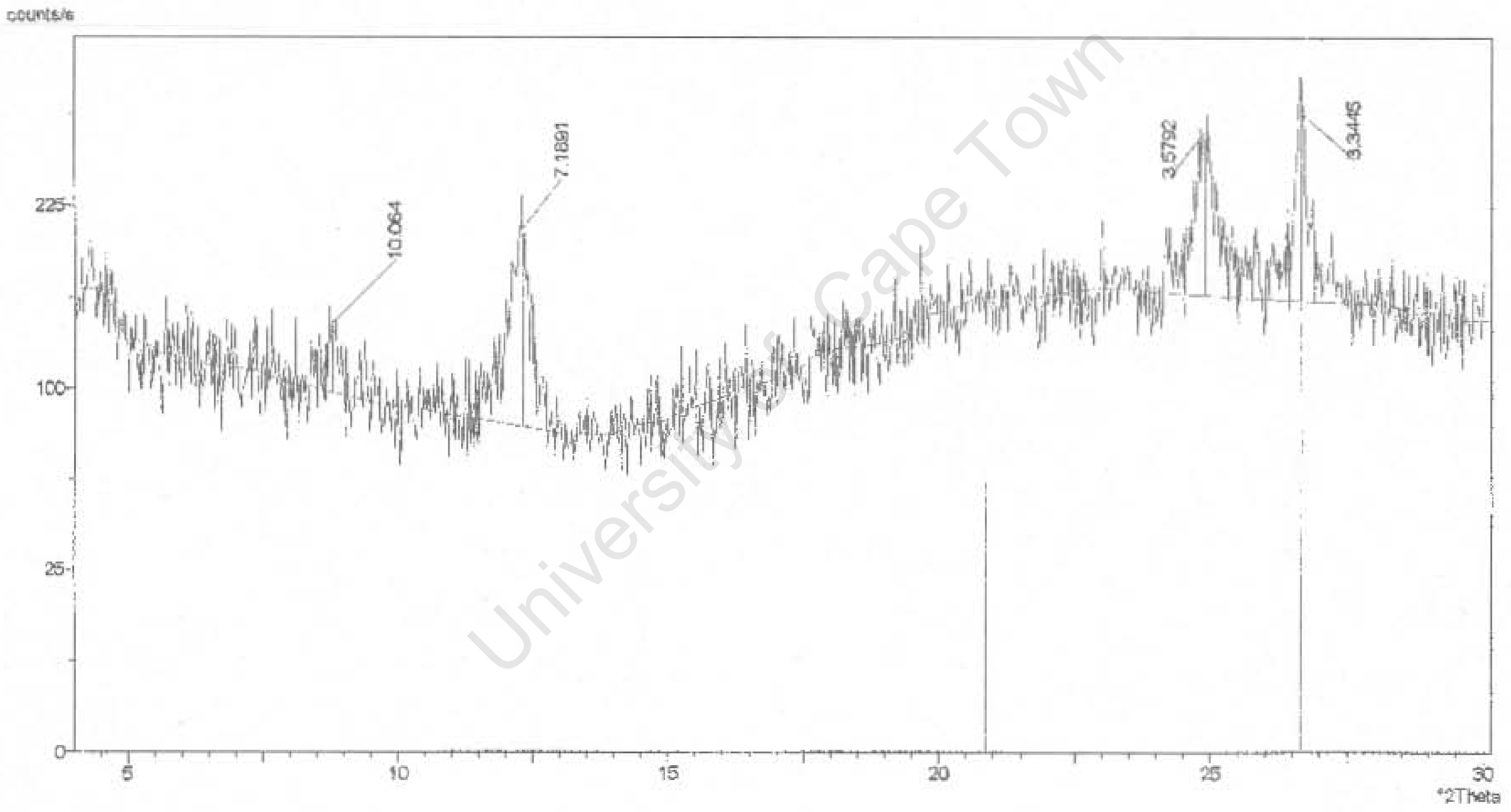

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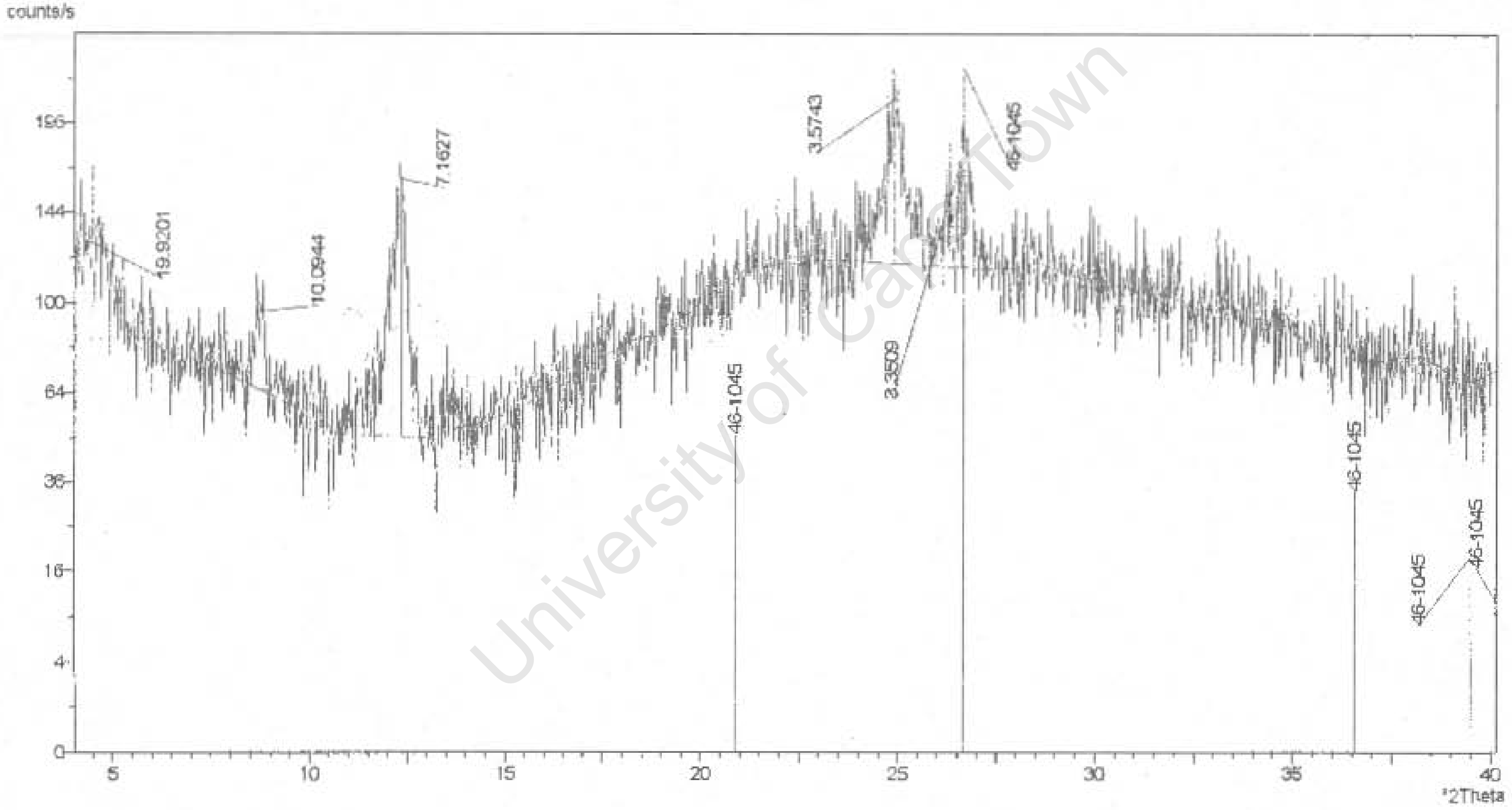

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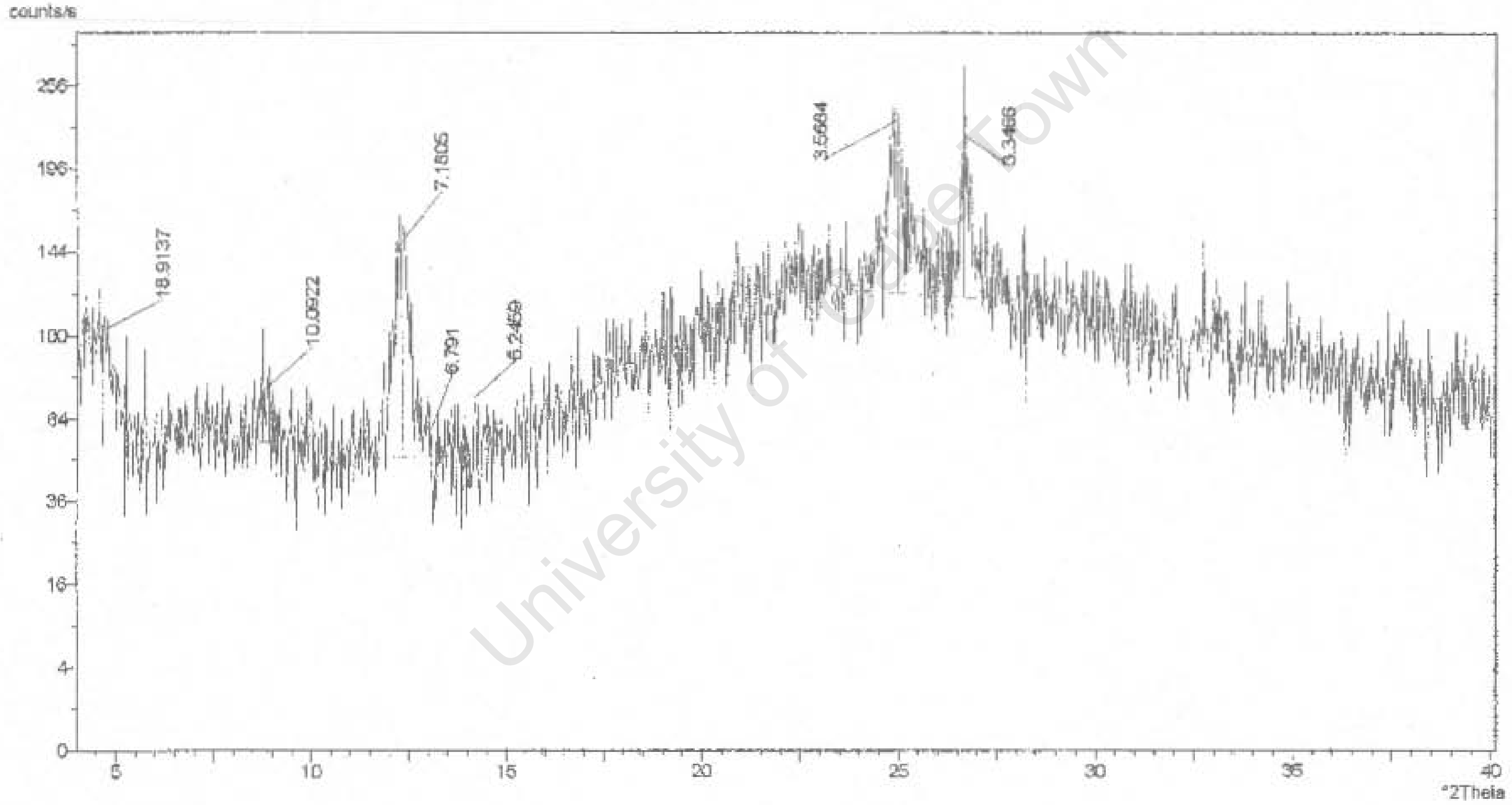

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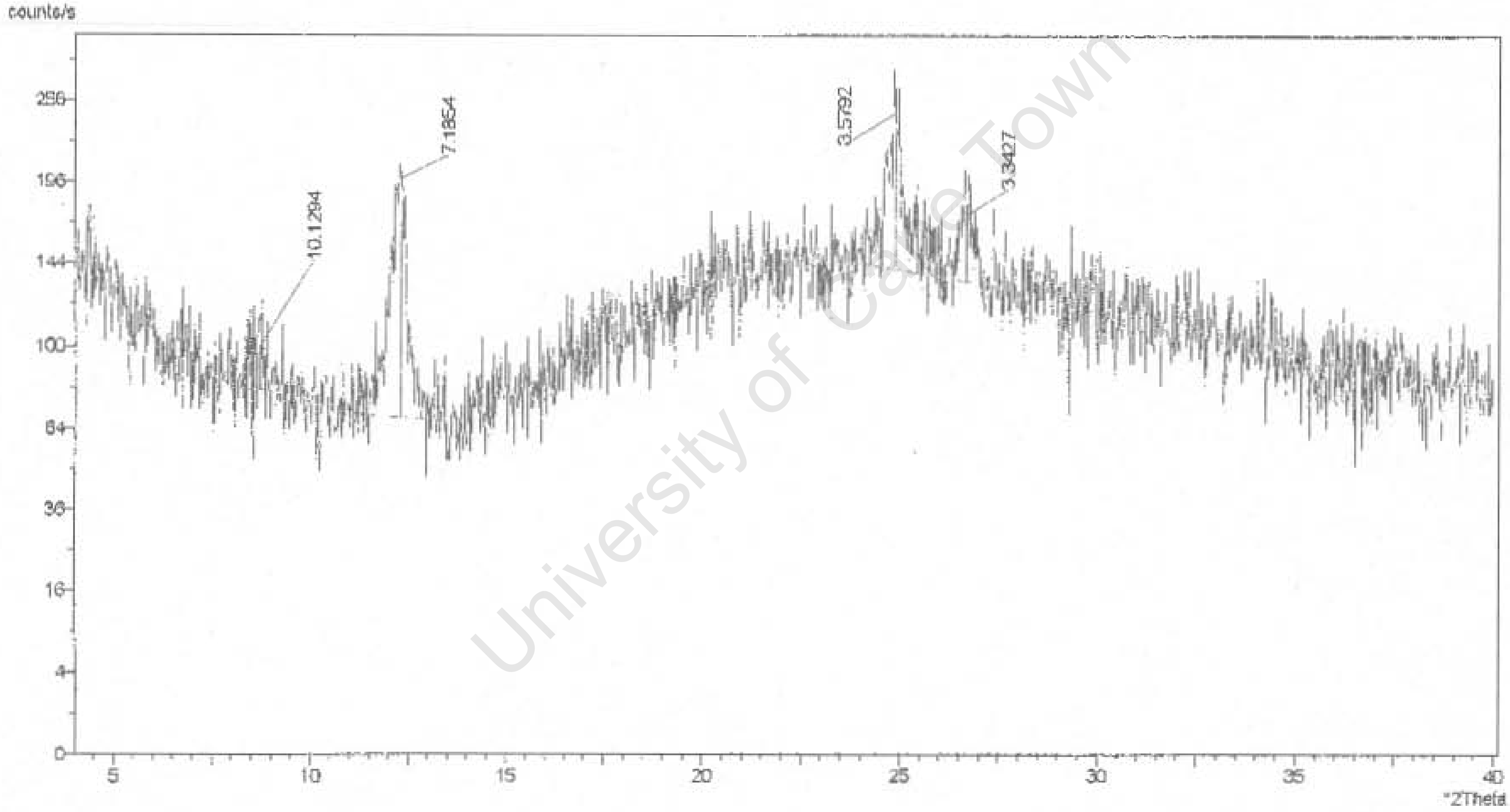

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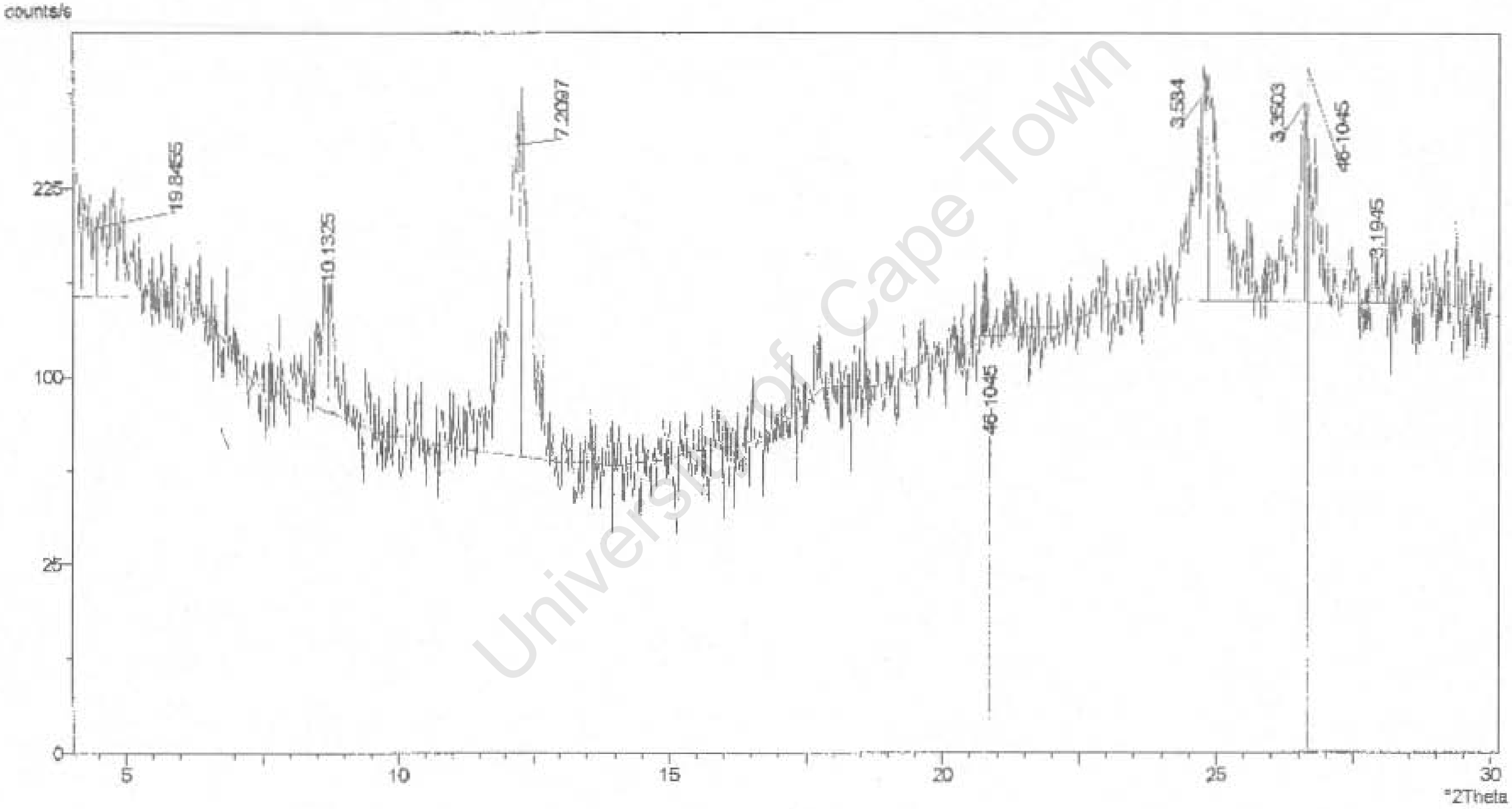
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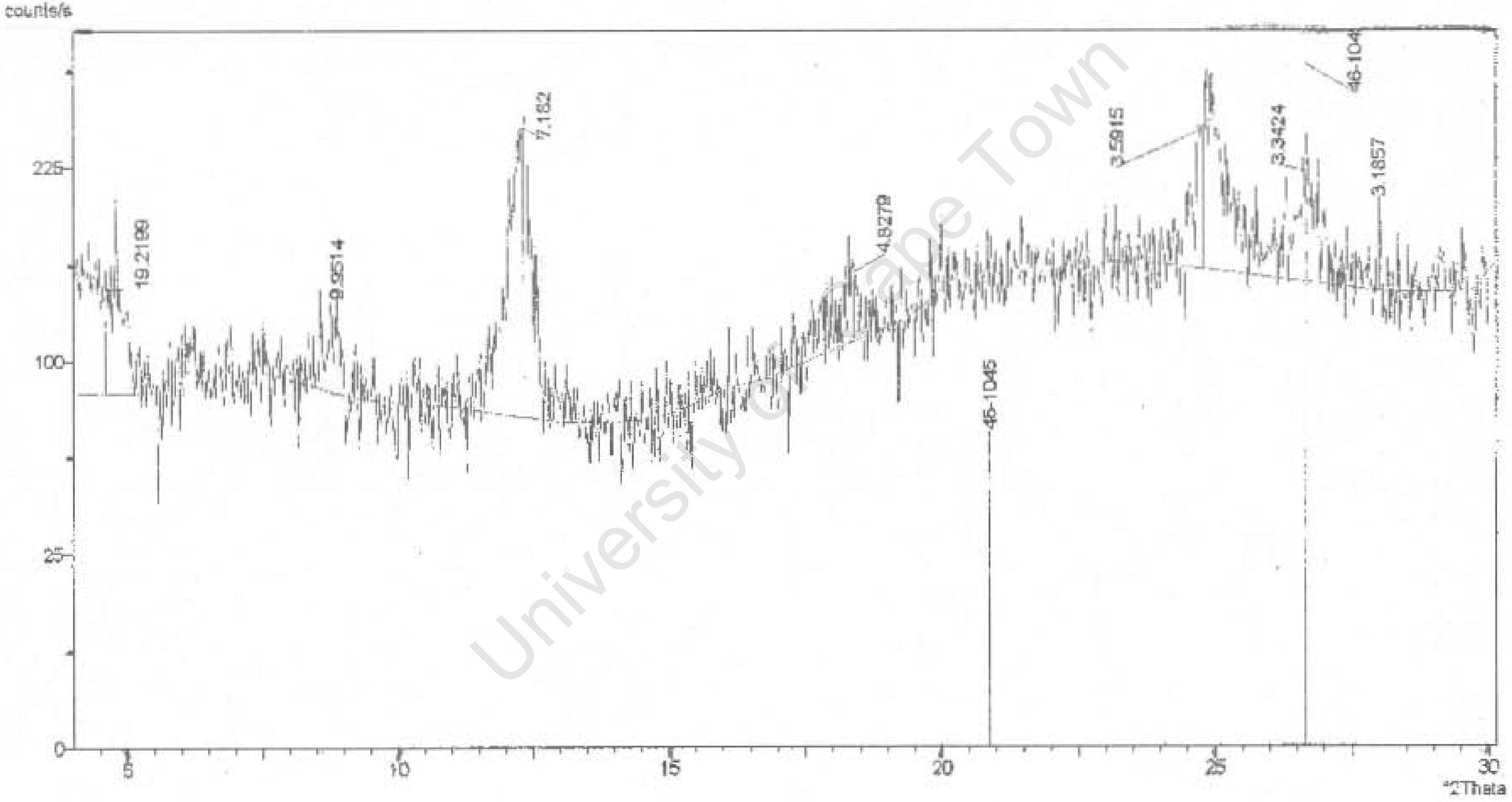

Philips Analytical

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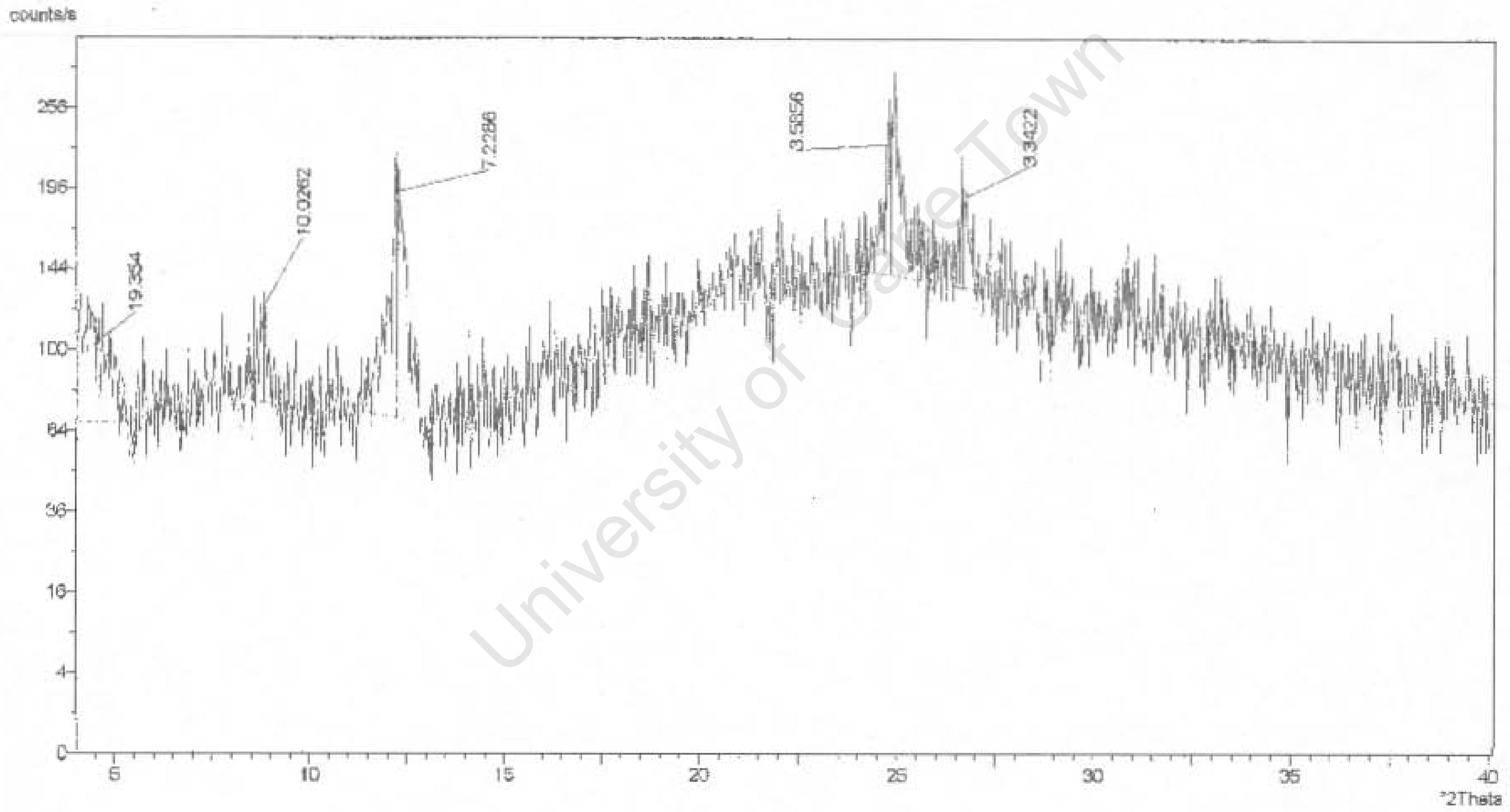

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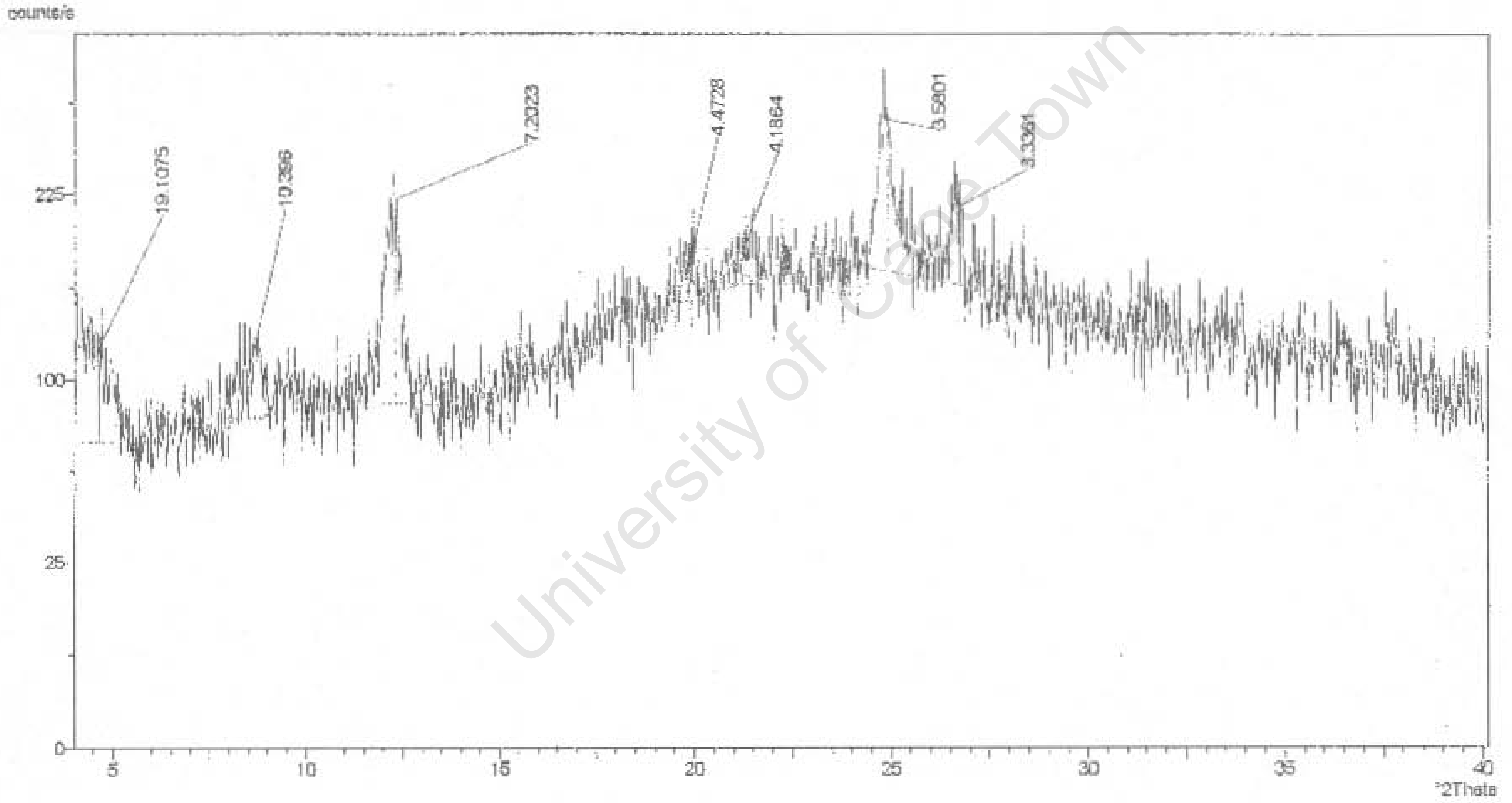

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Graph: P3(core sample)

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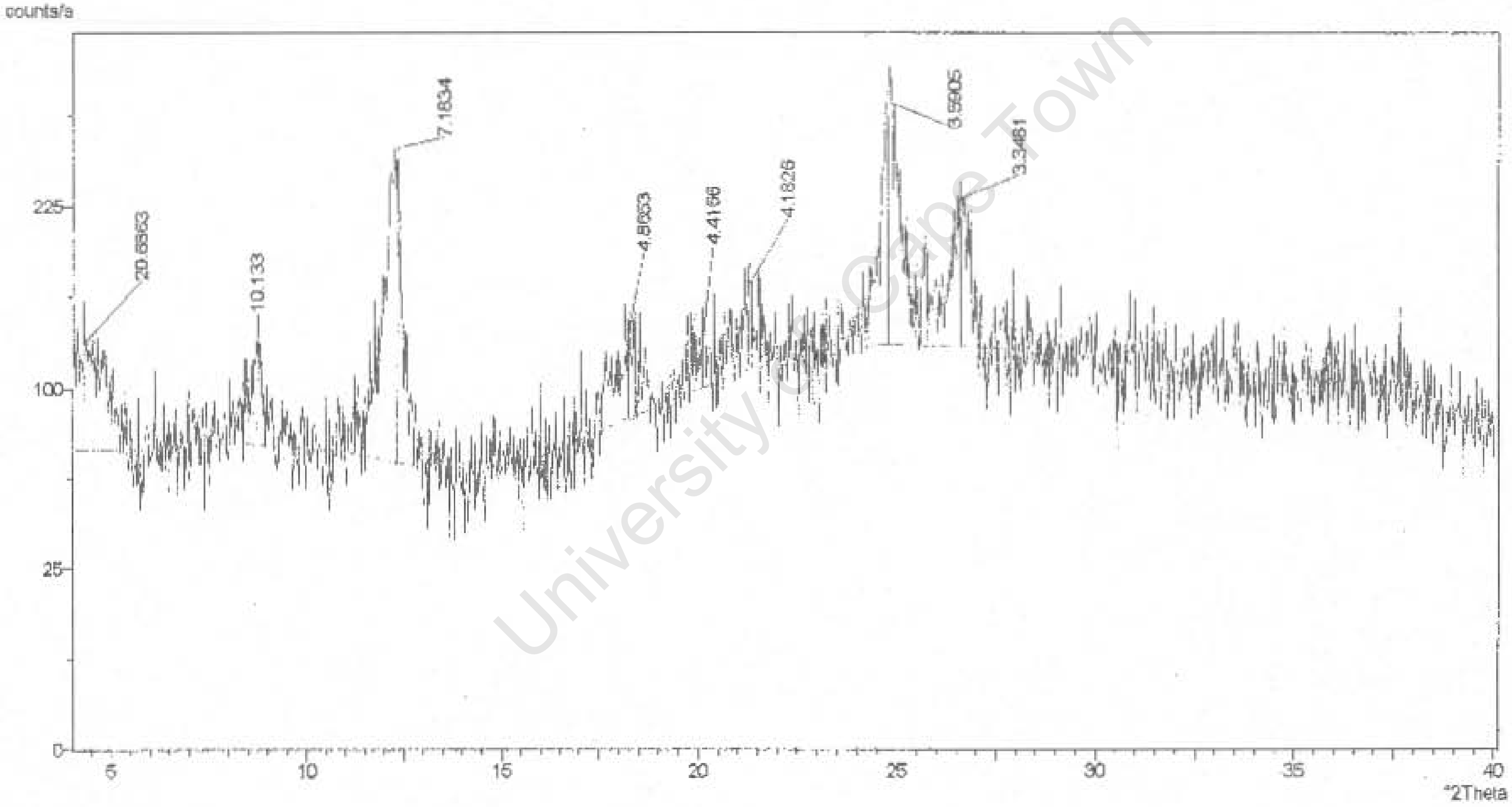

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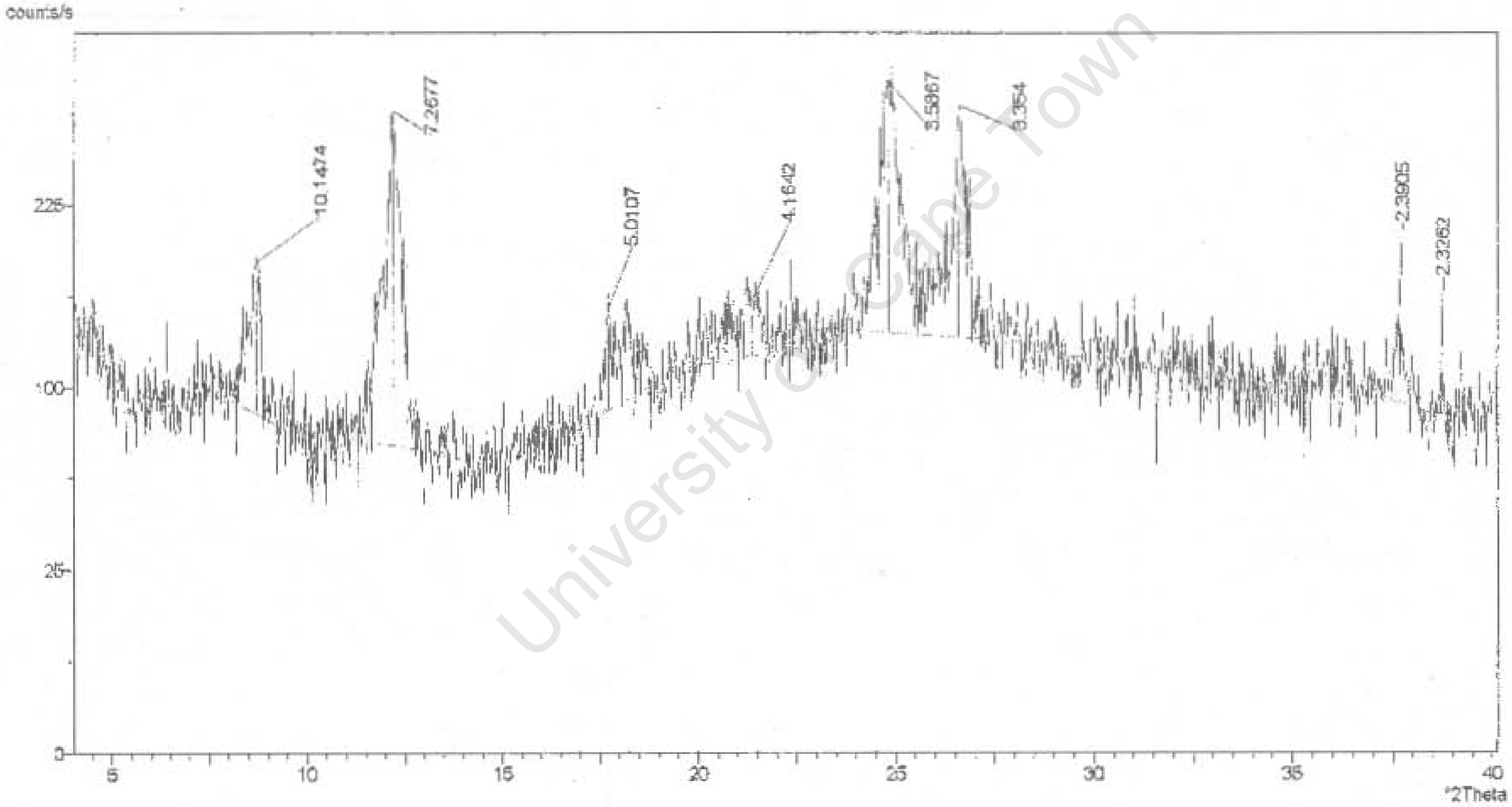

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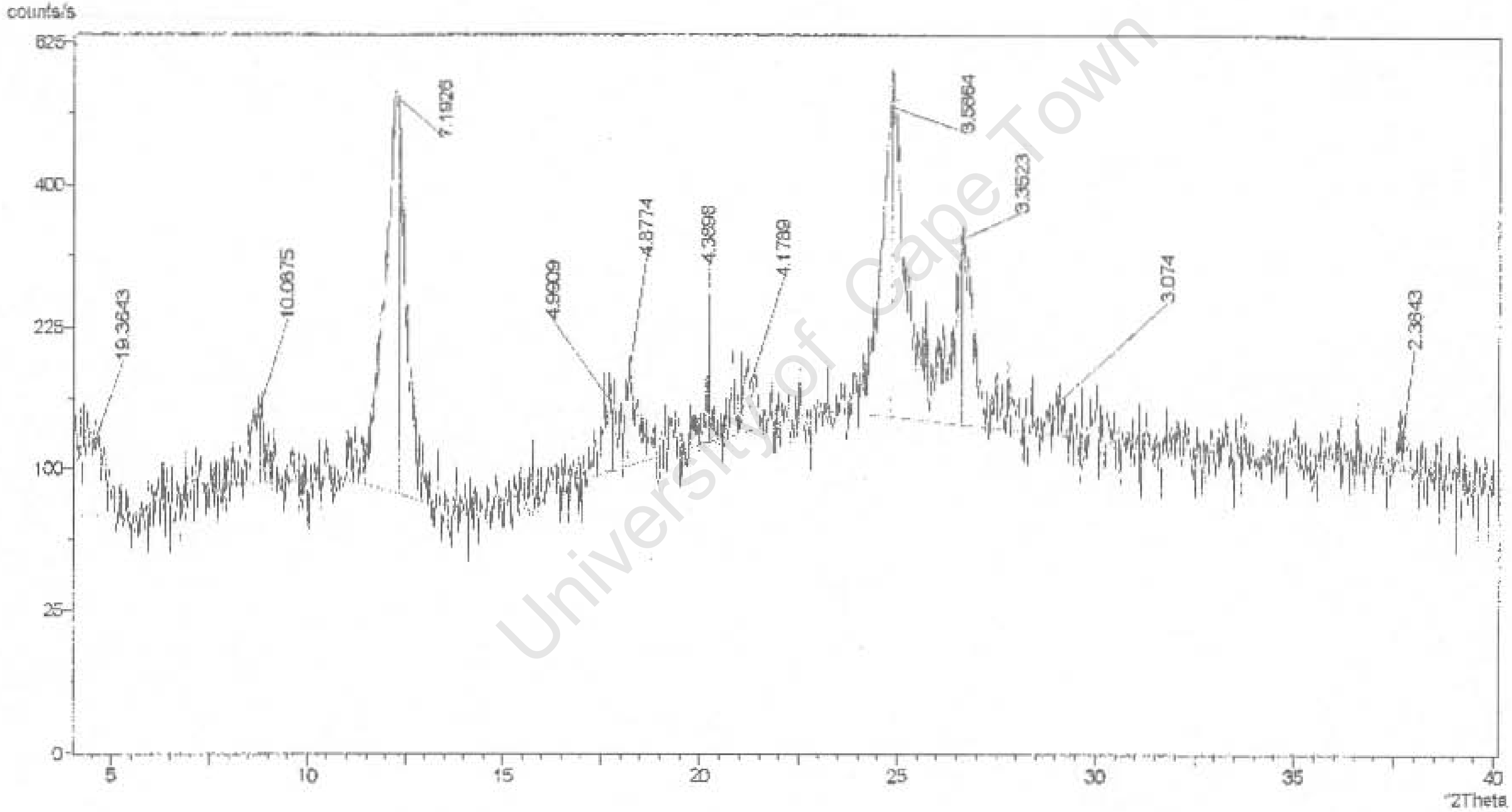

Philips Analytical

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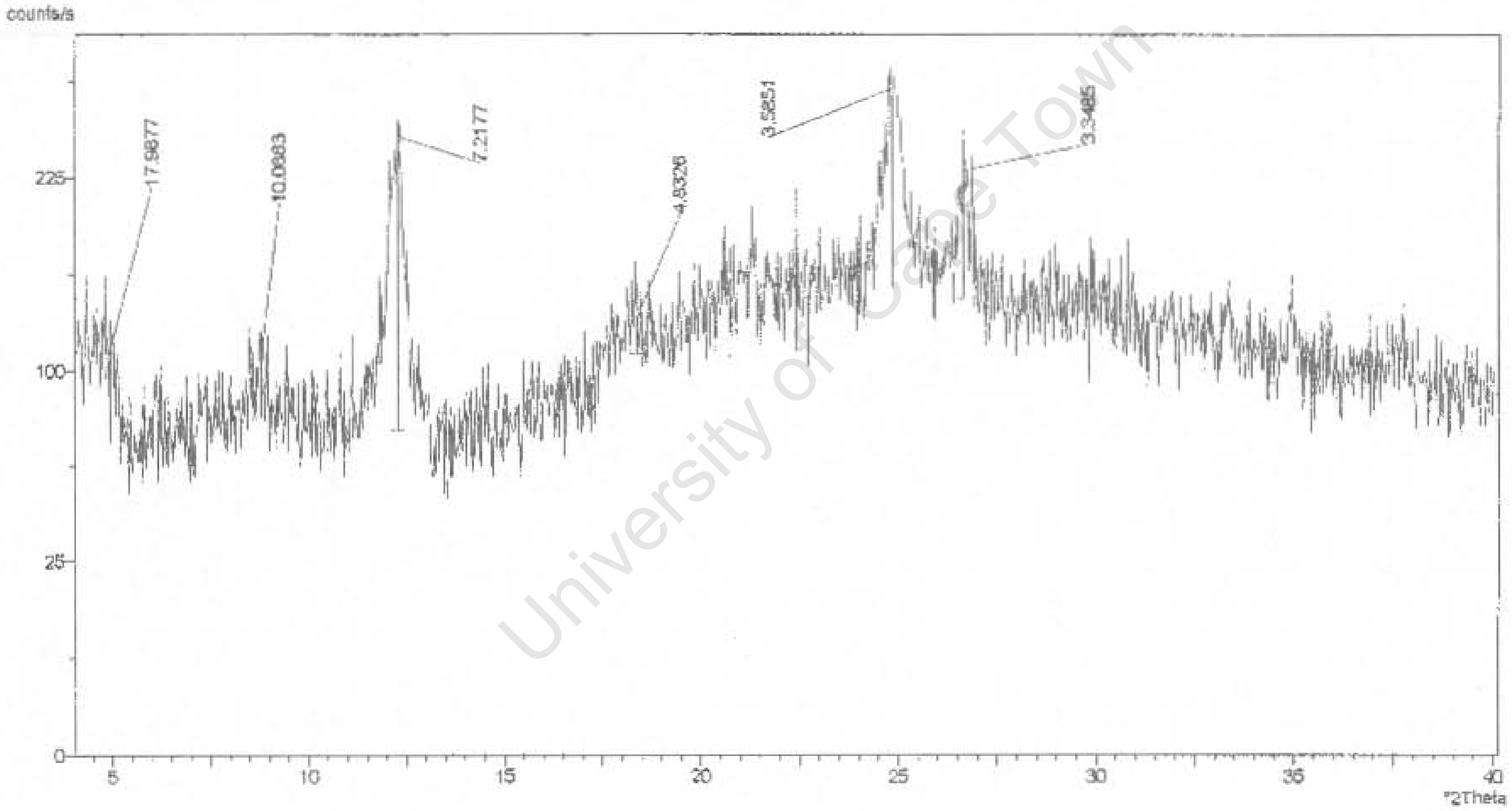

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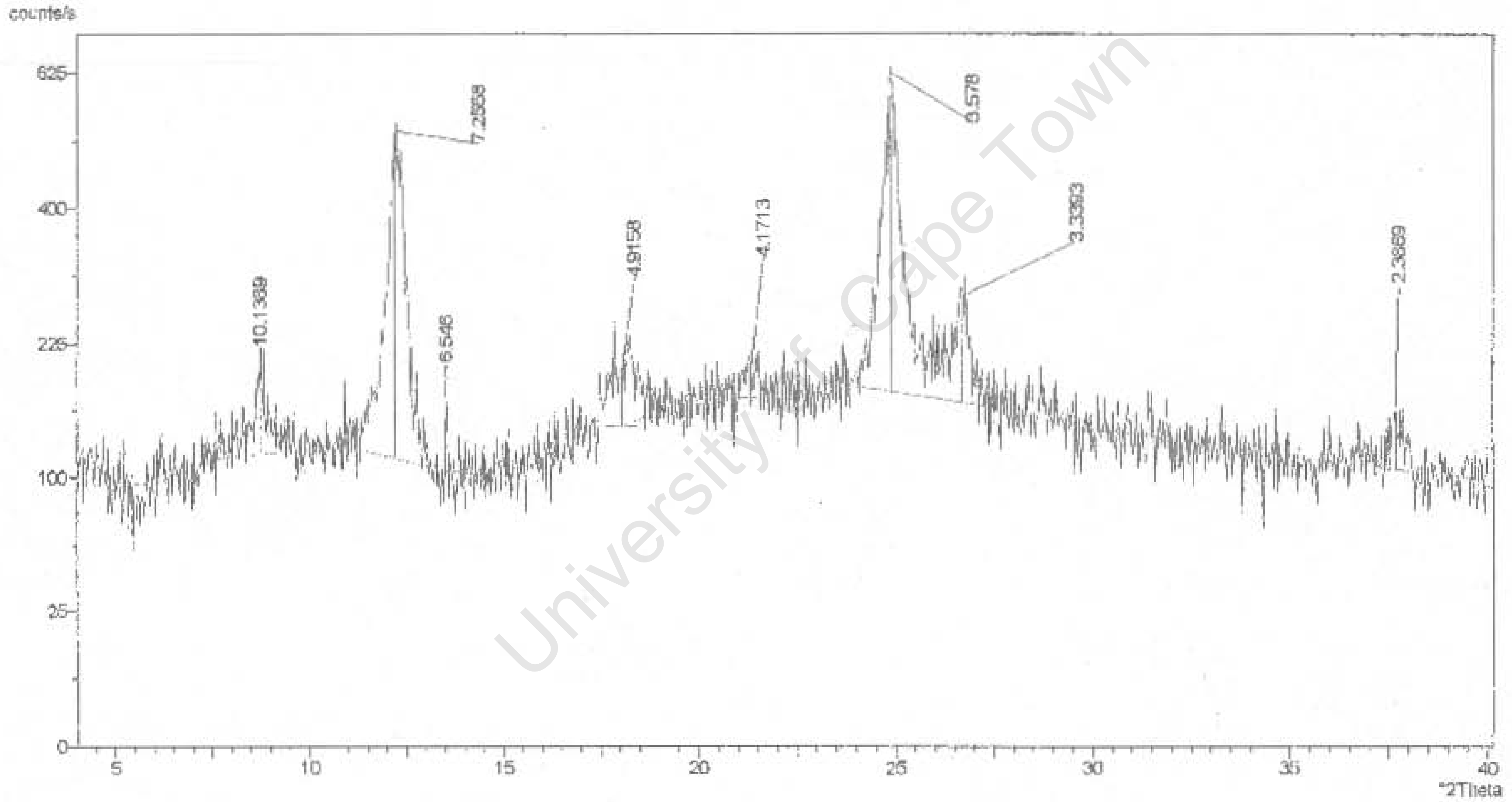

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Appendix 4

Whole sediment digestion graphs and associated analytical error for River sediment samples.

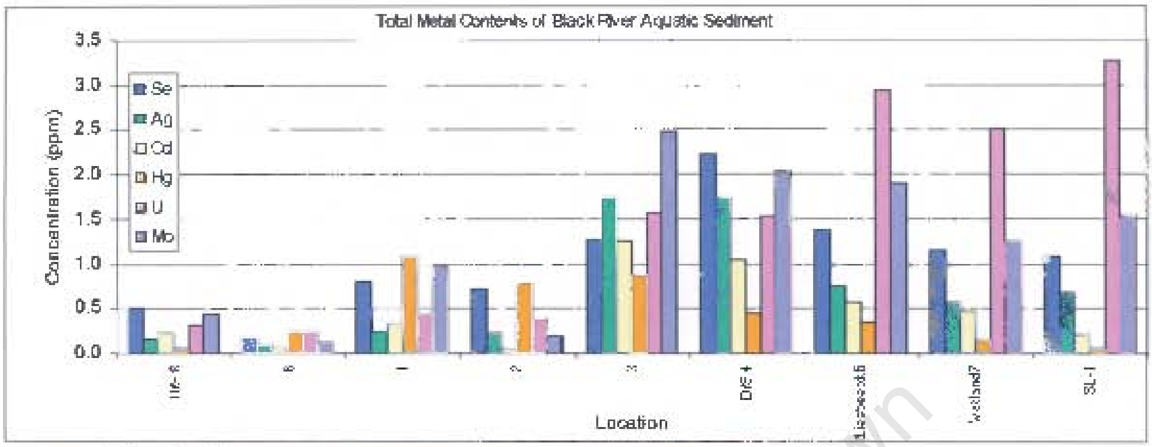

Figure A: Se, Ag, Cd, Hg, U, Mo concentrations in totally digested whole river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. SL-1 is the certified reference material.

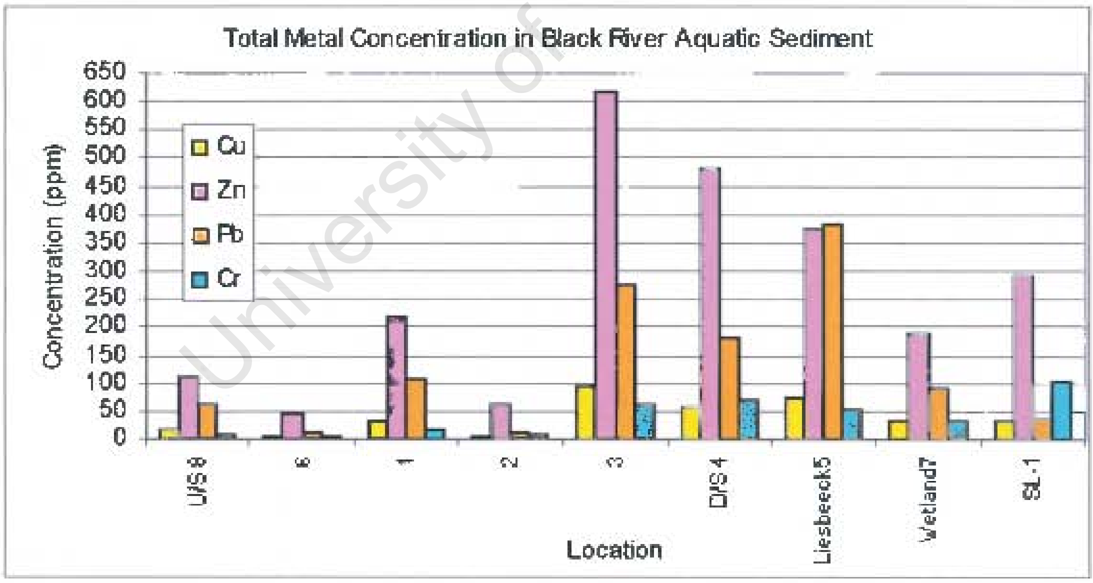

Figure B: Cu, Zn, Pb and Cr concentrations in totally digested whole river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. SL-1 is the certified reference material.

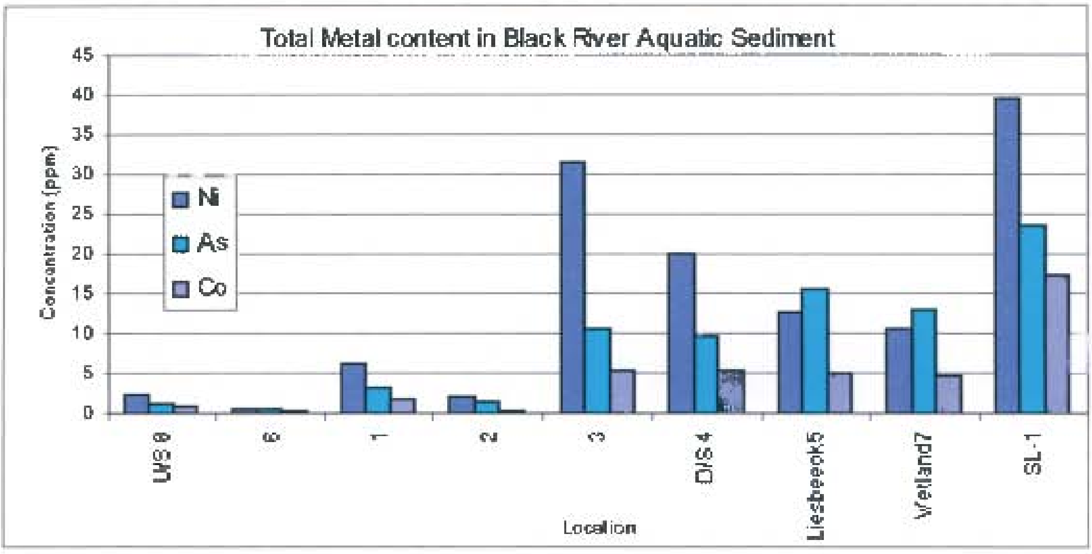

Figure C: Ni, As and Co concentrations in totally digested whole river sediment. Samples are in order from the most upstream, sample number 8 towards the most downstream, sample number 4. Sample 5 is from the Liesbeeck River, in line with number 4. The Raapenberg wetland, sample number 7, is adjacent to, and between sample 4 and sample 5. SL-1 is the certified reference material.

Table A: Analytical Error for Whole Digested River sediment samples at the 95% Confidence Limit (%P = (σ/mean)*200).

Means, σ and %P for three Duplicate Whole Digested River samples (Sample numbers 1, 3 & 7).

mg/kg soil	Cr	Mn	Ni	Co	Cu	Zn	As	Se	Rb	Sr	Mo	Ag	Cd	Sb	Hg	Tl	Pb	U
mean: 1	16.64	65.42	6.14	1.63	30.92	217.34	3.37	0.81	8.87	76.57	0.97	0.24	0.33	2.18	1.08	0.08	105.96	0.44
σ: 1	1.33	0.53	0.52	0.01	0.83	1.15	0.66	0.02	0.23	3.41	0.02	0.02	0.01	0.16	0.00	0.00	5.40	0.00
%P: 1	16.02	1.63	16.88	0.88	5.38	1.06	39.21	4.16	5.17	8.91	4.62	19.70	4.58	14.62	0.00	0.15	10.20	1.85
mean: 3	60.81	145.87	31.43	5.15	94.97	618.18	10.53	1.26	25.88	240.18	2.47	1.74	1.26	3.94	0.88	0.26	275.93	1.56
σ; 3	4.85	4.19	0.85	0.19	3.32	17.79	3.65	0.26	0.82	3.10	0.15	0.14	0.11	0.17	0.38	0.01	11.15	0.03
%P: 3	15.96	5.74	5.44	7.38	7.00	5.75	69.37	41.91	6.35	2.58	12.01	16.38	17.45	8.42	86.38	5.80	8.08	3.96
mean: 7	34.86	176.51	10.73	4.66	34.61	190.21	12.89	1.16	52.74	65.98	1.26	0.57	0.47	1.48	0.15	0.36	91.55	2.51
σ: 7	0.57	3.65	1.14	0.06	0.03	0.28	0.09	0.01	0.97	0.58	0.07	0.13	0.02	0.04	0.05	0.00	2.71	0.03
%P: 7	3.26	4.14	21.27	2.46	0.17	0.29	1.36	1.07	3.69	1.76	10.90	45.64	6.40	5.79	69.97	1.55	5.92	2.55

Appendix 5

Table A: Sampling Heterogeneity for porewater samples from the Raapenberg Wetland.

Element	PW1 (ppb)	PW2 (ppb)	mean (ppb)	st. dev. (σ)	%P((σ/mean)*200)
Cr	9.74	8.98	9.36	0.5400	11.54
Mn	609.0	689.0	648.98	56.5323	17.42
Fe	18999	17879	18438.83	792.1241	8.59
Ni	75.4	121.0	98.19	32.1867	65.56
Co	8.17	8.61	8.39	0.3117	7.43
Cu	21.44	25.66	23.55	2.9845	25.35
Zn	111.4	153.6	132.51	29.8670	45.08
As	18.17	18.85	18.51	0.4854	5.25
Se	17.94	18.77	18.36	0.5904	6.43
Mo	2.64	2.77	2.71	0.0933	6.89
Ag	0.06	0.05	0.05	0.0091	34.61
Cd	0.11	0.15	0.13	0.0238	36.45
Hg	0.43	0.33	0.38	0.0695	36.44
Tl	0.06	0.07	0.07	0.0094	28.45
Pb	64.26	68.68	66.47	3.1197	9.39

Table B: All elements analysed by ICP-MS and Analytical Error on duplicate analyses, for porewater samples from the Raapenberg Wetland. Mean concentrations in ppb or μg/l

Element	mean PW1	mean PW2	σ PW1	σ PW2	%P1	%P2	ave %P
Li	3.61	3.98	0.20	0.03	11.22	1.57	6.39
Be	1.24	1.23	0.33	0.50	52.90	80.94	66.92
B	555	583	4.60	19.98	1.66	6.85	4.25
Na	1125889	1257972	123567	312592	21.95	49.70	35.82
Mg	62749	62636	1699	571	5.41	1.82	3.62
Al	520	544	10.21	5.29	3.93	1.94	2.94
Si	7561	7607	77.29	94.32	2.04	2.48	2.26
K	28006	27657	699	423	4.99	3.06	4.03
Ca	69410	68960	1364	5622	3.93	16.30	10.12
Sc	2.93	2.56	1.16	0.66	79.14	51.29	65.21
Ti	108	111	0.99	5.34	1.83	9.58	5.70
V	16.35	17.57	1.49	3.06	18.18	34.78	26.48
Cr	9.74	8.98	2.67	1.04	54.91	23.18	39.04
Mn	609	689	0.68	15.29	0.22	4.44	2.33
Fe	18999	17879	555	881	5.84	9.86	7.85
Ni	75.43	121	7.95	5.74	21.08	9.49	15.29
Co	8.17	8.61	0.20	0.11	4.91	2.57	3.74
Cu	21.44	25.66	0.27	0.05	2.50	0.37	1.44
Zn	111	154	0.23	1.07	0.41	1.39	0.90
Ga	3.02	2.94	0.00	0.05	0.17	3.28	1.72
As	18.17	18.85	0.38	0.46	4.21	4.92	4.56
Se	17.94	18.77	0.01	0.79	0.09	8.43	4.26
Rb	11.80	12.35	0.03	0.21	0.43	3.39	1.91
Sr	735	787	4.16	2.31	1.13	0.59	0.86
Y	1.25	1.42	0.02	0.11	3.84	15.33	9.58
Zr	3.03	3.21	0.16	0.05	10.64	3.14	6.89
Mo	2.64	2.77	0.14	0.09	10.58	6.24	8.41
Ag	0.06	0.05	0.02	0.02	79.46	78.92	79.19
Cd	0.11	0.15	0.01	0.00	14.74	6.20	10.47
Sb	5.71	5.57	0.24	0.04	8.46	1.30	4.88
Cs	0.07	0.07	0.00	0.01	9.25	21.36	15.30
Ba	99.50	96.45	0.44	1.79	0.89	3.71	2.30
La	1.17	1.27	0.03	0.01	4.74	0.93	2.83
Ce	3.16	3.47	0.05	0.03	2.92	1.77	2.35
Nd	1.48	1.62	0.02	0.01	3.01	0.67	1.84
W	1.15	1.12	0.17	0.06	29.47	10.67	20.07
Hg	0.43	0.33	0.28	0.07	131.98	43.10	87.54
Tl	0.06	0.07	0.00	0.01	7.93	25.36	16.64
Pb	64.26	68.68	0.86	1.80	2.69	5.25	3.97
Th	0.39	0.43	0.01	0.01	6.84	4.43	5.64
U	0.72	0.76	0.01	0.03	2.11	7.83	4.97

Appendix 6

Temporal variation of concentrations during four steps of the sequential extraction procedure.

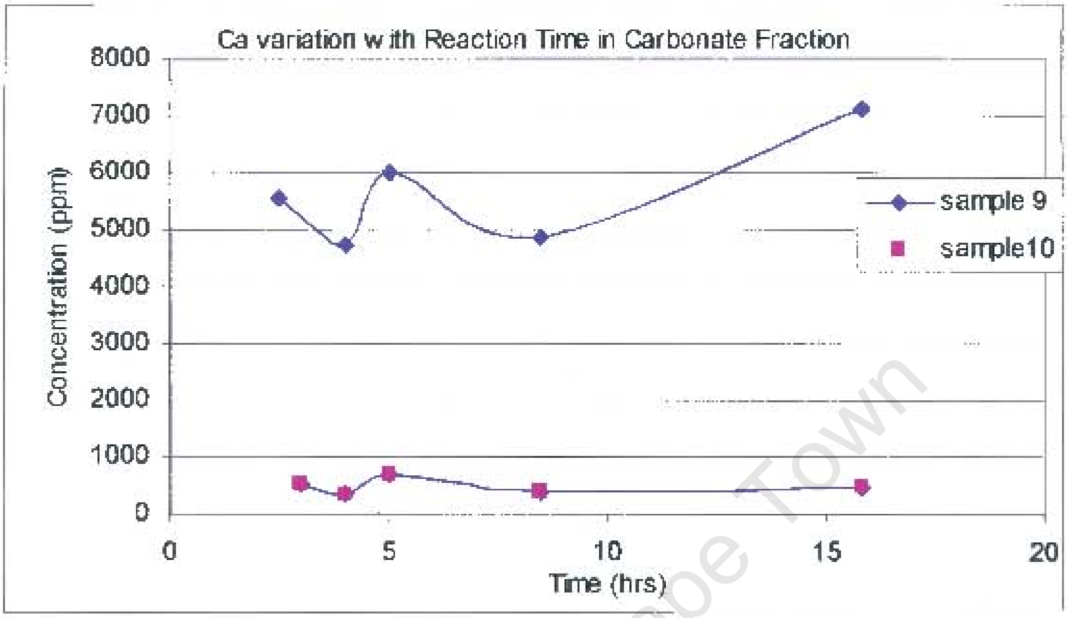

Figure 28: Temporal variation of Ca concentration in the supernatant in the second extraction step (carbonates). Reagent = 1 M NaOAc at pH 5 (with HOAc) added at 0 hrs. Total prescribed reaction time for this extraction step is 5 hours. All other samples reacted for 6 hrs for the river sediment and 5 hrs for the wetland core.

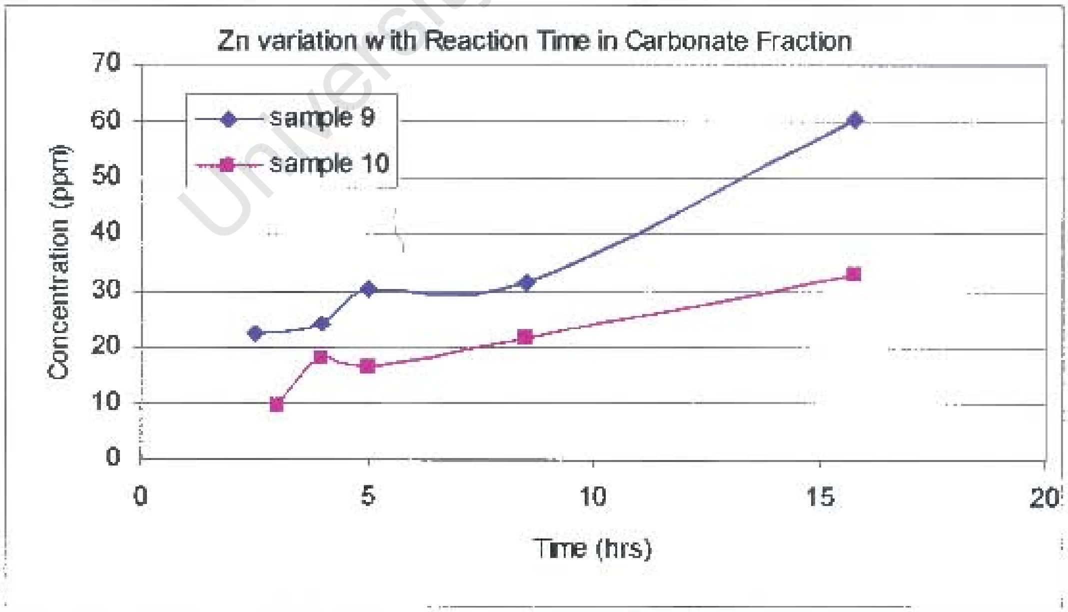

Figure 29: Temporal variation of Zn concentration in the supernatant in the second extraction step (carbonates). Reagent = 1 M NaOAc at pH 5 (with HOAc) added at 0 hrs. Total prescribed reaction time for this extraction step is 5 hours. All other samples reacted for 6 hrs for the river sediment and 5 hrs for the wetland core.

Figures 28 and 29 show the variation of Ca and Zn with time, in the supernatants for the second extraction step. Ca shows two adsorption events for these two river samples (samples 9 and 10, duplicates of samples 1 and 7). The Zn follows the Ca concentrations, implying that it is being released from the carbonate as it dissolves. The river samples were reacted for a total of 6 hours, and the wetland samples were reacted for 5 hours. This appears to be on the peak of desorption, which is desirable. Other trace metals show the same trend and follow the Ca concentration.

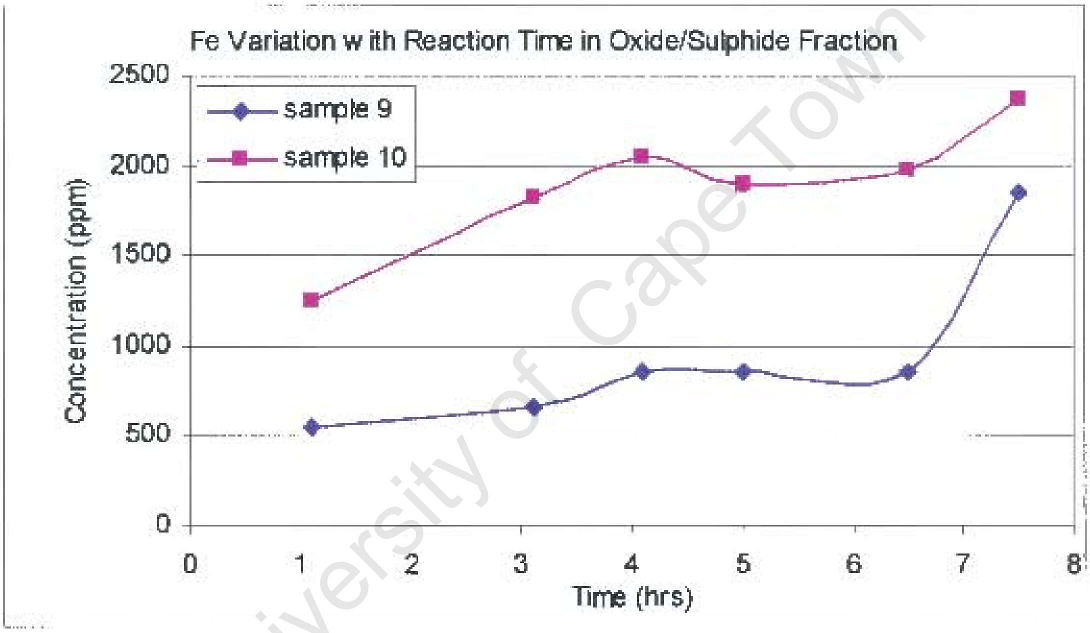

Figure 30: Temporal variation of Fe concentration in the supernatant in the third extraction step (Fe/Mn oxides or AVS fraction). Reagent = 20 ml of 0.04 M NH2OH.HCl in 25% v/v HOAc was added at 0 hrs and reacted at 96°C. Total prescribed reaction time for this extraction step is 6 hours. All river and wetland core sediment were reacted for 6 hrs.

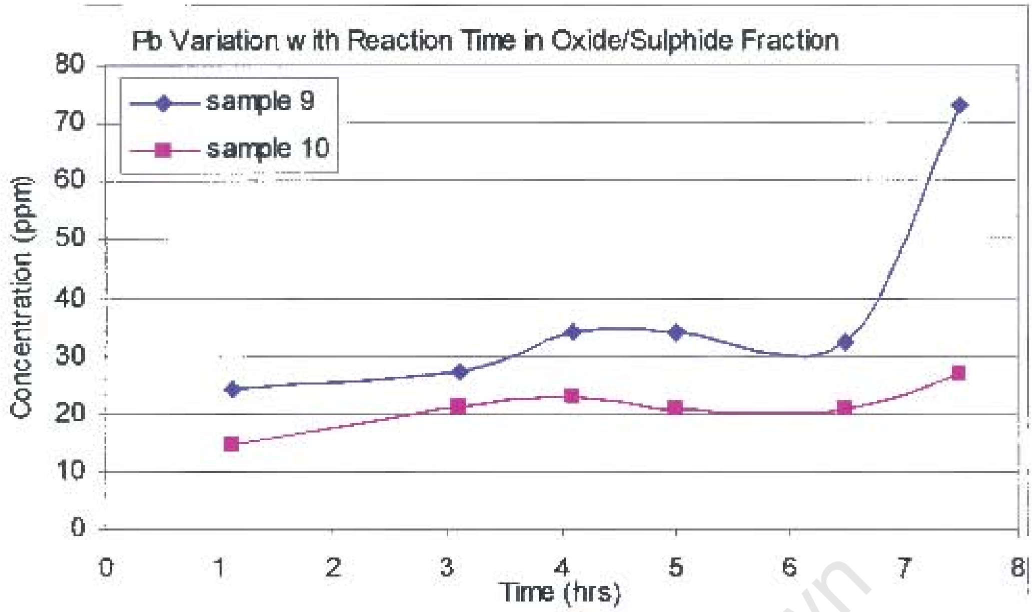

Figure 31: Temporal variation of Pb concentration in the supernatant in the third extraction step (Fe/Mn oxides or AVS fraction). Reagent = 20 ml of 0.04 M NH2OH.HCl in 25% v/v HOAc was added at 0 hrs and reacted at 96°C. Total prescribed reaction time for this extraction step is 6 hours. All river and wetland core sediment were reacted for 6 hrs.

Figures 30 and 31 show the variation of Fe and Pb with time for the third extraction step in two supernatants. Again, the trace element closely follows the major element concentration, and this is the case for all trace metals examined. All samples sequentially extracted were reacted for six hours, which is close to the peak concentration in the 0 to 6 hour reaction time.

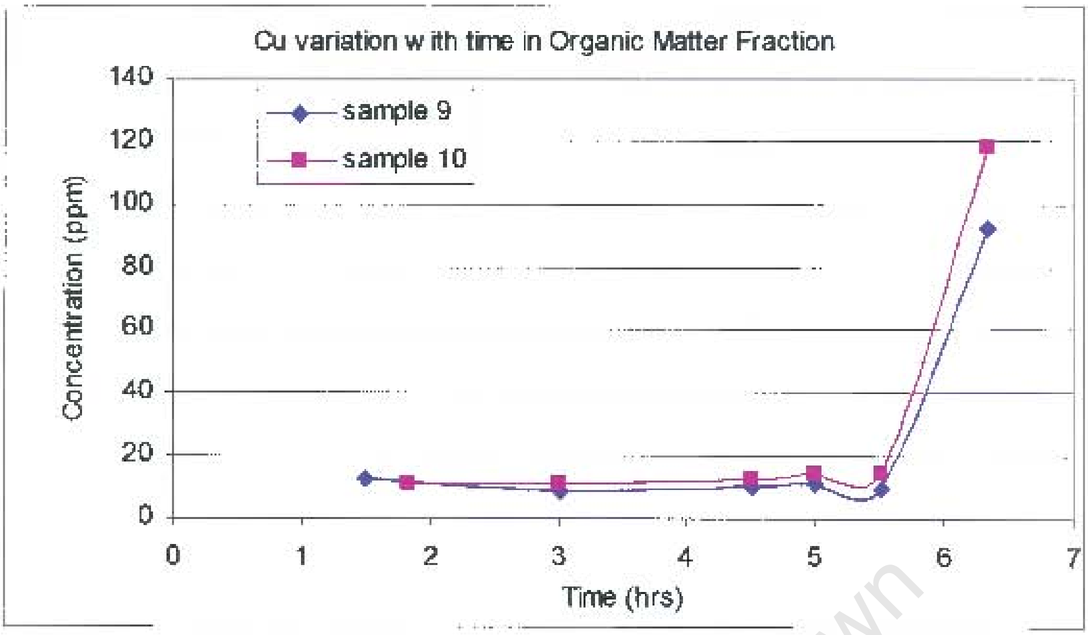

Figure 32: Temporal variation of Cu concentration in the superoatant in the fourth extraction step (organic fraction). Reagent = 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 at pH 2 was added at 0 hrs, 3 ml of 30% H_2O_2 at pH 2 was added at 2 hrs. Reacted till 5 hrs at 85°C. 5 ml 3.2 M NH4OAc in 20% v/v HNO3 added at 5 hrs. Total prescribed reaction time for this extraction step is 5.5 hours. All river and wetland core sediment were reacted for 5.5 hrs.

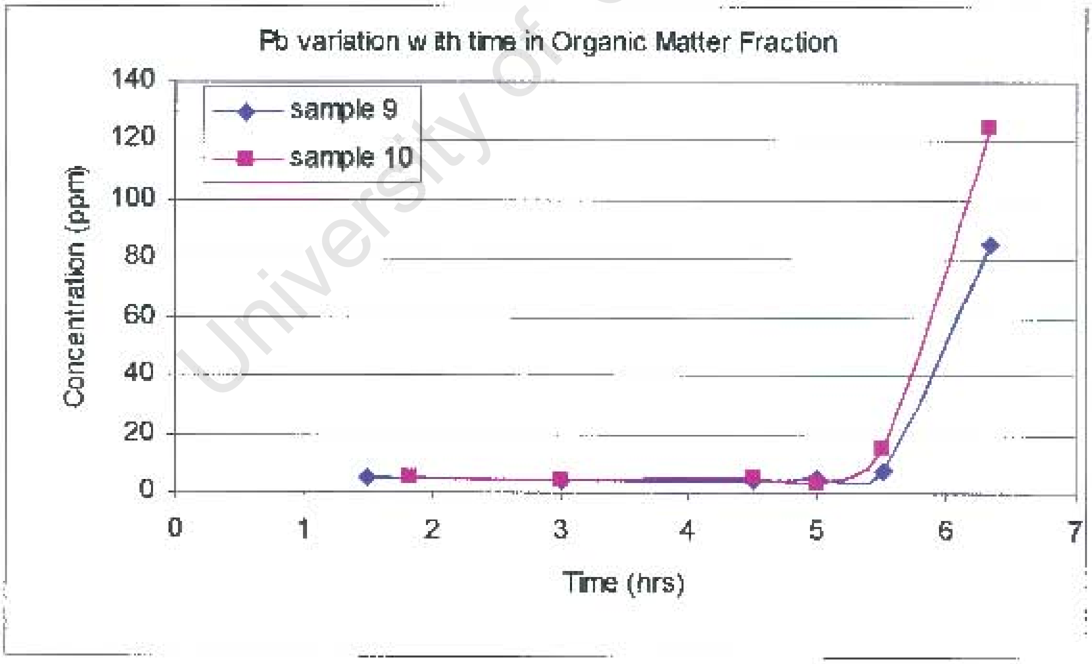

Figure 33: Temporal variation of Pb concentration in the supernatant in the fourth extraction step (organic fraction). Reagent = 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 at pH 2 was added at 0 hrs, 3 ml of 30% H_2O_2 at pH 2 was added at 2 hrs. Reacted till 5 hrs at 85°C. 5 ml 3.2 M NH4OAc in 20% v/v HNO3 added at 5 hrs. Total prescribed reaction time for this extraction step is 5.5 hours. All river and wetland core sediment were reacted for 5.5 hrs.

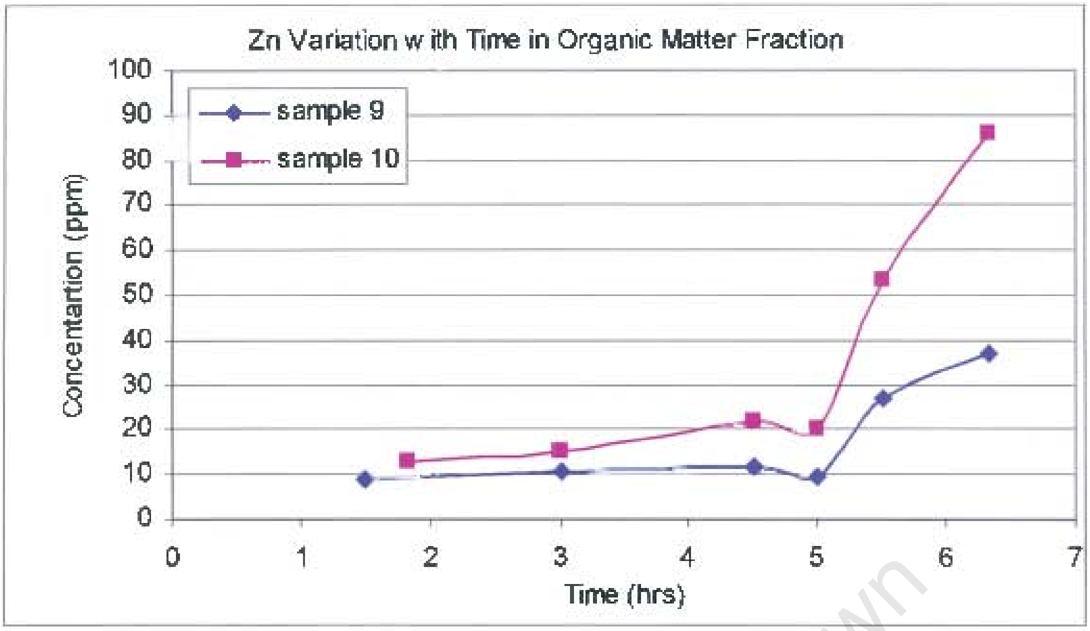

Figure 34: Temporal variation of Zn concentration in the supernatant in the fourth extraction step (organic fraction). Reagent = 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 at pH 2 was added at 0 hrs, 3 ml of 30% H_2O_2 at pH 2 was added at 2 hrs. Reacted till 5 hrs at 85°C. 5 ml 3.2 M NH4OAc in 20% v/v HNO3 added at 5 hrs. Total prescribed reaction time for this extraction step is 5.5 hours. All river and wetland core sediment were reacted for 5.5 hrs.

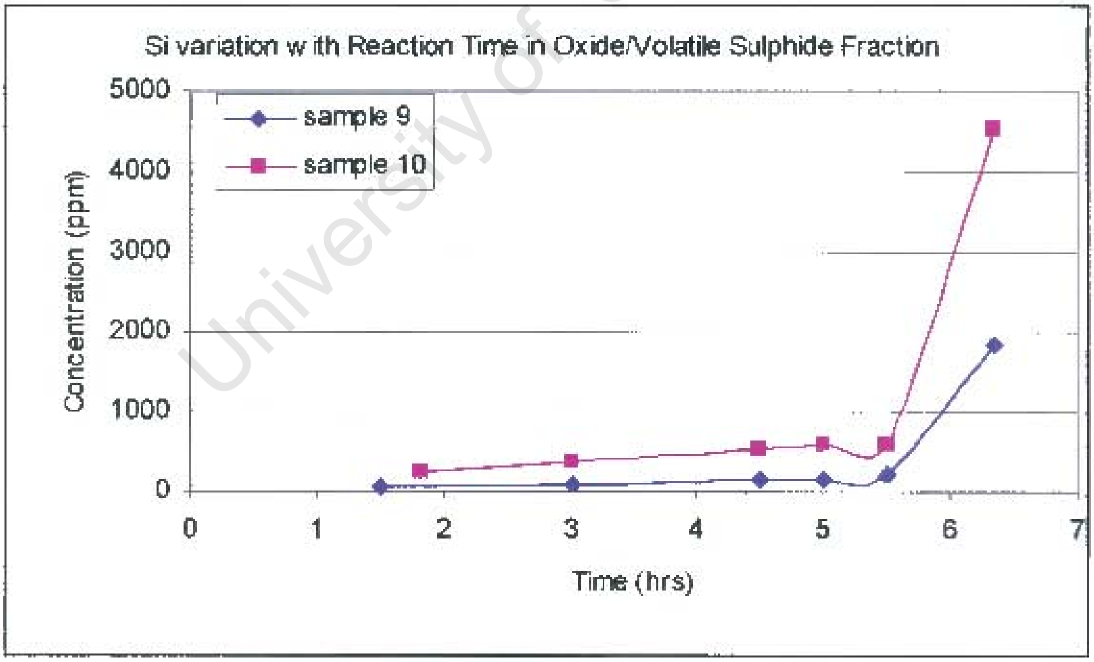

Figure 35: Temporal variation of Si concentration in the supernatant in the third extraction step (Fe/Mn oxide or AVS fraction). Reagent = 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 at pH 2 was added at 0 hrs, 3 ml of 30% H_2O_2 at pH 2 was added at 2 hrs. Reacted till 5 hrs at 85°C. 5 ml 3.2 M NH4OAc in 20% v/v HNO3 added at 5 hrs. Total prescribed reaction time for this extraction step is 5.5 hours. All river and wetland core sediment were reacted for 5.5 hrs.

Figures 32, 33, 34, 35 shows the Cu, Pb, Zn and Si variation for the fourth extraction step in two supernatants. The Si (**Fig. 35**) indicates that the residual silicate lattice is not attacked until after the 5.5 hours. All samples that were sequentially extracted, both the river and core samples, were reacted till the 5.5 hours. This is a lengthy step involving several reagent additions and the reaction time does not imply one uninterrupted step. The last aliquot of reagent added is 3.2M NH_4OAc in 20% v/v HNO_3 at 5 hours, which then begins to attack the silicate lattice at reaction times exceeding 5.5 hours. Most trace metal concentrations follow the major element concentration trend for all four fractions. Only Zn appears to reflect some liberation from the residual fraction of the sediment just before 5.5 hours in fraction 4 (**Fig. 34**). It is thus probable, that this very mobile and semi-volatile metal (MacBride, 1994) has been liberated partially from the residual fraction, during the extraction step intended to dissolve the organic matter. This may indicate that for certain metals, the residual fraction of metal may be as available as the organic fraction of other metals.