

**BIOMONITORING OF METAL CONTAMINATION IN  
THE LOWER DIEP RIVER, MILNERTON, WESTERN  
CAPE**

**BY**

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**Cape Town**

**April 2008**

## DECLARATION

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I Likentso Sylvia Shuping, declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed -----

Date 03-04-2008-----

## ABSTRACT

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The lower Diep River is a major freshwater ecosystem in the Western Cape. The river is surrounded by many possible sources of metal pollution such as an oil refinery, industries, a sewage treatment plant and a landfill site. However, metal contamination levels have not been monitored in this river. The aim of the study was therefore to monitor the degree of metal pollution in the lower Diep River, over a period of one year, and to investigate the use of the sedge *Bolboschoenus maritimus*, as biomonitor species.

Three sampling sites were used. Site 1 was located in the vicinity of landfill sites and farm areas. Site 2 was located 1 km upstream from a wetland reserve, surrounded by heavy industrial activity and continuous residential developments. Site 3 was located downstream of the wetland reserve, 2 km from the river mouth. The following metals were investigated: aluminium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel and zinc. Water and sediment samples were collected every two months for a period of one year. Plant specimens (roots, leaves and stems) were collected seasonally from site 1 and site 3. Samples were acid digested and metal analysis was done using an ICP – AES (Inductively Coupled Plasma- Atomic Emission Spectrophotometer). Statistical analyses were done to investigate possible differences between the sites, sampling occasions and various plant components.

The results showed that the water of the lower Diep River is contaminated in terms of aluminium, copper, zinc, manganese and iron, as their concentrations were higher than the DWAF guidelines for aquatic ecosystems at all sites. The high levels of these metals could pose a threat to the health of the ecosystem. The metals that were below detectable levels may also pose a similar threat, even if present in minute quantities. They may possibly be highly bioavailable to freshwater organisms and could lead to toxic effects at various levels of biological organisation. Metal concentrations in sediments were generally significantly higher at site 2 and significantly lower at site 3, compared to the other sites. The concentrations in the sediment of site 2 were generally high, compared to the Canadian Sediment Quality Guidelines (CSQG) and other South African studies. It seems that metals, originating from surrounding metal

sources (e.g. industries), settle into the sediments at a faster rate than they are washed downstream. Closer to the mouth of the river, large concentrations of metals have already been accumulated by plants such as *Bolboschoenus maritimus*, lessening the threat to the estuary. However, these accumulated metals have of course not been taken out of the ecosystem and, with decomposition of plants, and via food chains, these metals still pose a threat to the ecosystem.

Plant results revealed greater metal bioaccumulation by plants from site 3. This indicates higher bioavailability of metals at this site, which was probably influenced by salinity levels. Sediment clay content at site 1 probably played a major role in making metals less available to plants.

The results showed that *B. maritimus* is a root accumulator, as higher concentrations of metals were found in roots than in above-ground tissues. The distribution of metals from the roots to other plant parts was probably mainly influenced by factors such as seasonality and translocation of metals, as a result of a demand for essential micronutrients in the above-ground parts, limited storage capacity of the roots, saline river conditions and the presence of other metals in the plant.

Seasonal variations in metal concentrations in *B. maritimus* roots were observed, as well as some concentration peaks, but these did not follow similar patterns between the different metals or between the two sites. Neither did the results correspond with seasonal sediment concentrations. Again, the significance of bioavailability was highlighted.

Although root concentrations mostly did not indicate the actual level of contamination in the environment (sediment), or changes in contamination levels over time, using *B. maritimus* as test species in this study did provide additional information, that soil analyses alone could not have provided, namely the bioavailability of the metals in the sediment and water. With such mixed results it is therefore not possible to make final conclusions about the effective use of *B. maritimus* as biomonitor species in an environment such as the lower Diep River. More extensive research is needed.

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- Last but not least, I would like to thank the National Research Foundation for financial assistance. Opinions expressed in this thesis and the conclusions arrived at, are those of the author, and are not necessarily to be attributed to the National Research Foundation.

## **DEDICATION**

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This goes to my husband for encouraging and supporting me throughout the journey of this thesis. Also my mother for her words of encouragement. I love you.

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## GLOSSARY

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**DWAF:** Department of Water Affairs and Forestry.

**CCME:** Canadian Council of Ministers of the Environment.

**ISQG:** Interim Sediment Quality Guidelines.

**CSQG:** Canadian Sediment Quality Guidelines.

**ICP-AES:** Inductively Coupled Plasma-Atomic Emission Spectrophotometer.

**TDS:** Total dissolved solids.

**TWQR:** Target Water Quality Range.

**Bioaccumulation:** The process by which substances are accumulated by aquatic organisms from all routes of exposure (CCME, 2001).

**Pollutant:** An environmental chemical which exceeds normal background levels and has the potential to cause harm (Walker et al., 1996).

**Bioavailability:** Measure of the potential of a chemical for entry into ecological or human receptors (Lanno, 2003).

**Biomonitor:** A species that provides additional information about the health of an environment, that environmental analyses alone (e.g. soil analyses) cannot provide (Madejón et al., 2006b; Mertens et al., 2006).

**Biomarker:** Any biological response to an environmental chemical below individual level, measured inside an organism or in its products (urine, faeces, hairs, feathers, etc.), indicating a departure from the normal status, that cannot be detected from the intact organism (Van Gestel and Van Brummelen, 1996).

Rivers and wetlands play a significant role in human lives (Elangovan et al., 1999). Rivers provide humans with drinking water and recreational facilities. They provide habitat for freshwater animals and plants (Brix and Schierup, 1989). Wetlands provide habitat for migrating species. Vegetative matter is released into rivers, which helps feed aquatic organisms (Weis and Weis, 2004). In some countries wetland products form an important element in international trade (Matagi et al., 1998). Wetlands control soil erosion and act as water purifiers, and sinks for contaminants (Mattuck and Nikolaidis, 1996). Wetlands also prevent flooding by holding water, much like a sponge (Matagi et al., 1998).

Freshwater ecosystems are threatened by metal pollution throughout the world. Metals and other pollutants are introduced into rivers naturally through volcanic eruptions and erosion of rocks (Thawley et al., 2004; Van Aardt and Booysen, 2004). They occur in various forms in the aquatic environment: as ions dissolved in water, as vapour, as minerals in rocks and in particulate forms. Certain metals such as Nickel, Zinc, Copper, Chromium and Iron are essential micronutrients (Kempster et al., 1982; Rainbow, 1985). Although several metals have beneficial effects, all metals can be harmful when available in large quantities (Wright, 1980). They are pervasive and can remain for years in the environment (Hare et al., 2001).

Anthropogenically, metals can be released directly into rivers through effluent from municipal wastewater treatment plants, industrial processes such as galvanizing, combustion of fossil fuels and mining effluent. Metals can also be released indirectly by surface runoff from roads, farming lands and metal-contaminated groundwater from facilities such as metal manufacturing plants (Salomons, 1995; Grimalt et al., 1999; Hochella et al., 1999; Grabowski et al., 2001; Dalvie et al., 2004). They are also released as waste byproducts of industries or as residues from pesticide application (Hellawell, 1988).

When metals and other pollutants are discharged into rivers and lakes, they ultimately leach into soils and groundwater (Abernathy et al., 1984). Ecotoxicologists use sediments and water to assess pollution levels in aquatic ecosystems (Otte et al., 1991; Mohan and Hosetti, 1998). Numerous of these studies have been conducted worldwide (Knight et al., 1997; Grabowski et al., 2001; Ramessur and Ramjeawon, 2002; Audry et al., 2004; Singh et al., 2005). Similarly in South Africa, a large body of literature exists (Van Eeden and Schoonbee, 1991; Steenkamp et al., 1994; Binning and Baird, 2001; Snyman et al., 2002; Reinecke et al., 2003; Botes and Van Staden, 2005; Okonkwo et al., 2005).

Bioavailability, bioaccumulation and toxicity of metals to aquatic organisms depend strongly on the chemical form in which metals occur (their speciation). This speciation is affected by solution conditions, the nature of the metal ion and its reaction with other metals, pH, salinity and conductivity of the water (De Haan et al., 1993; Campbell, 1995; Rainbow, 1995; 1997; Sivakumar and Subbhuraam, 2005). Water and sediment concentrations reveal little about the bioavailability of metals in the river ecosystem. Therefore aquatic plants and animals must be incorporated as biomonitoring species (Mortimer, 1985) in the evaluation of metal bioavailability and toxicity.

In aquatic ecosystems metals are absorbed or ingested by organisms (Marsden and Rainbow, 2004) and bioaccumulated in organisms' tissues. The bioaccumulation of metals is well documented for freshwater plants (Jackson, 1998; Fitzgerald et al., 2003; Choi et al., 2006; Deng et al., 2006; Vardanyan and Ingole, 2006) and animals (Van Hattum et al., 1993; Sanders et al., 1999; Gyedu- Ababio et al., 1999; Nussey et al., 1999; Snyman et al., 2002; Wepener et al., 2005).

Effects of accumulated metals on organisms differ from species to species, depending on many factors such as feeding mode, the current stage in the life cycle, the type of metal and metal chemical form, as well as the season. The effects of metals do not only impact on individual organisms, but ultimately affect the population, community and the ecosystem as a whole (Elangovan et al., 1999). Sensitive species may disappear completely when an aquatic ecosystem is polluted with metals. When species disappear,

the entire ecosystem is affected through the food web and nutrient cycling interactions (Ward and Young, 1982; Rygg, 1985).

Aquatic macrophytes play a very important role in river ecosystems. Among other functions, macrophytes provide habitats and shelter for invertebrates and are capable of accumulating various metals and removing them from soil and water (St-Cry et al., 1994; Coquery and Welbourn, 1995; Greger et al., 1995; Jackson, 1998; Mohan and Hosetti, 1998; Ait Ali et al., 2004; Fritioff et al., 2005). Wetland plants, in particular, play an important role in the conservation of wetlands by retaining large amounts of nutrients and metals and storing them in their roots and / or leaves and stems (Stoltz and Greger, 2002). This has been documented for species such as *Phragmites australis* (Ye et al., 2001; Bragato et al., 2006), *Bolboschoenus maritimus* (Almeida et al., 2006; Bragato et al., 2006; Madejón et al., 2006a), and *Spartina alterniflora* (Weis and Weis, 2004; Weis et al., 2004), that can accumulate and store metals in their roots. Due to this bioaccumulation, and due to the fact that wetland plants have general fast growth and high biomass production (Bragato et al., 2006), they are also used for phytoremediation, which is a cheap and effective way of cleaning up wetlands contaminated with metals (Peeverly et al., 1995; Weis and Weis, 2004).

*Bolboschoenus maritimus* is widely used in the reconstruction, creation and rehabilitation of wetlands (Kantrud, 1996). Its basic biology is well known and documented (Otte et al., 1991; Zákavský and Hroudová, 1996; Clevering and Hundscheid, 1998; Sanchez et al., 1998; Archer, 2000; Merlin et al., 2002; Almeida et al., 2006; Bragato et al., 2006; Madejón et al., 2006a; Lillebo et al., 2007). This plant has been widely used as test species in ecotoxicology-related studies in various countries around the world (Otte et al., 1991; Clevering, 1995; Zákavský and Hroudová, 1996; Almeida et al., 2006; Madejón et al., 2006a). However, no such studies have been done in South Africa. The only South African literature available on this species is of a taxonomic or biodiversity-related nature (Goldblatt, 1978; Trinder-Smith et al., 1996; Archer, 2000; Goldblatt and Manning, 2000; 2002; Trinder-Smith, 2003).

*Bolboschoenus maritimus* is common on river banks around the Cape Peninsula (Trinder-Smith, 2003). The lower Diep River is one of the freshwater ecosystems where the plant is found in abundance (personal observation). There are various possible sources of pollution along the banks of the Diep River, which could lead to high metal contamination. Despite this, no comprehensive studies have been conducted on metal contamination in this ecosystem. Also, the use of a biomonitor species to determine the degree of metal bioaccumulation has not been investigated. According to Madejón et al. (2006b), biomonitors in a soil environment are species that indicate soil quality and that reveal information on soil quality that is difficult to measure using direct soil analyses. For example, they may confirm the availability of trace elements in the soil (Madejón et al., 2004). The latter authors suggested that plants that are trace element accumulators could possibly be used as biomonitors.

Based on the successful use of *B. maritimus* as a test species (although not a biomonitor) in other studies, particularly also in terms of its ability to accumulate metals (Otte et al., 1991; Zákavský and Hroudová, 1996; Clevering et al., 1998; Bragato et al., 2006; Madejón et al., 2006a), it was chosen as a potential biomonitor species for the present study.

## **THE AIM OF THE STUDY:**

The main aim of the study was to monitor the degree of metal pollution in the lower Diep River, over a period of one year, and to investigate the use of the sedge *Bolboschoenus maritimus*, as biomonitor species.

### **The specific objectives were:**

- To determine the concentrations of Al, Fe, Zn, Cd, Cr, Co, Pb, Mn, Ni and Cu in water and sediment from selected sites of the lower Diep River, every two months, over a one year period.
- To determine the type of sediment present at each site, through sediment characterization.
- To measure water pH, temperature and conductivity at all selected sites..
- To determine the degree of metal bioaccumulation in the sedge *Bolboschoenus maritimus*, over the biomonitoring period.
- To determine the distribution of metals in the parts of *Bolboschoenus maritimus*, i.e., the particular site of bioaccumulation (roots, leaves and / or stems).
- To statistically compare the different sampling occasions, in terms of all the above parameters, in order to investigate seasonal variations.
- To statistically compare the different sampling sites in terms of the above parameters, in order to investigate the influence of industries, urban areas and wetlands, on metal contamination.
- To determine the usefulness of *Bolboschoenus maritimus*, as biomonitor species of metal pollution.

**2.1 DESCRIPTION OF THE STUDY AREA**

The Diep River rises in the Kasteel Mountain near Malmesbury at an altitude of 420m above mean sea level. The river flows for about 65 km in a southwesterly direction, passing through Rietvlei Wetland Reserve before entering Table Bay (Atlantic Ocean) at Milnerton. The wetland itself is surrounded by densely populated residential areas and industries. The catchment comprises the Swartland and Sandveld regions in the Western lowland area of the Western Cape. The flat topography of the catchment makes it attractive for agricultural and urban development. More than 90% of the catchment is under cultivation, predominantly wheat and other grain crops. There has been an increase in vineyards and orchards in the area. Three wastewater treatment works discharge into the Diep River at Milnerton, Kraaifontein and Malmesbury. A large landfill site (Vissershok) and a number of general waste sites are found in the vicinity of the river. These landfill sites receive various hazardous wastes. There is also an incinerator for the disposal of medical waste (River Health Programme, 2003). The river possibly also receives waste from a large oil refinery and an informal settlement situated on its banks (personal observation).

**2.2 VEGETATION****Terrestrial vegetation:**

According to the River Health Programme (2003), farming practices along the river bank have disturbed the natural vegetation and consequently alien plants such as Black Wattle (*Acacia mearnsii*), Castor Oil (*Ricinus communis*), Large Cocklebur (*Xanthium strumarium*), Kikuyu Grass (*Pennisetum clandestinum*), Oak (*Quercus robur*), Red River Gum (*Eucalyptus camaldulensis*), Pampas Grass (*Cortaderia selloana*), Port Jackson (*Acacia saligna*), Red Sesbania (*Sesbania punicea*) infested the catchment.

### **Semi-aquatic / aquatic vegetation:**

According to Grindley and Dudley (1988), this area is dominated by rushes, sedges and reeds, such as *Juncus kraussii*, *Sarcocornia spp.*, *Phragmites australis*, *Typha capensis* and *Scirpus* (now *Bolboschoenus*) *spp.* The alien invasive Water Hyacinth (*Eichhornia crassipes*) is also common in the area and needs to be controlled on a regular basis.

*Bolboschoenus maritimus* was chosen for this study since it is known to accumulate metals in its different parts (Otte et al., 1991; Almeida et al., 2006; Bragato et al., 2006; Madejón et al., 2006a). *B. maritimus* is a quick growing sedge of the Cyperaceae family, which can grow up to 1.2 m in height (Goldblatt and Manning, 2000). It occurs in many places around the world. In South Africa it can be found from the Cape Peninsula, northwards (Trinder-Smith, 2003). It can be found in wet, marshy flats, seasonal and permanent wetlands, pond margins and estuaries (Clevering and Hundscheid, 1998). The plant can survive under both saline and non-saline conditions and can handle almost total submersion in water. During drier seasons the plant survives by means of dormant corms (Clevering, 1995). According to C. Archer (pers. comm. 2007), the growing season for the plant in the Milnerton area is in October.

*B. maritimus* can reproduce through vegetative as well as sexual reproduction. Vegetative reproduction: It is a rhizomatous plant (Kantrud, 1996; Archer, 2000) that grows from a corm and puts out a horizontal rhizome from which the next plant grows. In this way the plant can quickly form dense stands. Sexual reproduction: Both sexes are found on the same plant. Shiny, brown, tear-shaped fruits are produced, each containing one seed. Pollination is by wind (Huxley et al., 1999).

### **2.3 CLIMATE AND RAINFALL**

The Diep River and its tributaries lie within the winter rainfall region (Grindley and Dudley, 1988). The total monthly rainfall (mm), recorded for the Diep River area during the sampling months, is shown in Table 2.1.



**Table 2.1:** Total monthly rainfall (mm), recorded for the Diep River area during the sampling period. Sampling months are indicated with an asterisk (\*) (Source: South African Weather Services).

<b>Months</b>	<b>Rainfall (mm)</b>
August 2004	17.4
*September 2004	114.8
October 2004	3.8
*November 2004	2.0
December 2004	17.6
*January 2005	1.6
February 2005	4.0
*March 2005	65.8
April 2005	35.0
*May 2005	71.0
June 2005	22.8
*July 2005	67.8
August 2005	31.1
*September 2005	0

## **2.4 SAMPLING SITES**

Three sites were selected along the lower reaches of the river:

### **Site 1**

Site 1 (Figure 2.1) was located at the N7 Bridge, in the vicinity of the landfill sites and the farming areas, 6 km upstream of the wetland reserve. The site receives run-off from agricultural activities upstream.

### **Site 2**

Site 2 (Figure 2.1) was located 1 km upstream from the wetland reserve, surrounded by industries and residential areas. This site receives effluent from industries, households around the area and an informal settlement 2 km upstream of the site. It also receives effluent from the sewage treatment plant which discharges at this site.

### **Site3**

Site 3 (Figure 2.1) was located downstream of the wetland reserve, 2 km from the river mouth. This site receives run-off from a major road (R27), which is heavily congested with traffic in the mornings and the afternoons. It also receives storm water from the municipalities.

## **2.5 SAMPLING PROCEDURE**

Water and sediment samples were collected every 2 months for a period of 1 year, starting from September 2004 to September 2005. Plant specimens (*Bolboschoenus maritimus*) were collected seasonally, in November 2004, March 2005, July 2005 and September 2005. Plant specimens were only collected from site 1 and site 3 as the same species could not be found at site 2. All water, sediment and plant samples used for metal analysis were frozen at -18 °C until preparation for metal analysis could be done. Sediment samples used for characterisation were not frozen.

### **Water samples**

Water temperature, pH and conductivity were measured at all the sites, during every sampling occasion. For the temperature, a standard thermometer was used. Conductivity and pH were measured using a Hanna Hi 9810 Portable pH/EC/TDS meter. Water samples from each site were collected 1 meter away from the riverbank and stored at -18 °C in marked polyethylene containers.

### **Sediment samples**

Sediment samples from each site were collected 1 meter away from the riverbank and stored at -18 °C in marked polyethylene containers.

### **Plant (*Bolboschoenus maritimus*) samples**

An average of four plants was collected from site 1 and site 3, from the edge of the river. They were completely uprooted.

## **2.6 SEDIMENT CHARACTERISATION PER SITE**

### **Site 1**

Sediment samples were collected every two months for a one-year period, starting from September 2004 to September 2005. One sample of top sediment from each site was collected and stored in marked polyethylene containers. Samples were then analysed by Dr. J. Rogers, from the Geology Department, at the University of Cape Town.

The analysis procedure followed was according to the method described by Folk (1954). Salt was removed from the sediment samples overnight by dialysis in cellophane tubing in a tub of tap water, gently overflowing. The fine fraction (silt and clay) was separated from the coarse fraction (sand and gravel). The coarse fraction was dried overnight in the oven at 80 °C. The fine fraction was allowed to settle at the bottom of plastic tubs over two weeks. Pebbles were separated from sand using a 2 mm laboratory test sieve. Sand and pebbles fractions were weighed using an electronic balance to obtain the mass (g) of sand and pebbles. The supernatant water above the settled silt and clay in the plastic tubs was decanted, then transferred to a liter measuring cylinder and made up to a volume of 1 liter. The water was very turbid brown. Silt and clay were pipetted to obtain the mass (g). The percentages of clay, silt, sand and pebbles were determined.

### **Site 2**

The same procedure as for site 1 was followed. Decanted supernatant water was translucent green brown.

### **Site 3**

The same procedure as for sites 1 and 2 was followed. Decanted supernatant water was black (rich in organic matter and highly turbid).

## **2.7 PREPARATION AND ANALYSIS OF SAMPLES**

### **Preparation of samples for acid digestion**

Plant specimens from site 1 and site 3 were divided into roots, leaves and stems. The different plant components from site 1 and site 3 were then pooled. These plant specimens and the sediment samples were thawed before drying. They were oven dried for 48 hours at 60 °C to obtain the dry weight. Sediment was sieved to remove large particles, using a 1 mm sieve and plant specimens were ground using a pestle and mortar. All sediment and plant samples were divided into five replicates of 0.5 g each, using a XB 220A Precisa balance. Water samples were divided into five replicates per site. Each replicate consisted of 10 ml water.

### **Acid Digestion**

The methods described below were based on those given by Odendaal and Reinecke (1999).

**Water:** Five ml of 55% nitric acid were added to each sample and a 5 ml nitric acid blank was prepared. Samples were heated in a Grant UBD dry block heater in a fume cabinet, at 40 °C for 1 hour. The temperature was then increased to 120 °C and maintained for 3 hours. After acid digestion, samples were left to cool, and then diluted with distilled water to obtain a 20 ml sample. Samples were poured into 20 ml volumetric flasks and filtered using a syringe, needle and 0.45 µm Millipore filter paper. Samples were then poured into labelled 30 ml polyethylene plastic containers, and stored in a refrigerator.

**Sediment and plant samples:** Ten ml of 55% nitric acid were added to samples and a 10 ml blank was prepared. Samples were digested following the same procedure as the water samples. Afterwards they were left to cool and then diluted with distilled water to obtain 20 ml samples. Filtration was done using 0.4 mm or 0.6 mm Whatman filter paper to remove the slurry. Fine filtration was done using 0.45 µm cellulose nitrate membrane filter papers, a needle and a syringe. Samples were poured into labelled 30 ml polyethylene plastic containers and stored in a refrigerator.

## 2.8 METAL ANALYSIS

Metal concentrations were determined using the ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectrophotometer) of the University of Stellenbosch. ICP results were converted using the following formula:

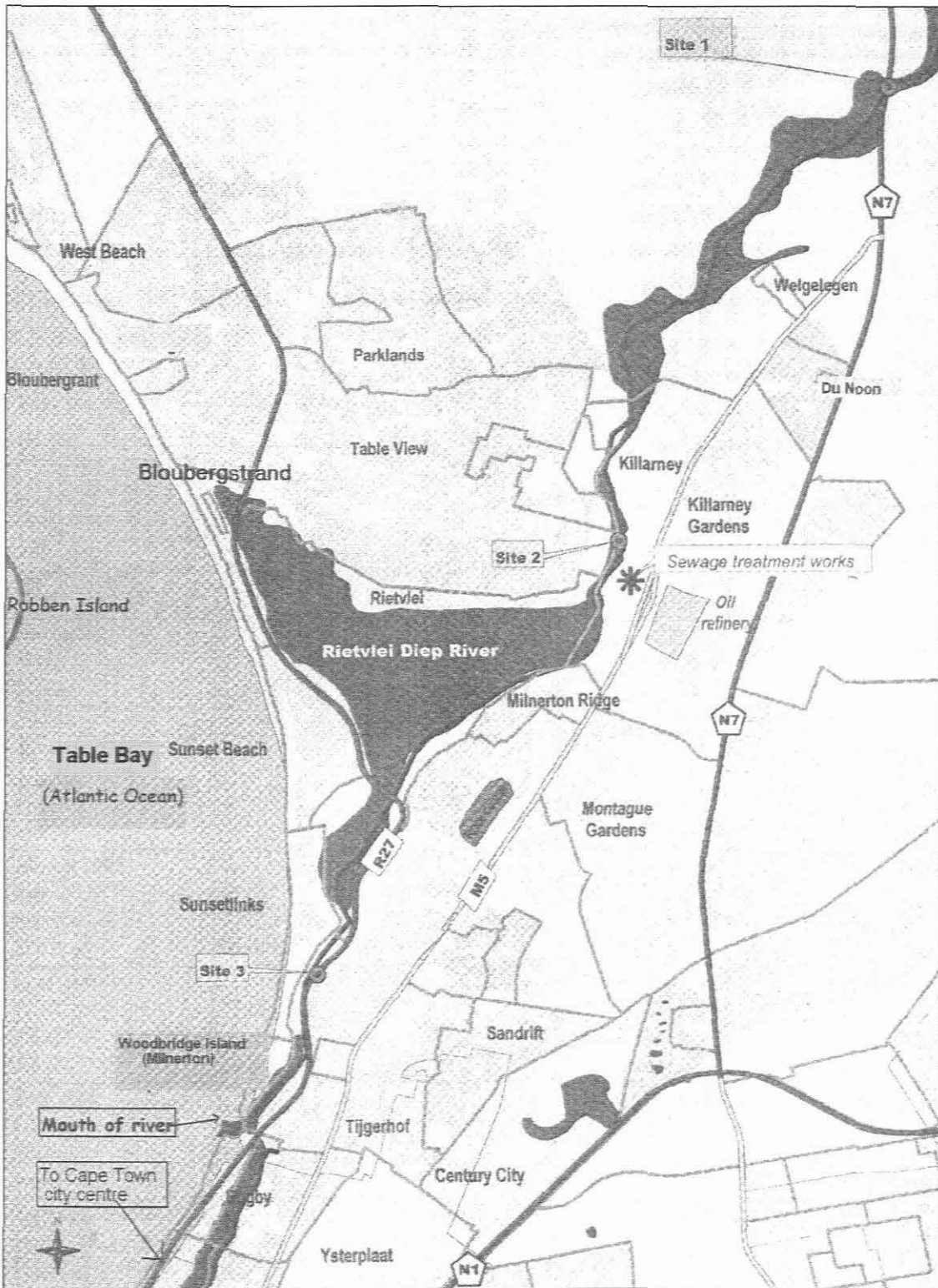
$$\text{For sediment and plants: } \left[ \frac{\text{ICP Readings} - \text{Blank}}{\text{Mass (g)}} \right] \times \text{dilution factor (20)}$$

$$\text{For water: } [\text{ICP Readings} - \text{Blank}] \times 2$$

All sediment and plant metal concentrations were expressed as mg/kg, and all water metal concentrations as mg/l.

## 2.9 STATISTICAL ANALYSIS

Kruskal-Wallis One Way Analysis of Variance on Ranks was carried out to compare the concentrations of metals at different sites, over the duration of the sampling period, in water, sediment and plant samples. The Student-Newman-Keuls Method was used to do pairwise multiple comparisons. Statistical analysis was done using Sigmastat 3.1 software package.



**Figure 2.1:** Map showing the Diep River sampling sites and surrounding areas. (Sources: Department of Environmental Affairs and Development Planning).

**RESULTS****3.1 Physico-chemical parameters**

Temperature, pH, and conductivity of the water were measured at each sampling site during each sampling occasion. These parameters are tabulated in Table 3.1.

Table 3.1: Temperature, pH and conductivity, measured at the three Diep River sampling sites, during each sampling occasion.

Sampling occasion	pH	Temperature (°C)	Conductivity (mS/m)
<b>September 2004</b>			
Site 1	6.5	20.6	523
Site2	6.8	22.8	199
Site3	6.8	22.2	288
<b>November 2004</b>			
Site 1	7	Not measured	428
Site 2	6.8	Not measured	133
Site 3	6.5	Not measured	263
<b>January 2005</b>			
Site 1	7.5	22	209
Site 2	7.5	23.4	1095
Site 3	9.5	25	460
<b>March 2005</b>			
Site 1	7.5	23	415
Site 2	7.6	24	808
Site 3	8.6	25	821
<b>May 2005</b>			
Site 1	7.8	15	257
Site 2	7.6	18	173
Site 3	7.2	16	971
<b>July 2005</b>			
Site 1	7.6	15.2	162
Site 2	7.4	15.9	152
Site 3	7.2	14.9	187
<b>September 2005</b>			
Site1	7.7	19	242
Site 2	7	19	204
Site 3	7	21	261

## **3.2 Comparisons of metal concentrations between the three sampling sites, per sampling occasion**

### **3.2.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in water from the three sampling sites, during each sampling occasion are shown in Table 3.2.1.

No significant differences ( $P>0.05$ ) were found between any of the sites during any of the sampling occasions.

### **3.2.2 Copper**

Mean ( $\pm$  SD) copper concentrations, measured in water from the three sampling sites, during each sampling occasion are shown in Table 3.2.2.

*November 2004:* No significant differences ( $P>0.05$ ) were found between the three sites.

*All other sampling occasions:* Copper was not detected at all (except in January 2005 at site 3), therefore statistical comparisons were not done.

### **3.2.3 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in water from the three sampling sites, during each sampling occasion are shown in Table 3.2.3.

*September 2004 and November 2004:* For each of these sampling occasions no significant differences were found between the three sampling sites ( $P>0.05$ ).

*January 2005:* Statistically significant differences ( $P<0.05$ ) were found between all three sampling sites. Site 1 had the highest mean iron concentration ( $4.24 \pm 1.48$  mg/l), and site 2 the lowest ( $0.05 \pm 0.09$  mg/l).



**March 2005:** Statistically significant differences ( $P < 0.05$ ), were found between all three sampling sites. Site 3 had the highest mean iron concentration ( $2.01 \pm 1.57$  mg/l), and site 2 the lowest ( $0.09 \pm 0.03$  mg/l).

**May 2005, July 2005 and September 2005:** For each of these sampling occasions, no significant differences were found between the three sampling sites ( $P > 0.05$ ).

### **3.2.4 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in water from the three sampling sites, during each sampling occasion are shown in Table 3.2.4.

**September 2004:** Statistically significant differences were found between sites 1 and 2, and between sites 2 and 3 ( $P < 0.05$ ). Site 1 had the highest mean manganese concentration ( $0.23 \pm 0.03$  mg/l), and site 2 the lowest ( $0.09 \pm 0.01$  mg/l).

**November 2004:** No significant differences were found between any of the sampling sites ( $P > 0.05$ ).

**January 2005:** Statistically significant differences were found between sites 3 and 2, and between sites 1 and 2 ( $P < 0.05$ ). Site 2 had the lowest mean manganese concentration ( $0.06 \pm 0.01$  mg/l).

**March 2005:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean manganese concentration was found at site 3 ( $0.43 \pm 0.07$  mg/l), and site 2 the lowest ( $0.05 \pm 0.06$  mg/l).

**May 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P < 0.05$ ). The highest mean manganese concentration was found at site 1 ( $0.27 \pm 0.18$  mg/l).

**July 2005:** No significant differences were found between any of the sampling sites ( $P>0.05$ ).

**September 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 2 and 3 ( $P<0.05$ ). The lowest mean manganese concentration was found at site 3 ( $0.10 \pm 0.01$  mg/l).

### **3.2.5 Zinc**

Mean ( $\pm$  SD) zinc concentrations, measured in water from the three sampling sites, during each sampling occasion are shown in Table 3.2.5.

**September 2004 and November 2004:** No significant differences were found between any of the sampling sites ( $P>0.05$ ).

**January 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P<0.05$ ). The highest mean zinc concentration was found at site 1 ( $0.60 \pm 0.37$  mg/l). Zinc was not detected in samples from sites 2 and 3.

**March 2005:** All comparisons between the three sampling sites showed statistically significant differences ( $P<0.05$ ). The highest mean zinc concentration was found at site 3 ( $1.7 \pm 0.04$  mg/l), and site 1 the lowest ( $1.09 \pm 0.03$  mg/l).

**May 2005:** Zinc was not detected in samples from the three sites.

**July 2005 and September 2005:** No significant differences were found between any of the sampling sites ( $P>0.05$ ).

**3.2.6 Cadmium, cobalt, chromium, lead and nickel:** None of these metals were detected in any water samples from the three sampling sites throughout the sampling period. Statistical comparisons could therefore not be done.

### **3.3 Comparisons of metal concentrations between consecutive sampling occasions, per sampling site**

#### **3.3.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in water from the three sampling sites, over time are shown in Table 3.2.1. These results are graphically portrayed in Figure 3.3.1.

##### **Site 1**

The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). However, March 2005 vs. May 2005 did not differ significantly. A concentration peak was seen during January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show any significant difference ( $P > 0.05$ ).

##### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). January 2005 vs. March 2005, and March 2005 vs. May 2005 did however not differ significantly. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

##### **Site 3**

The majority of the comparisons between consecutive sampling occasions did not show significant differences ( $P > 0.05$ ). January 2005 vs. March 2005, and March 2005 vs. May 2005, however, showed significant decreases ( $P < 0.05$ ). A concentration peak was seen in September 2004. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

### **3.3.2 Copper**

Mean ( $\pm$  SD) copper concentrations, measured in water of the three sampling sites, over time are shown in Table 3.2.2. These results are graphically portrayed in Figure 3.3.2.

#### **Site 1 and site 2**

Copper was not detected during the majority of the sampling occasions, therefore statistical comparisons were not done.

#### **Site 3**

Copper was not detected during the majority of the sampling occasions. It was however detected in water during November 2004 and January 2005, and a comparison between these two occasions showed a statistically significant increase ( $P < 0.05$ ).

### **3.3.3 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in water of the three sampling sites, over time are shown in Table 3.2.3. These results are graphically portrayed in Figure 3.3.3.

#### **Site 1**

Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a statistically significant increase ( $P < 0.05$ ).

#### **Site 2**

No significant differences were found between any of the consecutive sampling occasions ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a statistically significant increase ( $P < 0.05$ ).

### **Site 3**

Comparisons between March 2005 and May 2005, and between May 2005 and July 2005 showed a significant decrease and increase respectively ( $P < 0.05$ ). Comparisons between the other sampling occasions did not show any significant differences. However, a comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a statistically significant decrease ( $P < 0.05$ ).

### **3.3.4 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in water of the three sampling sites, over time are shown in Table 3.2.4. These results are graphically portrayed in Figure 3.3.4.

#### **Site 1 and site 2**

All comparisons between consecutive sampling occasions showed no significant differences ( $P > 0.05$ ), including a comparison between September 2004 and September 2005.

#### **Site 3**

The majority of the comparisons between consecutive sampling occasions did not differ significantly. However, March 2005 vs. May 2005 showed a significant decrease ( $P < 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference.

### **3.3.5 Zinc**

Mean ( $\pm$  SD) zinc concentrations, measured in water of the three sampling sites, over time are shown in table 3.2.5. These results are graphically portrayed in Figure 3.3.5.

#### **Site 1**

March 2005 vs. May 2005 showed a significant decrease ( $P < 0.05$ ). Comparisons between all other consecutive sampling occasions did not show any significant differences ( $P > 0.05$ ). A particularly low mean concentration was seen in September 2005 compared

to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), therefore showed a significant decrease ( $P < 0.05$ ).

### **Site 2 and site 3**

For both of these sites, January 2005 vs. March 2005 and March 2005 vs. May 2005 showed statistically significant increases and decreases respectively ( $P < 0.05$ ). Comparisons between other consecutive sampling occasions did not show significant differences ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), for each site, did not show a significant difference ( $P > 0.05$ ).

**Table 3.2.1** Mean ( $\pm$ SD) aluminium concentrations (mg/L), measured in water from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	0.04 $\pm$ 0.00 <sup>a</sup>	0.04 $\pm$ 0.00 <sup>a</sup>	7.45 $\pm$ 6.74 <sup>a</sup>
November 2004	*1.47 $\pm$ 2.18 <sup>a</sup>	*0.80 $\pm$ 0.65 <sup>a</sup>	2.28 $\pm$ 4.12 <sup>a</sup>
January 2005	*5.52 $\pm$ 1.56 <sup>a</sup>	*0.25 $\pm$ 0.04 <sup>a</sup>	2.02 $\pm$ 0.11 <sup>a</sup>
March 2005	*0.25 $\pm$ 0.08 <sup>a</sup>	0.19 $\pm$ 0.01 <sup>a</sup>	*1.43 $\pm$ 0.81 <sup>a</sup>
May 2005	N.D. <sup>a</sup>	N.D. <sup>a</sup>	*N.D. <sup>a</sup>
July 2005	1.83 $\pm$ 1.72 <sup>a</sup>	1.31 $\pm$ 0.62 <sup>a</sup>	1.60 $\pm$ 0.69 <sup>a</sup>
September 2005	*0.13 $\pm$ 0.10 <sup>a</sup>	*0.38 $\pm$ 0.14 <sup>a</sup>	0.27 $\pm$ 0.06 <sup>a</sup>

Different letters indicate statistical differences between different sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk.

**Table 3.2.2** Mean ( $\pm$  SD) copper concentrations (mg/L), measured in water from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	N.D. <sup>a</sup>	N.D. <sup>a</sup>	N.D. <sup>a</sup>
November 2004	0.002 $\pm$ 0.006 <sup>a</sup>	0.07 $\pm$ 0.16 <sup>a</sup>	0.04 $\pm$ 0.10 <sup>a</sup>
January 2005	N.D. <sup>a</sup>	N.D. <sup>a</sup>	*0.26 $\pm$ 0.16 <sup>a</sup>
March 2005	N.D. <sup>a</sup>	N.D. <sup>a</sup>	N.D. <sup>a</sup>
May 2005			
July 2005			
September 2005			

Different letters indicate statistical differences between different sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk.

**Table 3.2.3** Mean ( $\pm$  SD) iron concentrations (mg/L), measured in water from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	N.D. <sup>a</sup>	N.D. <sup>a</sup>	6.32 $\pm$ 6.32 <sup>a</sup>
November 2004	*2.63 $\pm$ 5.28 <sup>a</sup>	0.97 $\pm$ 1.07 <sup>a</sup>	1.91 $\pm$ 3.98 <sup>a</sup>
January 2005	*4.24 $\pm$ 1.48 <sup>a</sup>	0.05 $\pm$ 0.09 <sup>b</sup>	0.72 $\pm$ 0.30 <sup>c</sup>
March 2005	*0.62 $\pm$ 0.36 <sup>a</sup>	0.09 $\pm$ 0.03 <sup>b</sup>	2.01 $\pm$ 1.57 <sup>c</sup>
May 2005	*N.D. <sup>a</sup>	0.43 $\pm$ 0.98 <sup>a</sup>	*N.D. <sup>a</sup>
July 2005	*1.88 $\pm$ 1.88 <sup>a</sup>	1.11 $\pm$ 0.81 <sup>a</sup>	*1.48 $\pm$ 0.53 <sup>a</sup>
September 2005	*0.24 $\pm$ 0.17 <sup>a</sup>	0.26 $\pm$ 0.29 <sup>a</sup>	0.11 $\pm$ 0.10 <sup>a</sup>

Different letters indicate statistical differences between different sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk.

**Table 3.2.4** Mean ( $\pm$  SD) manganese concentrations (mg/L), measured in water from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	0.23 $\pm$ 0.03 <sup>a</sup>	0.09 $\pm$ 0.01 <sup>b</sup>	0.21 $\pm$ 0.09 <sup>a</sup>
November 2004	0.21 $\pm$ 0.31 <sup>a</sup>	0.18 $\pm$ 0.20 <sup>a</sup>	18.06 $\pm$ 40.09 <sup>a</sup>
January 2005	0.31 $\pm$ 0.07 <sup>a</sup>	0.06 $\pm$ 0.01 <sup>b</sup>	0.31 $\pm$ 0.03 <sup>a</sup>
March 2005	0.10 $\pm$ 0.00 <sup>a</sup>	0.05 $\pm$ 0.06 <sup>a</sup>	0.43 $\pm$ 0.07 <sup>a</sup>
May 2005	0.27 $\pm$ 0.18 <sup>a</sup>	0.05 $\pm$ 0.06 <sup>b</sup>	*0.05 $\pm$ 0.05 <sup>b</sup>
July 2005	0.07 $\pm$ 0.03 <sup>a</sup>	0.04 $\pm$ 0.01 <sup>a</sup>	0.06 $\pm$ 0.01 <sup>a</sup>
September 2005	0.19 $\pm$ 0.07 <sup>a</sup>	0.13 $\pm$ 0.01 <sup>a</sup>	0.10 $\pm$ 0.01 <sup>b</sup>

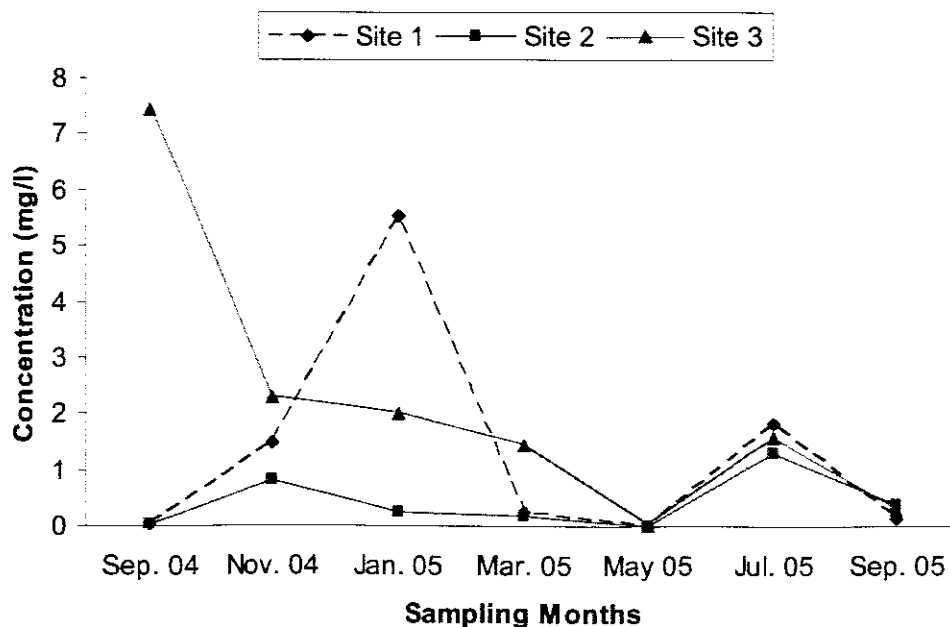
Different letters indicate statistical differences between different sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk.



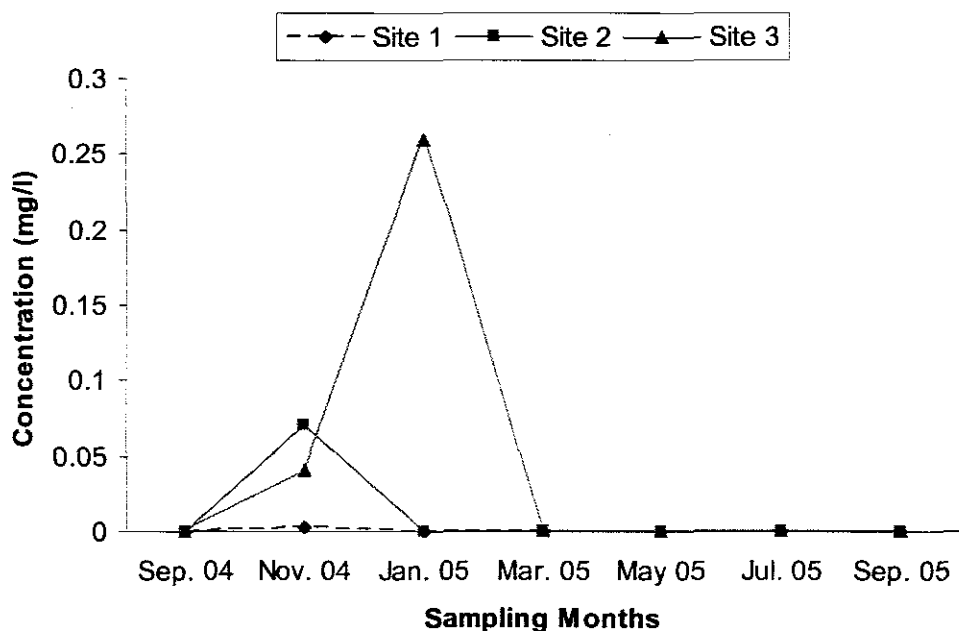
**Table 3.2.5** Mean ( $\pm$  SD) zinc concentrations (mg/L), measured in water from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	0.52 $\pm$ 1.05 <sup>a</sup>	N.D. <sup>a</sup>	N.D. <sup>a</sup>
November 2004	0.21 $\pm$ 0.22 <sup>a</sup>	0.33 $\pm$ 0.17 <sup>a</sup>	0.12 $\pm$ 0.08 <sup>a</sup>
January 2005	0.60 $\pm$ 0.37 <sup>a</sup>	N.D. <sup>b</sup>	N.D. <sup>b</sup>
March 2005	1.07 $\pm$ 0.03 <sup>a</sup>	*1.39 $\pm$ 0.15 <sup>b</sup>	*1.70 $\pm$ 0.04 <sup>c</sup>
May 2005	*N.D. <sup>a</sup>	*N.D. <sup>a</sup>	*N.D. <sup>a</sup>
July 2005	0.02 $\pm$ 0.01 <sup>a</sup>	0.012 $\pm$ 0.008 <sup>a</sup>	0.032 $\pm$ 0.027 <sup>a</sup>
September 2005	0.008 $\pm$ 0.017 <sup>a</sup>	0.02 $\pm$ 0.02 <sup>a</sup>	0.02 $\pm$ 0.01 <sup>a</sup>

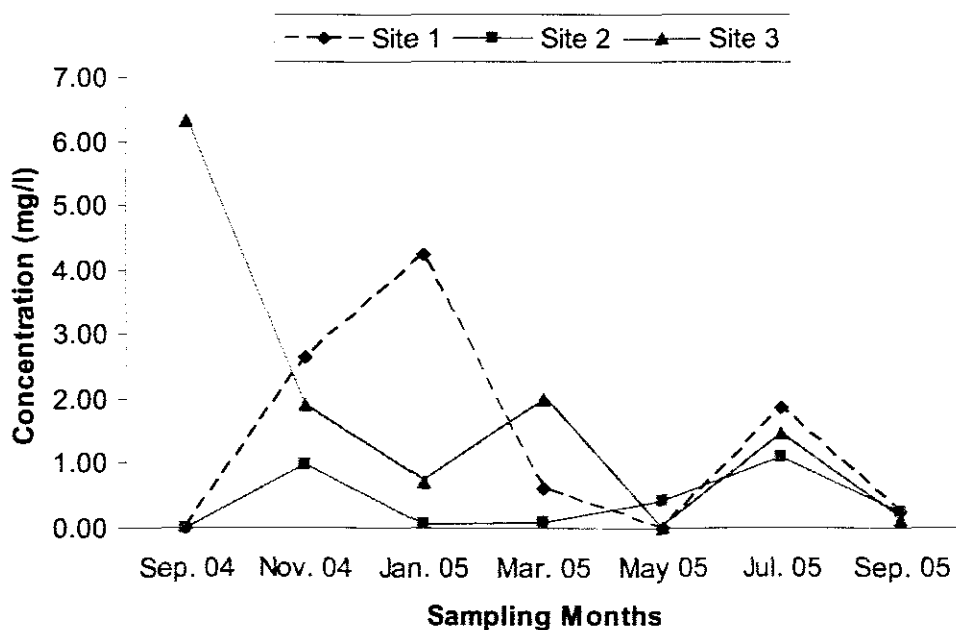
Different letters indicate statistical differences between different sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk.



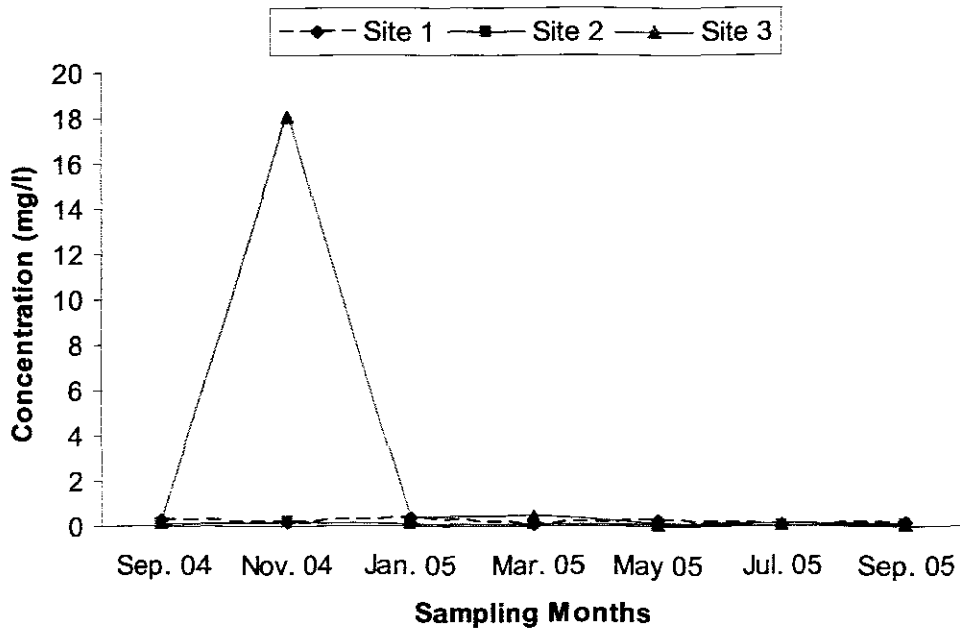
**Figure 3.3.1:** Mean aluminium concentrations (mg/l), measured in the water from three sampling sites in the Diep River, between September 2004 and September 2005.



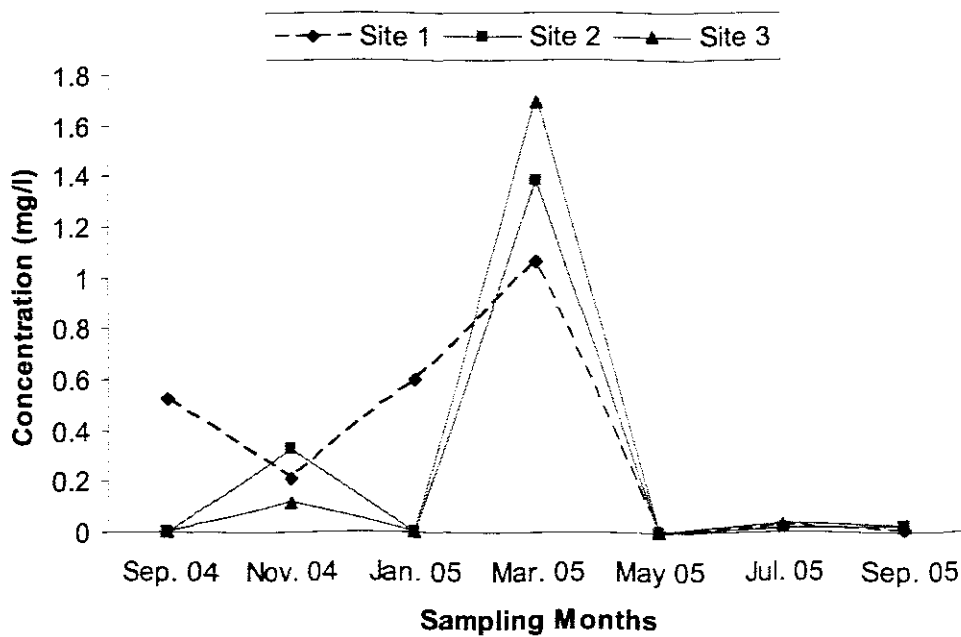
**Figure 3.3.2:** Mean copper concentrations (mg/l), measured in the water from three sampling sites in the Diep River, between September 2004 and September 2005.



**Figure 3.3.3:** Mean iron concentrations (mg/l), measured in the water from three sampling sites in the Diep River, between September 2004 and September 2005.



**Figure 3.3.4:** Mean manganese concentrations (mg/l), measured in the water from three sampling sites in the Diep River, between September 2004 and September 2005.



**Figure 3.3.5:** Mean zinc concentrations (mg/l), measured in the water from three sampling sites in the Diep River, between September 2004 and September 2005.

## DISCUSSION

Based on the South African Water Quality Guidelines from the Department of Water Affairs and Forestry, the Target Water Quality Range (TWQR) for pH of agricultural irrigation water is 6.5 to 8.5 (DWAF, 1996a), of domestic water is 6.0 to 9.0 (DWAF, 1996b) and of recreational water is 6.5 to 8.5 (DWAF, 1996c). Water with a pH within these ranges has the least negative effects on crops, livestock, humans, soil and farming equipment. In the case of aquatic ecosystems, no definite guidelines are available, since according to DWAF (1996d), pH values should not be allowed to vary by more than 0.5 of a pH unit, from the range of the background pH values for a specific site and time of day, and one should use the background site-specific pH regime. These data are not available for the lower Diep River. All of the pH values obtained for all the sampling sites in the lower Diep River fell within the ranges available, except site 3 in January 2005, when the pH was above these ranges (Table 3.1). Therefore, the pH of the river water probably would not affect its use for irrigation, domestic and recreational purposes.

Electrical conductivity (EC) measured in the present study ranged from 133 to 1095 mS/m (Table 3.1). Electrical conductivity measured was converted to the total dissolved solids (TDS) using the formula provided by DWAF (1996d) in order to compare the data with the DWAF guidelines. The TWQR for TDS concentrations of all inland waters should not change by more than 15% from the normal cycles of the water body under unimpacted conditions at any time of the year. For lack of background site-specific data in the present study, the given DWAF TDS range of 200-1100 mg/ml, for water in contact with Palaeozoic and Mesozoic sedimentary rock formation was used for comparison with the results of the present study. The readings in this study were much higher than the DWAF guideline, except at site 2 in November 2004 and July 2005, when readings were lower. This could have been due to several factors such as, for example, leachate from the dumping site upstream of site 1, and effluent from the sewage treatment plant close to site 2 which, during rainy seasons, overflows (personal observation) and may contribute to an increase in conductivity. Other possible explanations could be groundwater seepage into surface waters (Westbrook et al., 2005). The mixing of

seawater and riverwater during high tide (Grindley and Dudley, 1988) is a strong possibility for high EC readings at site 3. Run-offs from the roads and farms surrounding the river, may also have been a contributing factor.

Water temperature measured in the present study ranged from 14.9 to 25 °C at all the sampling sites (Table 3.1). For river water temperature, no definite guidelines are available to compare with, since according to DWAF (1996d), one should also use the background site specific temperature regime, which is unavailable for the lower Diep River. It is assumed that fluctuations in water temperature at each site were probably merely due to natural seasonal fluctuations. Water temperature did not differ greatly between the different sites at all.

In the case of the water metal data, several metals were not detected in any of the water samples at all: Cr, Co, Pb, Ni and Cd. Detected metals (Al, Cu, Fe, Mn and Zn) were compared with the South African Water Quality Guidelines for Aquatic Ecosystems (DWAF, 1996d). The Target Water Quality Range (TWQR) for aquatic ecosystems for aluminium is 10 µg/l (0.01 mg/l), for manganese is 180 µg/l (0.18 mg/l), for copper is 1.4 µg/l (0.0014 mg/l), and for zinc is 2 µg/l (0.002 mg/l). Guideline values for iron are not available. Concentrations of the detected metals were mostly higher than the guideline concentrations. Aluminium, copper, and zinc concentrations were almost always higher than the guideline concentrations except on a few occasions when they were below detectable levels. Manganese concentrations varied greatly but were extremely high in November 2004 at site 3, compared to the manganese guideline limit.

Apart from the comparisons with the guideline concentrations, the metal results were also compared with previous studies on metal contamination in South African freshwater ecosystems. However, differences in the types of freshwater ecosystems, geochemistry of the freshwater ecosystems, climatic changes and the location of the freshwater ecosystems, complicated such comparisons and varying results were obtained: Manganese concentrations were compared with the results of De Wet et al. (1990) for polluted sites in the Blesbokspruit wetland ecosystem. Manganese concentrations in the

present study were generally lower than their concentration range, except in March 2005 at site 3 when the concentrations were similar to theirs. Copper concentrations were compared with the results of Steenkamp et al. (1994) for polluted sites in the Natalspruit River, Bronkhorstspuit River and Nooitgedacht dam. Copper concentrations in the present study were generally lower than their concentration range, except in November 2004 at site 3 when the concentrations were higher than their range. Aluminium, iron and zinc were compared with the results of Fatoki et al. (2002) for polluted sites in the Umtata River. However, for all three metals in the present study, the concentration ranges were too wide for such a comparison. It must however be noted that these metals were, at times, well above the concentrations found by these authors.

When comparing metal concentrations between the sites and between sampling occasions, there seems to be no clear patterns or trends. The metals that were detected are all either micronutrients (Mn, Zn, Cu and Fe) or metals contained in clay minerals (aluminium and iron) (Ghobary, 1983; Warren and Rudolph, 1997). The small fluctuations in concentrations between sampling occasions and minor differences between sites were probably mainly due to natural metal fluctuations as a result of biological processes such as decomposition, and ion uptake and excretion by plants and animals. Other possible reasons could be occasional suspension of sediment into the water, or cation exchange between the clay minerals in the sediment and the water (Warren and Rudolph, 1997).

Finally, from the results it can be concluded that the water of the lower Diep River is contaminated in terms of the detected metals as they were higher than the DWAF guidelines for freshwater ecosystems. Metals such as aluminium, zinc and iron were higher than some of the South African studies compared with. This indicates that, at times, the lower Diep River may be more contaminated with these metals, than the other river systems that have been investigated. Several point sources of pollution, such as agricultural runoff and landfill sites near site 1, industries at site 2, and a sewage treatment plant before site 3, may contribute to this contamination.

The high levels of these metals could pose a threat to the health of the ecosystem. It must be noted that the metals that were below detectable levels (cadmium, lead, nickel, cobalt and chromium) may also pose a similar threat, even if present in minute quantities. It is known that metal bioaccumulation depends on the bioavailability of metals (Nussey et al., 1999), which in turn depends on the metal speciation (Batty and Younger, 2007), and various other factors including pH of the water (Alloway et al., 1988). Therefore, these undetected metals particularly the non-essential metals, might, due to some of these factors, actually be available to freshwater organisms of the lower Diep River and could lead to toxic effects at various levels of biological organisation.

**RESULTS****4.1 Sediment characterisation**

Table 4.1 illustrates relative percentages of the various fractions in sediment samples. Results showed that sediment at site 1 is slightly gravelly sandy mud (gsM), sandy gravel (sG) at site 2, and gravelly sandy (gS) at site 3.

Table 4.1: Relative percentages of the various fractions in sediment samples collected from the three sampling sites in the Diep River.

<b>Sampling site</b>	<b>Sediment fraction</b>	<b>Percentage (%)</b>
Site 1	Clay	19.78
	Silt	49.85
	Sand	29.35
	Pebbles	1.02
Site 2	Clay	0.43
	Silt	0.07
	Sand	25.39
	Pebbles	74.11
Site 3	Clay	0.44
	Silt	5.63
	Sand	79.41
	Pebbles	14.51

**4.2 Comparisons of metal concentrations between the three sampling sites, per sampling occasion****4.2.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.1.



**September 2004:** Statistically significant differences were found between sites 1 and 2, and between sites 1 and 3 ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $13964.25 \pm 1098.43$  mg/kg).

**November 2004, January 2005 and March 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sampling sites. Site 2 had the highest mean aluminium concentration during November 2004 ( $17694.22 \pm 462.07$  mg/kg) and January 2005 ( $15450.22 \pm 614.49$  mg/kg), while site 3 had the highest mean concentration during March 2005 ( $6455.71 \pm 275.53$  mg/kg). The lowest mean aluminium concentrations were found at site 3 during November 2004 ( $2837.31 \pm 377.64$  mg/kg) and January 2005 ( $3044.01 \pm 202.91$  mg/kg), while site 1 had the lowest mean concentration during March 2005 ( $1456.55 \pm 238.24$  mg/kg).

**May 2005 and July 2005:** Comparisons between site 1 and site 2, as well as between site 1 and site 3, showed statistically significant differences ( $P < 0.05$ ). Site 1 had the highest mean aluminium concentration during May 2005 ( $12127.58 \pm 1011.31$  mg/kg) and July 2005 ( $12455.35 \pm 681.58$  mg/kg).

**September 2005:** Statistically significant differences ( $P < 0.05$ ) were found between all three sampling sites. Site 1 had the highest mean aluminium concentration ( $13702.36 \pm 1389.47$  mg/kg), and site 3 the lowest ( $2756.91 \pm 143.45$  mg/kg).

#### **4.2.2 Cadmium**

Mean ( $\pm$  SD) cadmium concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.2.

**September 2004:** No statistically significant differences ( $P > 0.05$ ) were found between any of the sites.

**November 2004 and January 2005:** Statistically significant differences were found between sites 2 and 1, and between sites 2 and 3 ( $P < 0.05$ ). The highest mean cadmium

concentrations were found at site 2 during November 2004 ( $3.16 \pm 0.11$  mg/kg) and January 2005 ( $3.21 \pm 3.21$  mg/kg). Cadmium was not detected in sediment from site 1 and site 3.

**March 2005:** Cadmium was not detected in sediment during March 2005, therefore statistical comparisons were not done.

**May 2005, July 2005 and September 2005:** For each of these sampling occasions, statistically significant differences were found between sites 2 and 1, and between sites 2 and 3 ( $P < 0.05$ ). Site 2 had the highest mean cadmium concentrations during May 2005 ( $0.57 \pm 0.14$  mg/kg), July 2005 ( $0.84 \pm 0.06$  mg/kg) and September 2005 ( $0.40 \pm 0.01$  mg/kg). Cadmium was not detected in sediments from site 1 and site 3.

### 4.2.3 Chromium

Mean ( $\pm$  SD) chromium concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.3.

**September 2004:** Statistically significant differences were found between sites 1 and 3 and between sites 1 and 2 ( $P < 0.05$ ). The highest mean chromium concentration was found at site 1 ( $21.28 \pm 1.64$  mg/kg).

**November 2004, January 2005, March 2005 and May 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sampling sites. Site 2 had the highest mean chromium concentration during November 2004 ( $40.82 \pm 1.17$  mg/kg) and January 2005 ( $43.96 \pm 1.91$  mg/kg), site 3 during March 2005 ( $12.15 \pm 0.60$  mg/kg), and site 1 during May 2005 ( $22.22 \pm 0.86$  mg/kg). The lowest mean chromium concentrations were found at site 1 during November 2004 ( $3.34 \pm 0.94$  mg/kg) and March 2005 ( $3.03 \pm 0.81$  mg/kg), and at site 3 during January 2005 ( $5.87 \pm 0.43$  mg/kg) and May 2005 ( $8.66 \pm 0.44$  mg/kg).

**July 2005:** Statistically significant differences were found between sites 1 and 3 and between sites 1 and 2 ( $P < 0.05$ ). The highest mean chromium concentration was found at site 1 ( $24.52 \pm 1.17$  mg/kg)

**September 2005:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean chromium concentration was found at site 1 ( $20.16 \pm 0.73$  mg/kg), and the lowest at site 3 ( $4.88 \pm 0.35$  mg/kg).

#### **4.2.4 Cobalt**

Mean ( $\pm$  SD) cobalt concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.4.

**September 2004 and November 2004:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sampling sites. Site 1 had the highest mean cobalt concentration during September 2004 ( $8.66 \pm 0.49$  mg/kg), and site 3 during November 2004 ( $10.09 \pm 0.15$  mg/kg). The lowest mean concentrations were found at site 2 during September 2004 ( $0.60 \pm 0.07$  mg/kg), and site 1 during November 2005 ( $1.14 \pm 0.15$  mg/kg).

**January 2005:** Statistically significant differences were found between sites 2 and 3 and between sites 1 and 3 ( $P < 0.05$ ). The lowest mean cobalt concentration was found at site 3 ( $0.93 \pm 0.09$  mg/kg).

**March 2005, May 2005 and July 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all sampling sites. Site 3 had the highest mean cobalt concentration during March 2005 ( $6.23 \pm 0.23$  mg/kg), while site 1 had the highest concentrations during May 2005 ( $0.38 \pm 0.01$  mg/kg) and July 2005 ( $8.66 \pm 0.51$  mg/kg). The lowest mean cobalt concentrations were found at site 1 during March 2005 ( $0.51 \pm 0.05$  mg/kg), site 3 during May 2005 ( $0.05 \pm 0.00$  mg/kg), and site 2 during July 2005 ( $1.94 \pm 0.20$  mg/kg).

**September 2005:** Statistically significant differences were found between sites 1 and 3 and between sites 1 and 2 ( $P < 0.05$ ). The highest mean cobalt concentration was found at site 1 ( $7.48 \pm 0.28$  mg/kg).

#### 4.2.5 Copper

Mean ( $\pm$  SD) copper concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.5.

**September 2004:** No statistically significant differences ( $P > 0.05$ ) were found between any of the sites.

**November 2004:** All comparisons showed statistically significant differences between the three sites ( $P < 0.05$ ). The highest mean copper concentration was found at site 2 ( $108.28 \pm 1.60$  mg/kg), and the lowest at site 1 ( $4.18 \pm 1.20$  mg/kg).

**January 2005:** Statistically significant differences were found between sites 2 and 1 and between sites 2 and 3 ( $P < 0.05$ ). The highest mean copper concentration was found at site 2 ( $115.23 \pm 5.70$  mg/kg).

**March 2005:** Statistically significant differences were found between sites 1 and 2 and between sites 1 and 3 ( $P < 0.05$ ). The highest mean copper concentration was found at site 2 ( $16.84 \pm 5.22$  mg/kg).

**May 2005:** All comparisons showed statistically significant differences between the three sites ( $P < 0.05$ ). The highest mean copper concentration was found at site 2 ( $33.73 \pm 10.66$  mg/kg), and the lowest at site 3 ( $10.45 \pm 0.75$  mg/kg).

**July 2005:** Statistically significant differences were found between sites 2 and 3 and between sites 1 and 2 ( $P < 0.05$ ). The lowest mean copper concentration was found at site 1 ( $12.42 \pm 0.83$  mg/kg).

**September 2005:** All comparisons showed statistically significant differences between the three sites ( $P < 0.05$ ). The highest mean copper concentration was found at site 2 ( $24.45 \pm 2.50$  mg/kg), and the lowest at site 3 ( $5.59 \pm 1.45$  mg/kg).

#### **4.2.6 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.6.

**September 2004:** Statistically significant differences were found between sites 1 and 2 and between sites 1 and 3 ( $P < 0.05$ ). The highest mean iron concentration was found at site 1 ( $15566.41 \pm 748.63$  mg/kg).

**November 2004, January 2005 and March 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sampling sites. Site 2 had the highest mean iron concentration during November 2004 ( $28116.77 \pm 429.49$  mg/kg) and January 2005 ( $13925.03 \pm 396.56$  mg/kg), while site 3 had the highest mean concentration during March 2005 ( $10608.05 \pm 369.59$  mg/kg). The lowest mean concentrations were found at site 1 during November 2004 ( $4133.44 \pm 1443.40$  mg/kg) and March 2005 ( $1818.26 \pm 238.09$  mg/kg), and at site 3 during January 2005 ( $3294.89 \pm 220.48$  mg/kg).

**May 2005 and July 2005:** Statistically significant differences were found between sites 1 and 3 and between sites 1 and 2 ( $P < 0.05$ ). The highest mean iron concentrations were found at site 1 during May 2005 ( $15561.02 \pm 479.40$  mg/kg) and January 2005 ( $17951.47 \pm 793.07$  mg/kg).

**September 2005:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean iron concentration was found at site 1 ( $16150.37 \pm 682.04$  mg/kg), and the lowest at site 3 ( $3072.31 \pm 131.04$  mg/kg).

#### **4.2.7 Lead**

Mean ( $\pm$  SD) lead concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.7.

**September 2004:** No statistically significant differences ( $P>0.05$ ) were found between any of the sites.

**November 2004:** Statistically significant differences were found between all three sites ( $P<0.05$ ). The highest mean concentration was found at site 2 ( $70.05 \pm 9.14$  mg/kg), and the lowest at site 1 ( $6.08 \pm 0.68$  mg/kg).

**January 2005:** Statistically significant differences were found between sites 2 and 1, and between sites 2 and 3 ( $P<0.05$ ). The highest mean lead concentration was found at site 2 ( $52.53 \pm 1.94$  mg/kg).

**March 2005:** No statistically significant differences ( $P>0.05$ ) were found between any of the sites.

**May 2005, July 2005 and September 2005:** For each of these sampling occasions, statistically significant differences were found between sites 2 and 1, and between sites 2 and 3 ( $P<0.05$ ). The highest concentrations were found at site 2 during May 2005 ( $20.83 \pm 4.90$  mg/kg) and September 2005 ( $17.34 \pm 2.26$  mg/kg), and at site 3 during July 2005 ( $25.95 \pm 36.70$  mg/kg).

#### **4.2.8 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.8.

**September 2004:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P<0.05$ ). The highest mean concentration was found at site 1 ( $396.78 \pm 24.49$  mg/kg).

**November 2004, January 2005, March 2005, and May 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sites. Site 3 had the highest mean manganese concentration during November 2004 ( $581.35 \pm 30.02$  mg/kg) and March 2005 ( $387.37 \pm 14.65$  mg/kg), and site 1 during January 2005 ( $237.23 \pm 11.08$  mg/kg) and May 2005 ( $209.48 \pm 5.00$  mg/kg). The lowest mean concentrations were found at site 1 during November 2004 ( $19.46 \pm 8.79$  mg/kg) and March 2005 ( $7.85 \pm 1.22$  mg/kg), and at site 3 during January 2005 ( $15.20 \pm 3.03$  mg/kg) and May 2005 ( $16.47 \pm 1.35$  mg/kg).

**July 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $315.16 \pm 43.82$  mg/kg).

**September 2005:** Comparisons between all three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $283.84 \pm 17.19$  mg/kg), and the lowest at site 3 ( $15.36 \pm 0.74$  mg/kg).

#### **4.2.9 Nickel**

Mean ( $\pm$  SD) nickel concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.9.

**September 2004:** Statistically significant differences were found between sites 1 and 3, and between sites 2 and 3 ( $P < 0.05$ ). The lowest mean concentration was found at site 3 ( $1.27 \pm 0.77$  mg/kg).

**November 2004 and January 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sites. Site 2 had the highest mean concentrations during November 2004 ( $26.82 \pm 0.93$  mg/kg) and January 2005 ( $30.16 \pm 0.95$  mg/kg). The lowest mean concentrations were found at site 1 during November 2004 ( $1.73 \pm 0.30$  mg/kg), and at site 3 during January 2005 ( $3.11 \pm 1.80$  mg/kg).

**March 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P < 0.05$ ). The lowest mean nickel concentration was found at site 1 ( $2.00 \pm 1.81$  mg/kg).

**May 2005:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $11.02 \pm 0.68$  mg/kg), and the lowest at site 3 ( $3.62 \pm 0.27$  mg/kg).

**July 2005:** Statistically significant differences were found between sites 1 and 3, and between sites 1 and 2 ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $13.44 \pm 0.61$  mg/kg).

**September 2005:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). The highest mean concentration was found at site 1 ( $10.95 \pm 0.76$  mg/kg), and the lowest at site 3 ( $1.89 \pm 0.64$  mg/kg).

#### **4.2.10 Zinc**

Mean ( $\pm$  SD) zinc concentrations, measured in sediments from the three sampling sites, during each sampling occasion are shown in Table 4.2.10.

**September 2004:** All comparisons between the three sites showed statistically significant differences ( $P < 0.05$ ). Site 1 had the highest mean concentration during ( $33.17 \pm 1.43$  mg/kg), and the lowest at site 2 ( $15.87 \pm 2.25$  mg/kg).

**November 2004:** Statistically significant difference was found between sites 2 and 3 ( $P < 0.05$ ). Site 2 had the highest mean concentration ( $290.57 \pm 11.91$  mg/kg). Zinc was not detected in sediment at site 1.

**January 2005:** Statistically significant differences were found between sites 1 and 2, and between sites 2 and 3 ( $P < 0.05$ ). The highest mean zinc concentration was found at site 2 ( $331.32 \pm 12.76$  mg/kg).



**March 2005 and May 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between all three sites. Site 3 had the highest mean concentration during March 2005 ( $589.7 \pm 159.67$  mg/kg), and site 2 during May 2005 ( $74.98 \pm 16.66$  mg/kg). The lowest mean concentrations were found at site 1 during March 2005 ( $15.87 \pm 2.25$  mg/kg) and May 2005 ( $35.95 \pm 1.74$  mg/kg).

**July 2005 and September 2005:** For each of these sampling occasions, statistically significant differences ( $P < 0.05$ ) were found between the three sites. The highest mean zinc concentrations were found at site 2 during July 2005 ( $85.23 \pm 16.97$  mg/kg) and September 2005 ( $52.35 \pm 2.07$  mg/kg). Site 1 had the lowest mean concentrations during July 2005 ( $28.60 \pm 1.43$  mg/kg) and September 2005 ( $29.53 \pm 1.77$  mg/kg).

### **4.3 Comparisons of metal concentrations between consecutive sampling occasions, per sampling site**

#### **4.3.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in sediments of the three sampling sites over time are shown in Table 4.2.1. These results are graphically portrayed in Figure 4.3.1.

##### **Site 1**

Comparisons between the following consecutive sampling occasions showed significant ( $P < 0.05$ ) increases or decreases: September 2004 vs November 2004, November 2004 vs. January 2005, January 2005 vs. March 2005, March 2005 vs. May 2005, and July 2005 vs. September 2005. A particularly low mean concentration was found in March 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed no significant difference ( $P > 0.05$ ).

### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed statistically significant ( $P < 0.05$ ) increases or decreases. The following consecutive sampling occasions did not differ significantly: March 2005 vs. May 2005 and May 2005 vs. July 2005. Major concentration peaks were seen in November 2004 and January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

The majority of the comparisons between consecutive sampling occasions showed statistically significant ( $P < 0.05$ ) increases or decreases. The comparisons between November 2004 and January 2005, and between July 2005 and September 2005 did not show significant differences ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

## **4.3.2 Cadmium**

Mean ( $\pm$  SD) cadmium concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.2. These results are graphically portrayed in Figure 4.3.2.

### **Site 1**

Cadmium was mostly not detected in sediment samples from site 1, except during September 2004. However, the comparison between September 2004 and November 2004 did not show a significant difference ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), also did not show a significant difference ( $P > 0.05$ ).

### **Site 2**

The majority of the comparisons between the consecutive sampling occasions, except between November 2004 and January 2005, showed significant ( $P < 0.05$ ) increases or

decreases. Concentration peaks were seen in November 2004 and January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

Cadmium was mostly not detected in sediment samples from site 3, except during September 2004. However, the comparison between September 2004 and November 2004 did not show a significant difference ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), also did not show a significant difference ( $P > 0.05$ ).

### **4.3.3 Chromium**

Mean ( $\pm$  SD) chromium concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.3. These results are graphically portrayed in Figure 4.3.3.

### **Site 1**

All comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). Particularly low mean concentrations were found in November 2004 and March 2005, compared to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed significant ( $P < 0.05$ ) increases or decreases. The following sampling occasions did not show significant differences: May 2005 vs. July 2005 and July 2005 vs. September 2005. Major concentration peaks were seen in November 2004 and January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

All comparisons between consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed that the data did not differ significantly ( $P > 0.05$ ).

### **4.3.4 Cobalt**

Mean ( $\pm$  SD) cobalt concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.4. These results are graphically portrayed in Figure 4.3.4.

#### **Site 1**

All comparisons between consecutive sampling occasions showed statistically significant ( $P < 0.05$ ) increases or decreases. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P > 0.05$ ).

**Site 2 and Site 3:** All comparisons between consecutive sampling occasions showed statistically significant ( $P < 0.05$ ) increases or decreases. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed statistically significant increase ( $P < 0.05$ ).

### **4.3.5 Copper**

Mean ( $\pm$  SD) copper concentrations, measured in sediments of the three sampling sites, over time, are shown in Table 4.2.5. These results are graphically portrayed in Figure 4.3.5.

#### **Site 1**

The majority of the comparisons between consecutive sampling occasions showed significant ( $P < 0.05$ ) increases or decreases. May 2005 vs. July 2005 did however not differ significantly ( $P > 0.05$ ). A comparisons between the first sampling occasion

(September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

#### **Site 2**

Comparisons between September 2004 and November 2004, and between January 2005 and March 2005 showed a significant ( $P<0.05$ ) increase and decrease respectively. Major concentration peaks were seen in November 2004 and January 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

#### **Site 3**

The majority of the comparisons between the consecutive sampling occasions showed significant ( $P<0.05$ ) increases or decreases. Comparisons between January 2005 and March 2005, and between March 2005 and May 2005 showed no significant differences ( $P>0.05$ ). A concentration peak was seen in July 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

### **4.3.6 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.6. These results are graphically portrayed in Figure 4.3.6.

#### **Site 1**

All comparisons between the consecutive sampling occasions showed statistically significant increases or decreases ( $P<0.05$ ). Particularly low mean concentrations were seen in November 2004 and March 2005, compared to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed significant ( $P < 0.05$ ) increases or decreases. The comparisons between March 2005 and May 2005, and between May 2005 and July 2005, did not show significant differences ( $P > 0.05$ ). Concentration peaks were seen during November 2004 and January 2005. A comparison between the first sampling occasion (September 2004) and the last sampling occasion (September 2005), showed significant increase ( $P < 0.05$ ).

### **Site 3**

The comparisons between the majority of the consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). Comparisons between May 2005 and July 2005, and between July 2005 and September 2005 did not show significant differences ( $P > 0.05$ ). A concentration peak was seen in November 2004. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P > 0.05$ ).

## **4.3.7 Lead**

Mean ( $\pm$  SD) lead concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.7. These results are graphically portrayed in Figure 4.3.7.

### **Site 1**

Comparisons between November 2004 and January 2005, and between January 2005 and March 2005 did not show any significant differences ( $P > 0.05$ ). All other comparisons showed significant differences ( $P < 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P > 0.05$ ).

### **Site 2**

Comparisons between November 2004 and January 2005, and between January 2005 and March 2005 showed significant decreases ( $P < 0.05$ ). Comparisons between the rest of the sampling occasions did not show any significant differences ( $P > 0.05$ ). Major

concentration peaks were seen during November 2004 and January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

### **Site 3**

The majority of the comparisons between the consecutive sampling occasions did not differ significantly ( $P>0.05$ ). However, a significant increase was seen between May 2005 and July 2005, and a significant decrease between July 2005 and September 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

## **4.3.8 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.8. These results are graphically portrayed in Figure 4.3.8.

### **Site 1**

The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P<0.05$ ). July 2005 vs. September 2005 did however not differ significantly ( $P>0.05$ ). Particularly low mean manganese concentrations were seen in November 2004 and March 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P<0.05$ ).

### **Site 2**

The majority of comparisons between consecutive sampling occasions showed significant increases or decreases ( $P<0.05$ ). Comparisons between November 2004 and January 2005, and between May 2005 and July 2005 did not differ significantly ( $P>0.05$ ). The mean manganese concentration determined for September 2004 was particularly low, and for November 2004 and January 2005 particularly high, compared to the rest of the sampling occasions. A comparison between the first sampling occasion (September

2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

The majority of the comparisons between the consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). However, July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). Major concentration peaks were observed during November 2004 and March 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P > 0.05$ ).

## **4.3.9 Nickel**

Mean ( $\pm$  SD) nickel concentrations, measured in sediments of the three sampling sites, over time are shown in Table 4.2.9. These results are graphically portrayed in Figure 4.3.9.

### **Site 1**

The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). The comparisons between May 2005 and July 2005, and between July 2005 and September 2005 did not show significant differences ( $P > 0.05$ ). Mean concentrations determined for November 2004 and March 2005 were particularly low compared to the rest of the sampling period. No significant difference was found between September 2004 and September 2005.

### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). Comparisons between March 2005 and May 2005 and between May 2005 and July 2005 did not show any significant differences. Mean concentration peaks were seen in November 2004 and January 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).



### **Site 3**

The majority of the comparisons between consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). However, comparisons between May 2005 and July 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not differ significantly ( $P > 0.05$ ).

### **4.3.10 Zinc**

Mean ( $\pm$  SD) zinc concentrations, measured in sediments of the three sampling sites, over time, are shown in Table 4.2.10. These results are graphically portrayed in Figure 4.3.10.

#### **Site 1**

The majority of the comparisons between consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). No significant difference was found between July 2005 and September 2005. A concentration peak was seen during March 2005. During November 2004 zinc was not detected in the sediments. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P > 0.05$ ).

#### **Site 2**

The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). However, May 2005 vs. July 2005 did not differ significantly ( $P > 0.05$ ). Major concentration peaks were observed during November 2004, January 2005 and March 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

#### **Site 3**

Comparisons between May 2005 and July 2005, and between July 2005 and September 2005 did not show significant differences ( $P > 0.05$ ). All other comparisons between consecutive sampling occasions showed statistically significant differences ( $P < 0.05$ ). A

major concentration peak was observed during March 2005. A comparison between the first sampling occasion (September 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Table 4.2.1: Mean ( $\pm$  SD) aluminium concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.**

Sampling occasion	Site 1	Site 2	Site 3
September 2004	13964.25 $\pm$ 1098.43 <sup>a</sup>	1454.55 $\pm$ 140.48 <sup>b</sup>	1594.75 $\pm$ 149.57 <sup>b</sup>
November 2004	*13271.42 $\pm$ 501.05 <sup>a</sup>	*17694.22 $\pm$ 462.07 <sup>b</sup>	*2837.31 $\pm$ 377.64 <sup>c</sup>
January 2005	*10861.33 $\pm$ 280.36 <sup>a</sup>	*15450.22 $\pm$ 614.49 <sup>b</sup>	3044.01 $\pm$ 202.91 <sup>c</sup>
March 2005	*1456.54 $\pm$ 238.24 <sup>a</sup>	4270.45 $\pm$ 207.61 <sup>b</sup>	*6455.70 $\pm$ 275.53 <sup>c</sup>
May 2005	*12127.58 $\pm$ 1011.31 <sup>a</sup>	4071.82 $\pm$ 701.98 <sup>b</sup>	*4323.83 $\pm$ 436.65 <sup>b</sup>
July 2005	*12455.35 $\pm$ 681.58 <sup>a</sup>	3757.25 $\pm$ 485.68 <sup>b</sup>	*7108.64 $\pm$ 9866.31 <sup>b</sup>
September 2005	*13702.36 $\pm$ 1389.47 <sup>a</sup>	*5030.42 $\pm$ 138.64 <sup>b</sup>	2756.90 $\pm$ 143.45 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.2: Mean ( $\pm$  SD) cadmium concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.**

Sampling occasion	Site 1	Site 2	Site 3
September 2004	0.10 $\pm$ 0.17 <sup>a</sup>	0.10 $\pm$ 0.00 <sup>a</sup>	0.23 $\pm$ 0.29 <sup>a</sup>
November 2004	N.D. <sup>a</sup>	*3.16 $\pm$ 0.11 <sup>b</sup>	N.D. <sup>a</sup>
January 2005	N.D. <sup>a</sup>	3.21 $\pm$ 3.21 <sup>b</sup>	N.D. <sup>a</sup>
March 2005	N.D. <sup>a</sup>	N.D. <sup>a</sup>	N.D. <sup>a</sup>
May 2005	N.D. <sup>a</sup>	0.57 $\pm$ 0.14 <sup>b</sup>	N.D. <sup>a</sup>
July 2005	N.D. <sup>a</sup>	*0.83 $\pm$ 0.06 <sup>b</sup>	N.D. <sup>a</sup>
September 2005	N.D. <sup>a</sup>	*0.40 $\pm$ 0.01 <sup>b</sup>	N.D. <sup>a</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.3:** Mean ( $\pm$  SD) chromium concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	21.28 $\pm$ 1.64 <sup>a</sup>	2.64 $\pm$ 0.93 <sup>b</sup>	3.42 $\pm$ 1.36 <sup>b</sup>
November 2004	*3.34 $\pm$ 0.94 <sup>a</sup>	*40.82 $\pm$ 1.17 <sup>b</sup>	*19.30 $\pm$ 0.59 <sup>c</sup>
January 2005	*15.85 $\pm$ 0.30 <sup>a</sup>	*43.96 $\pm$ 1.91 <sup>b</sup>	*5.87 $\pm$ 0.43 <sup>c</sup>
March 2005	*3.03 $\pm$ 0.81 <sup>a</sup>	*9.35 $\pm$ 0.19 <sup>b</sup>	*12.15 $\pm$ 0.60 <sup>c</sup>
May 2005	*22.21 $\pm$ 0.86 <sup>a</sup>	*12.78 $\pm$ 2.44 <sup>b</sup>	*8.66 $\pm$ 0.44 <sup>c</sup>
July 2005	*24.52 $\pm$ 1.17 <sup>a</sup>	10.80 $\pm$ 1.19 <sup>b</sup>	*14.91 $\pm$ 21.90 <sup>b</sup>
September 2005	*20.16 $\pm$ 0.73 <sup>a</sup>	10.33 $\pm$ 0.70 <sup>b</sup>	*4.88 $\pm$ 0.35 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.4:** Mean ( $\pm$  SD) cobalt concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	8.66 $\pm$ 0.49 <sup>a</sup>	0.60 $\pm$ 0.07 <sup>b</sup>	0.77 $\pm$ 0.23 <sup>c</sup>
November 2004	*1.14 $\pm$ 0.15 <sup>a</sup>	*7.27 $\pm$ 0.12 <sup>b</sup>	*10.09 $\pm$ 0.15 <sup>c</sup>
January 2005	*5.82 $\pm$ 0.15 <sup>a</sup>	*5.80 $\pm$ 0.22 <sup>a</sup>	*0.93 $\pm$ 0.09 <sup>b</sup>
March 2005	*0.51 $\pm$ 0.05 <sup>a</sup>	*1.89 $\pm$ 0.11 <sup>b</sup>	*6.23 $\pm$ 0.23 <sup>c</sup>
May 2005	*0.38 $\pm$ 0.01 <sup>a</sup>	*0.09 $\pm$ 0.01 <sup>b</sup>	*0.05 $\pm$ 0.00 <sup>c</sup>
July 2005	*8.37 $\pm$ 0.51 <sup>a</sup>	*1.94 $\pm$ 0.20 <sup>b</sup>	*2.20 $\pm$ 2.80 <sup>c</sup>
September 2005	*7.48 $\pm$ 0.28 <sup>a</sup>	*2.44 $\pm$ 0.17 <sup>b</sup>	*1.18 $\pm$ 0.00 <sup>b</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.5:** Mean ( $\pm$  SD) copper concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	13.58 $\pm$ 2.87 <sup>a</sup>	39.34 $\pm$ 53.50 <sup>a</sup>	9.71 $\pm$ 7.13 <sup>a</sup>
November 2004	*4.18 $\pm$ 1.20 <sup>a</sup>	*108.28 $\pm$ 1.60 <sup>b</sup>	*12.83 $\pm$ 0.98 <sup>c</sup>
January 2005	*6.87 $\pm$ 1.59 <sup>a</sup>	115.23 $\pm$ 5.70 <sup>b</sup>	6.78 $\pm$ 1.74 <sup>a</sup>
March 2005	*4.92 $\pm$ 1.13 <sup>a</sup>	*16.84 $\pm$ 5.22 <sup>b</sup>	9.61 $\pm$ 5.09 <sup>a</sup>
May 2005	*12.35 $\pm$ 1.41 <sup>a</sup>	33.73 $\pm$ 10.66 <sup>b</sup>	10.45 $\pm$ 0.75 <sup>c</sup>
July 2005	12.42 $\pm$ 0.83 <sup>a</sup>	22.46 $\pm$ 2.50 <sup>b</sup>	*24.30 $\pm$ 36.74 <sup>a</sup>
September 2005	*10.00 $\pm$ 0.91 <sup>a</sup>	24.45 $\pm$ 21.10 <sup>b</sup>	*5.59 $\pm$ 1.45 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.6:** Mean ( $\pm$  SD) iron concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	15566 $\pm$ 748.63 <sup>a</sup>	1872.60 $\pm$ 248.82 <sup>b</sup>	1992.76 $\pm$ 189.37 <sup>b</sup>
November 2004	*4133.44 $\pm$ 1443.40 <sup>a</sup>	*28116.77 $\pm$ 429.49 <sup>b</sup>	*24960.13 $\pm$ 364.94 <sup>c</sup>
January 2005	*11857.95 $\pm$ 239.11 <sup>a</sup>	*13925.03 $\pm$ 396.56 <sup>b</sup>	*3294.89 $\pm$ 220.48 <sup>c</sup>
March 2005	*1818.26 $\pm$ 238.09 <sup>a</sup>	*6007.80 $\pm$ 426.59 <sup>b</sup>	*10608.05 $\pm$ 369.59 <sup>c</sup>
May 2005	*15561.02 $\pm$ 479.40 <sup>a</sup>	5083.04 $\pm$ 897.73 <sup>b</sup>	*4483.67 $\pm$ 694.52 <sup>b</sup>
July 2005	*17951.47 $\pm$ 793.07 <sup>a</sup>	6028.10 $\pm$ 567.87 <sup>b</sup>	7639.92 $\pm$ 10828.00 <sup>b</sup>
September 2005	*16150.37 $\pm$ 682.04 <sup>a</sup>	*6935.06 $\pm$ 477.78 <sup>b</sup>	3072.31 $\pm$ 131.04 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.7:** Mean ( $\pm$  SD) lead concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	13.63 $\pm$ 1.65 <sup>a</sup>	37.71 $\pm$ 36.37 <sup>a</sup>	9.50 $\pm$ 4.24 <sup>a</sup>
November 2004	*6.08 $\pm$ 0.68 <sup>a</sup>	70.05 $\pm$ 9.14 <sup>b</sup>	16.67 $\pm$ 0.72 <sup>c</sup>
January 2005	9.55 $\pm$ 0.75 <sup>a</sup>	*52.53 $\pm$ 1.94 <sup>b</sup>	10.97 $\pm$ 1.61 <sup>a</sup>
March 2005	8.38 $\pm$ 6.57 <sup>a</sup>	*20.61 $\pm$ 9.06 <sup>a</sup>	11.18 $\pm$ 7.41 <sup>a</sup>
May 2005	*13.04 $\pm$ 1.87 <sup>a</sup>	20.83 $\pm$ 4.90 <sup>b</sup>	12.41 $\pm$ 1.65 <sup>a</sup>
July 2005	*11.15 $\pm$ 0.70 <sup>a</sup>	22.62 $\pm$ 9.28 <sup>b</sup>	*25.95 $\pm$ 36.70 <sup>a</sup>
September 2005	*12.28 $\pm$ 0.49 <sup>a</sup>	17.34 $\pm$ 2.26 <sup>b</sup>	*11.89 $\pm$ 1.72 <sup>a</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.8:** Mean ( $\pm$  SD) manganese concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	396.78 $\pm$ 24.49 <sup>a</sup>	14.99 $\pm$ 1.68 <sup>b</sup>	14.05 $\pm$ 0.93 <sup>b</sup>
November 2004	*19.46 $\pm$ 8.79 <sup>a</sup>	*214.12 $\pm$ 4.36 <sup>b</sup>	*581.35 $\pm$ 30.02 <sup>c</sup>
January 2005	*237.23 $\pm$ 11.08 <sup>a</sup>	208.98 $\pm$ 5.92 <sup>b</sup>	*15.20 $\pm$ 3.02 <sup>c</sup>
March 2005	*7.85 $\pm$ 1.22 <sup>a</sup>	*54.55 $\pm$ 4.65 <sup>b</sup>	*387.37 $\pm$ 14.65 <sup>c</sup>
May 2005	*209.48 $\pm$ 5.00 <sup>a</sup>	*84.84 $\pm$ 17.16 <sup>b</sup>	*16.47 $\pm$ 1.35 <sup>c</sup>
July 2005	*315.16 $\pm$ 43.82 <sup>a</sup>	104.26 $\pm$ 8.53 <sup>b</sup>	*31.49 $\pm$ 44.20 <sup>b</sup>
September 2005	283.84 $\pm$ 17.19 <sup>a</sup>	*61.66 $\pm$ 4.02 <sup>b</sup>	15.36 $\pm$ 0.74 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

**Table 4.2.9:** Mean ( $\pm$  SD) nickel concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. Sample size (n) =5.

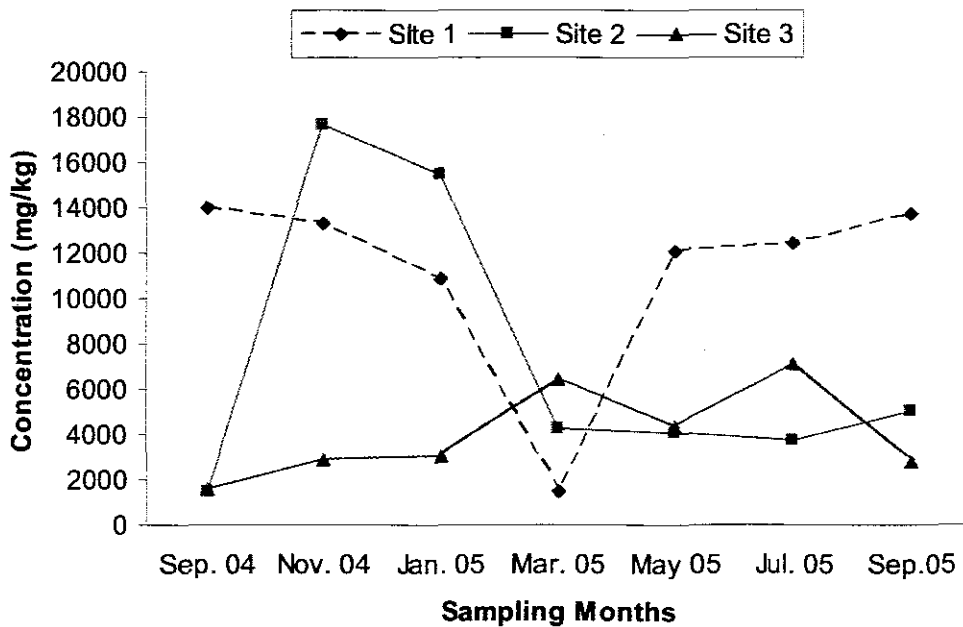
Sampling occasion	Site 1	Site 2	Site 3
September 2004	10.88 $\pm$ 0.97 <sup>a</sup>	10.88 $\pm$ 0.97 <sup>a</sup>	1.27 $\pm$ 0.77 <sup>b</sup>
November 2004	*1.73 $\pm$ 0.30 <sup>a</sup>	*26.82 $\pm$ 0.93 <sup>b</sup>	*11.49 $\pm$ 0.85 <sup>c</sup>
January 2005	*10.26 $\pm$ 0.31 <sup>a</sup>	*30.16 $\pm$ 0.95 <sup>b</sup>	*3.11 $\pm$ 1.80 <sup>c</sup>
March 2005	*2.00 $\pm$ 1.81 <sup>a</sup>	*8.37 $\pm$ 1.05 <sup>b</sup>	*8.56 $\pm$ 0.34 <sup>b</sup>
May 2005	*11.02 $\pm$ 0.68 <sup>a</sup>	8.44 $\pm$ 1.58 <sup>b</sup>	*3.62 $\pm$ 0.27 <sup>c</sup>
July 2005	13.44 $\pm$ 0.61 <sup>a</sup>	7.17 $\pm$ 0.34 <sup>b</sup>	6.46 $\pm$ 7.86 <sup>b</sup>
September 2005	10.94 $\pm$ 0.76 <sup>a</sup>	*6.38 $\pm$ 0.75 <sup>b</sup>	*1.89 $\pm$ 0.64 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

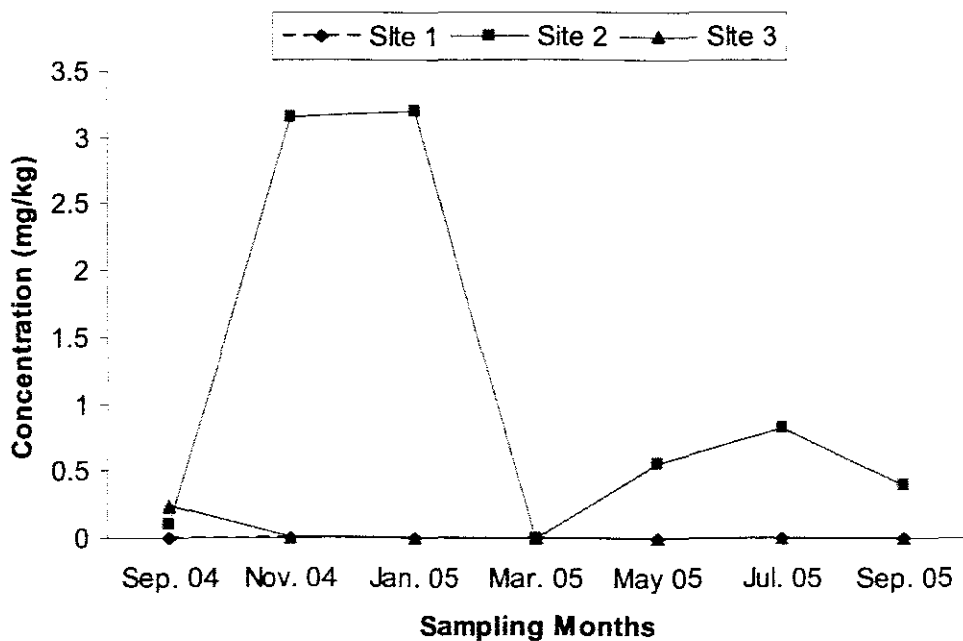
**Table 4.2.10:** Mean ( $\pm$  SD) zinc concentrations (mg/kg), measured in the sediments from the three Diep River sampling sites, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling occasion	Site 1	Site 2	Site 3
September 2004	33.17 $\pm$ 1.43 <sup>a</sup>	15.87 $\pm$ 2.25 <sup>b</sup>	19.20 $\pm$ 2.16 <sup>c</sup>
November 2004	N.D. <sup>a</sup>	*290.57 $\pm$ 11.91 <sup>b</sup>	*11.57 $\pm$ 3.04 <sup>c</sup>
January 2005	23.09 $\pm$ 14.14 <sup>a</sup>	*331.32 $\pm$ 12.76 <sup>b</sup>	*23.54 $\pm$ 4.98 <sup>a</sup>
March 2005	*83.39 $\pm$ 40.28 <sup>a</sup>	*191.35 $\pm$ 89.27 <sup>b</sup>	*589.77 $\pm$ 159.67 <sup>c</sup>
May 2005	*35.95 $\pm$ 1.74 <sup>a</sup>	*74.98 $\pm$ 16.66 <sup>b</sup>	*40.95 $\pm$ 2.29 <sup>c</sup>
July 2005	*28.60 $\pm$ 1.43 <sup>a</sup>	85.23 $\pm$ 16.97 <sup>b</sup>	82.52 $\pm$ 115.06 <sup>c</sup>
September 2005	29.53 $\pm$ 1.77 <sup>a</sup>	*52.35 $\pm$ 2.07 <sup>b</sup>	32.61 $\pm$ 1.12 <sup>c</sup>

Different letters indicate statistical significant differences between different sites. An asterisk (\*) indicates a statistical difference from the previous sampling occasion.

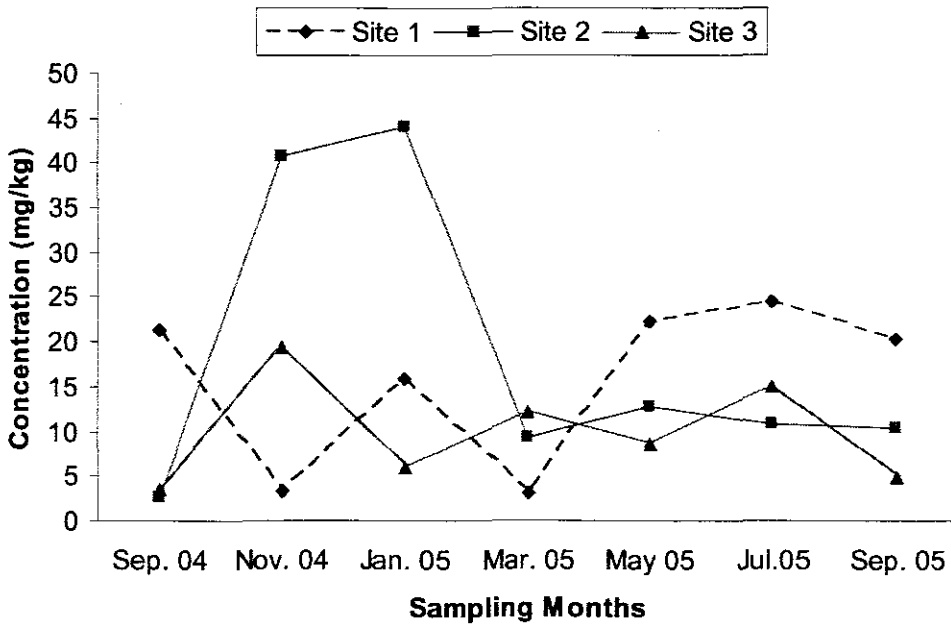


**Figure 4.3.1:** Mean aluminium concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.

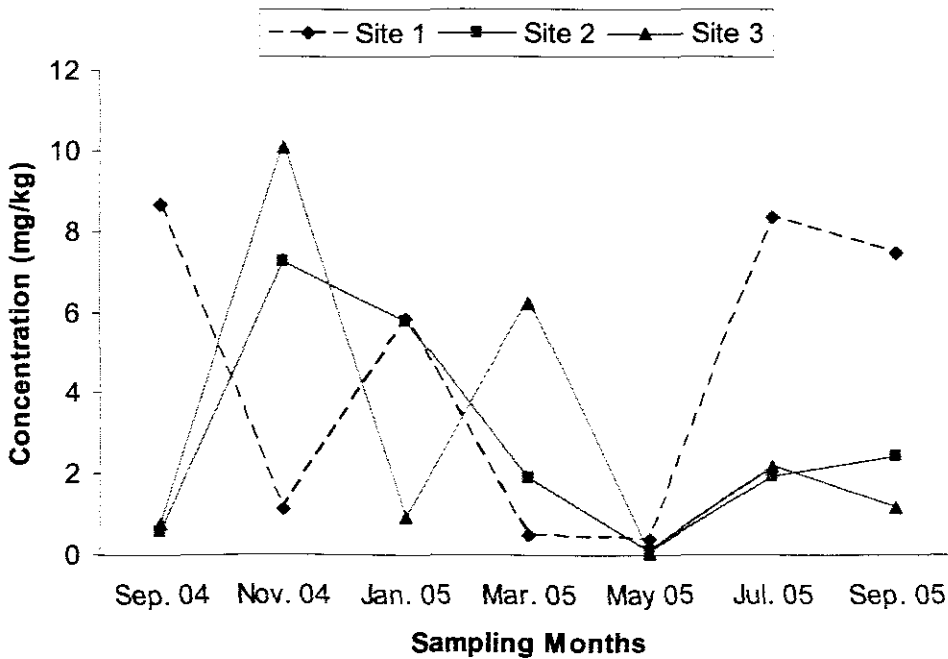


**Figure 4.3.2:** Mean cadmium concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.

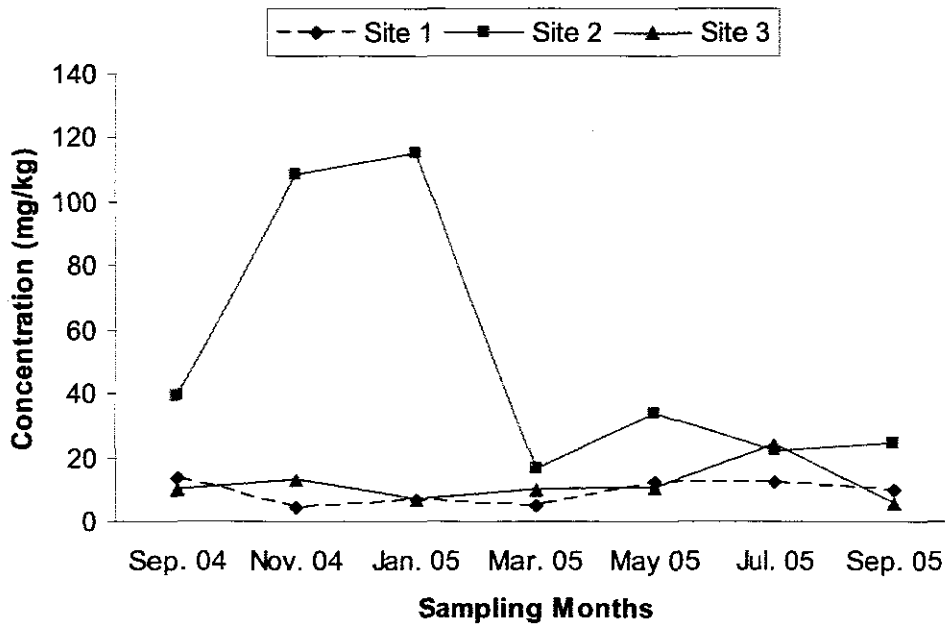




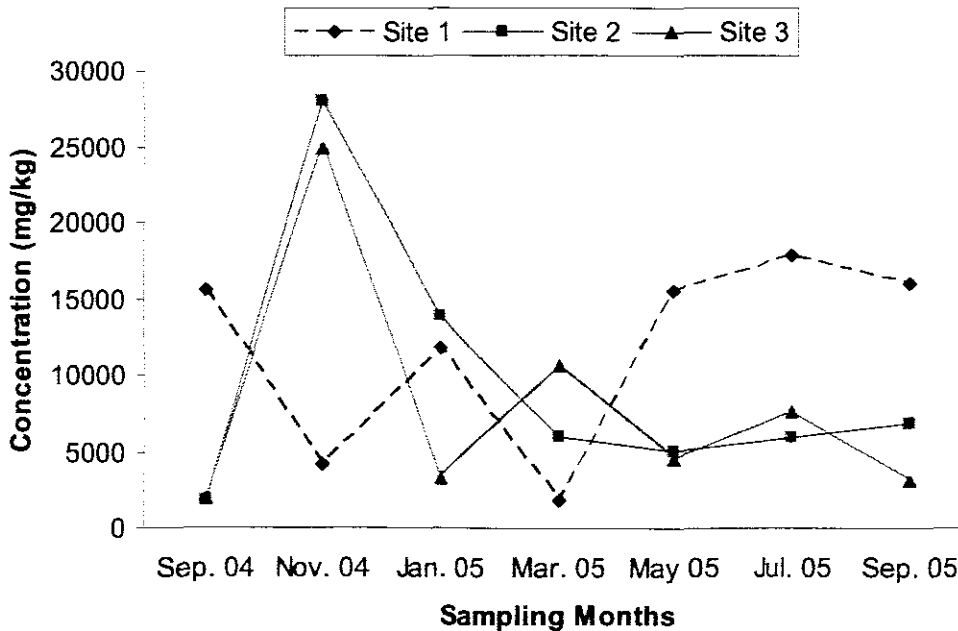
**Figure 4.3.3:** Mean chromium concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



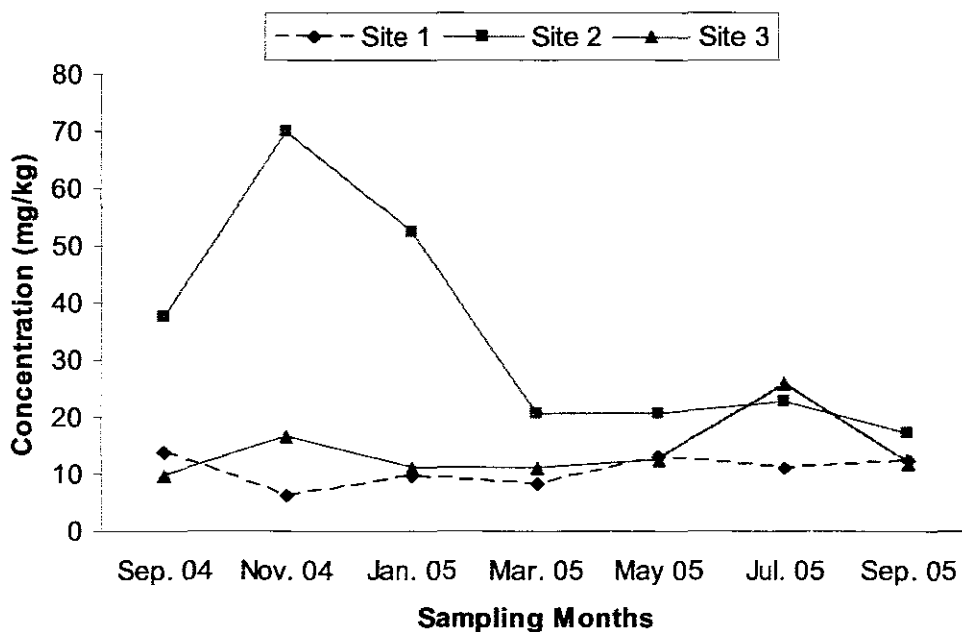
**Figure 4.3.4:** Mean cobalt concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



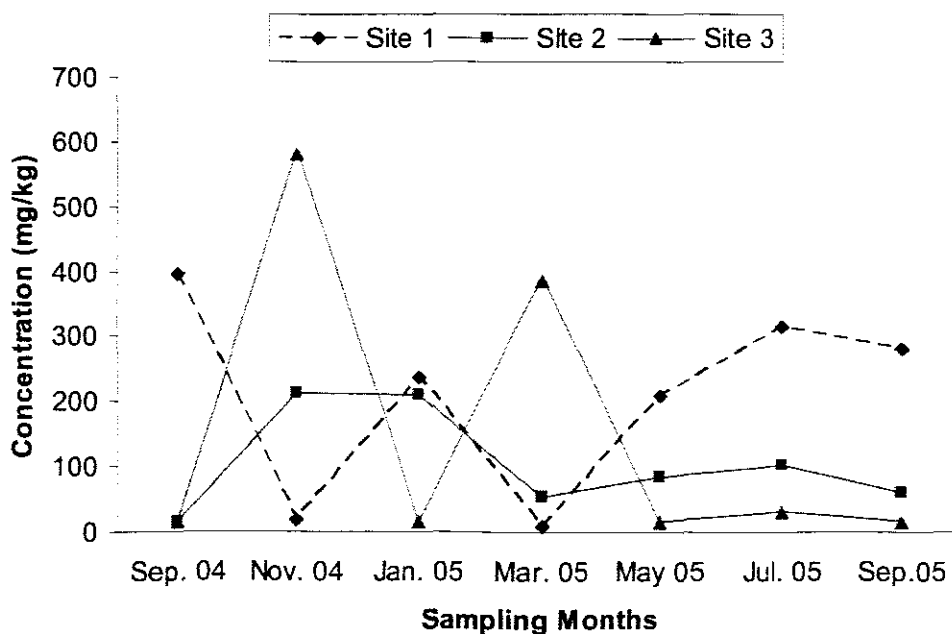
**Figure 4.3.5:** Mean copper concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



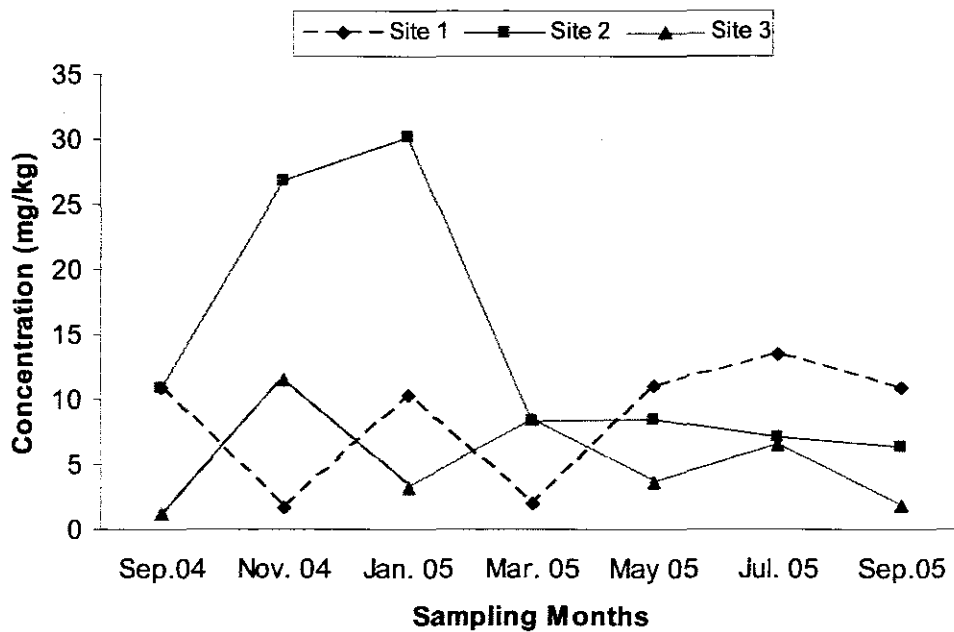
**Figure 4.3.6:** Mean iron concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



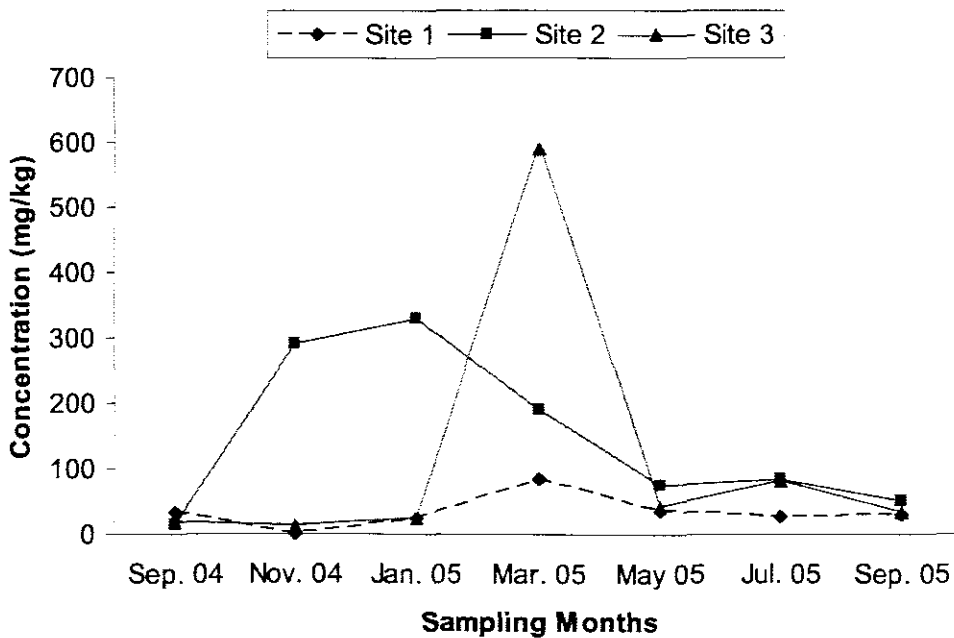
**Figure 4.3.7:** Mean lead concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



**Figure 4.3.8:** Mean manganese concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005



**Figure 4.3.9:** Mean nickel concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.



**Figure 4.3.10:** Mean zinc concentrations (mg/kg), measured in the sediments from three sampling sites in the Diep River, between September 2004 and September 2005.

## DISCUSSION

The sediments of the three Diep River sites were characterised. Site 1 sediment was found to be slightly gravelly sandy mud, with a high percentage of silt, followed by sand and clay respectively. Site 2 sediment was found to be sandy gravel, with a high percentage of pebbles and sand, whilst site 3 sediment was gravelly sandy, with a high percentage of sand, followed by pebbles. This site's sediment also was rich in organic material (Table 4.1). The clay and organic material content of soils or sediments are of particular importance, as it is these components that are responsible for cation adsorption and retention in soils (Otte et al., 1993; Van Hattum et al., 1993; Ashman and Puri, 2002). This needs to be taken into account when different sites with different sediment types are compared. In this study all three sites have different types of sediment, with site 1 containing the highest percentage of clay of the three, and site 3 containing high organic matter content. Site 2, on the other hand, has a low content of both clay and organic material. These differences may influence the accumulation of metals in the sediment.

Metal concentrations in sediment from the lower Diep River were compared with the Canadian Sediment Quality Guidelines (CSQG) for the protection of aquatic life as no sediment guidelines exist for South Africa. The guidelines are as follows: cadmium (0.6 mg/kg), copper (35.7 mg/kg), chromium (37.3 mg/kg), lead (35.0 mg/kg) and zinc (123 mg/kg) (CCME, 2001). Similar Canadian guidelines do not exist for the other metals investigated. Cadmium concentrations were low at site 1 and site 3 compared to the CSQG. Site 2 had high concentrations in November 2004 ( $3.16 \pm 0.11$  mg/kg), January 2005 ( $3.21 \pm 3.21$  mg/kg) and July 2005 ( $0.83 \pm 0.06$  mg/kg) compared to the CSQG (Table 4.2.2). Chromium (Table 4.2.3) and zinc (Table 4.2.10) had low concentrations at site 1 and 3 compared to the CSQG, but high concentrations were found at site 2 in November 2004 ( $40.82 \pm 1.17$  mg/kg;  $290.57 \pm 11.91$  mg/kg) and January 2005 ( $43.96 \pm 0.19$  mg/kg;  $331.32 \pm 12.76$  mg/kg) respectively. Copper (Table 4.2.5) and lead (Table 4.2.7) also had low concentrations at site 1 and 3, but high concentrations were found at site 2 in September 2004 ( $39.34 \pm 53.50$  mg/kg;  $37.71 \pm 36.37$  mg/kg), November 2004

(108.28 ± 1.60 mg/kg; 70.05 ± 9.14 mg/kg) and January 2006 (115.23 ± 5.70 mg/kg; 52.53 ± 1.94 mg/kg), respectively.

Nickel was compared with the Australian Interim Sediment Quality guidelines (ISQG) for fresh and marine waters. The ISQG for nickel is 21 mg/kg (ANZECC, 1992). Nickel concentrations were lower than the ISQG limit at all 3 sampling sites except during November 2004 (26.82 ± 0.93 mg/kg), and January 2005 (30.16 ± 11.91 mg/kg) at site 2 (Table 4.2.9).

Aluminium, cobalt, iron and manganese were compared with the World Shale Standard. The standard for aluminium is (8.0 mg/kg), cobalt (19 mg/kg), iron (4.6 mg/kg) and manganese (850 mg/kg) (Turekian and Wedepohl, 1961). Aluminium (Table 4.2.1) and iron (Table 4.2.6) concentrations at all three sites were much higher than the World Shale Standard. Cobalt concentrations were low compared to the World Shale Standard at all three sites (Table 4.2.4). Manganese concentrations (Table 4.2.8) were in general lower than the World Shale Standard, especially at site 1 in November (19.46 ± 8.79 mg/kg) and March (7.85 ± 1.22 mg/kg) when they were much lower than the standard. Site 2 had much lower concentrations than the standard in September 2004 (14.99 ± 1.69 mg/kg), March 2005 (54.55 ± 4.65 mg/kg), May 2005 (84.84 ± 17.16 mg/kg) and September 2005 (61.66 ± 4.02 mg/kg). Site 3 had much lower concentrations in September 2004 (14.05 ± 0.93 mg/kg), January 2005 (15.20 ± 3.02 mg/kg), May 2005 (16.47 ± 1.35 mg/kg) and July 2005 (31.49 ± 44.20 mg/kg), than the Standard.

Apart from the comparisons with the guideline concentrations, attempts were also made to compare the results with previous studies on metal contamination in South African sediments, even though the environments and types of sediment may differ. Comparisons with the findings of Reinecke et al. (2003) for a polluted site in the Eerste River showed that sediment cadmium concentrations in the present study were much higher at site 2 in November 2004 and January 2005, whilst lead concentrations in the present study were higher for all three sites. Zinc concentrations in the present study were much higher than the concentrations measured by Thawley et al. (2004) at all their sampling sites in the

Legarane River, Elands River and Hex River, of which some were considered polluted and some unpolluted. Copper concentrations in the present study were compared with the results of Snyman et al. (2002). Comparisons were done with a polluted site in the Eerste River. Concentrations were generally much higher than their concentrations. Chromium, iron and manganese concentrations were compared with the results of Steenkamp et al. (1994) for polluted sites in the Natalspruit River, Bronkhorstspuit River and Nooitgedacht Dam. Chromium concentrations in the present study were within their concentration range or lower. Iron concentrations in the present study were also within their concentration range, whilst the manganese concentration range was too wide for such comparisons. Finally, nickel concentrations were compared with the results of Van Eeden and Schoonbee (1991) for polluted sites in the Heidelberg wetland. Nickel concentrations in the present study were much lower at all three sites compared with their concentrations. Aluminium and cobalt concentrations could not be compared with the results of other studies, since information on these metals in South African rivers is lacking.

It is clear that the results of the present study compare favourably with those of other South African studies and also that all three sampling sites can be considered contaminated with metals in various degrees. The comparisons with sediment guidelines indicate that, particularly at site 2, metal concentrations (except manganese), were very high, especially for micronutrients zinc and copper in November 2004 and January 2005. These peaks observed in these months could have been due to several reasons, such as extra inputs of metals from the industries and sewage treatment works surrounding this area, since site 2 is within the major industrial area, and/or due to seasonal influences, as rainfall was low during this time (Table 2.1). The water level tended to be low, and water flow was slower, which according to Lee et al. (2003), may lead to metals being deposited into the sediment.

Comparisons between the three sampling sites revealed a number of trends in terms of metal contamination: firstly, cadmium, lead and the micronutrients copper and zinc were higher at site 2 than at the other two sites, throughout most of the year. All other metals,

except manganese, had concentration peaks at site 2 during November and January (not only higher than the other two sites but often also higher than the various sediment guideline concentrations that they were compared with). The possible explanations for these results have already been discussed in the previous paragraph.

Secondly, concentrations of aluminium, iron, chromium, manganese, nickel and cobalt tended to be higher at site 1 during September 2004, May, July and September 2005. These concentrations were however mainly not higher than the guideline concentrations. Site 1 was found to have higher clay content than the other sites (Table 4.2.1). Aluminium and iron are metals that are naturally included in the clay mineral structure (Watling and Watling, 1983; Modak et al., 1992; Ashman and Puri, 2002). The higher clay content at site 1 might possibly explain elevated concentrations of these two metals but such results would be expected throughout the year. Clay minerals also have an important adsorbing function (Salomons, 1995; Dassenakis et al., 1995), which may explain the elevated concentrations of chromium, manganese, nickel and cobalt. However, the exact sources of these four metals are uncertain, since no major industries exist above this site. It is possible that other anthropogenic activities, such as agriculture and waste disposal may have contributed to these metal levels. September 2004, May and July 2005 had the highest mean rainfall (Table 2.1), thus also the largest water volume and fastest flow, which would have increased the chances of site 1 being contaminated by sources upstream.

A third trend that was revealed from the results was that site 3 seemed to have generally lower metal contamination than the other two sites, or at least lower than site 2. Since site 3 was situated close to the estuary and directly downstream of the wetland system, these results were to be expected. Water from the estuary occasionally pushed up into the river, up to site 3 (personal observations). This probably had a dilution effect on metals at this site and possibly washed metals downstream into the ocean as the water receded. Grindley and Dudley (1988) documented the diluting effect of seawater influxes at high tide, in the Diep River estuary and Rietvlei. Furthermore, and probably far more importantly, wetlands are known to filter out metals from surface waters by means of



wetland vegetation. Plants such as *Phragmites australis*, *Bolboschoenus maritimus* (which both occur in this area), *Spartina alterniflora* and many others play a significant role in phytoremediation of wetlands as they accumulate metals in their tissues (Weis and Weis, 2004; Bragato et al., 2006; Madejón et al., 2006a). The problem with phytoremediation is of course that when the plants die and decay, the accumulated metals could increase the concentrations of metals in the sediment. This could pose a health risk to the organisms living in the particular wetland (Vardanyan and Ingole, 2006).

Finally, it seems that the lower Diep River ecosystem is threatened by metal pollution, particularly in the vicinity of the sensitive Rietvlei reserve (close to site 2), since the industries and surrounding urban areas are sources of metal contamination. These metals settle into the sediments at a faster rate than they are washed downstream. Closer to the mouth of the river, large concentrations of metals have already been accumulated by plants such as *Bolboschoenus maritimus* (see chapter 5), lessening the threat to the estuary. However, these accumulated metals have of course not been taken out of the ecosystem and, with decomposition of plants, and via food chains, these metals still pose a threat to the ecosystem.

**RESULTS****5.1 Comparisons of metal concentrations between sampling sites 1 and 3, per sampling occasion (as mentioned in chapter 2)****5.1.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3 during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.1.

***November 2004:***

Aluminium concentrations measured in leaves and stems of plants from site 1 were significantly higher ( $P < 0.05$ ) than those from site 3. However, the opposite results were found for the roots.

***March 2005:***

Aluminium concentrations measured in leaves and stems of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1, whereas the opposite results were found for the roots.

***July 2005:***

Aluminium concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the 2 sites in terms of aluminium in the stems.

### ***September 2005:***

Aluminium concentrations measured in the stems from site 1 were significantly higher ( $P < 0.05$ ) than the one from site 3. However, aluminium concentrations in the other plant parts did not differ significantly between the two sites.

## **5.1.2 Cadmium**

Mean ( $\pm$  SD) cadmium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3 during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.2.

***November 2004 and March 2005:*** Cadmium was not detected at all during November 2004 and March 2005.

***July 2005 and September 2005:*** Cadmium concentrations in roots from site 3 were significantly higher ( $P < 0.05$ ) than in roots from site 1. Cadmium was not detected in leaves and stems at all, therefore, statistical comparisons were not done.

## **5.1.3 Chromium**

Mean ( $\pm$  SD) chromium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.3.

***November 2004:*** Comparisons between leaves and between stems from site 1 and site 3 did not show any statistically significant differences ( $P > 0.05$ ). However, chromium concentrations in roots from site 1 were significantly higher ( $P < 0.05$ ) than in roots from site 3.

***March 2005:*** Comparisons between leaves and between roots from site 1 and site 3 did not show statistically significant differences ( $P > 0.05$ ). However, chromium concentrations in stems from site 3 were significantly higher ( $P < 0.05$ ) than in stems from site 1.

**July 2005:** Chromium concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, no statistically significant differences were found between the two sites in terms of chromium in the stems ( $P > 0.05$ ).

**September 2005:** Comparisons between roots, leaves and stems from site 1 and site 3 did not show any significant differences ( $P > 0.05$ ).

#### **5.1.4 Cobalt**

Mean ( $\pm$  SD) cobalt concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.4.

**November 2004 and March:** Cobalt concentrations measured in leaves, stems and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) higher than those from site 1.

**July 2005:** Comparisons between roots and between stems from the two sites did not show significant differences ( $P > 0.05$ ). However, cobalt concentrations in leaves from site 3 were significantly higher ( $P < 0.05$ ) than in leaves from site 1.

**September 2005:** Cobalt concentrations measured in leaves, stems and roots from site 1 were significantly higher ( $P < 0.05$ ) than those from site 3.

#### **5.1.5 Copper**

Mean ( $\pm$  SD) copper concentrations measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.5.

**November 2004:** Copper concentrations measured in leaves, stems and roots from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1.

**March 2005:** Copper concentrations measured in leaves and stems from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of copper in the roots.

**July 2005:** Copper concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. Copper concentrations in stems were significantly higher ( $P < 0.05$ ) at site 1 than site 3.

**September 2005:** Copper concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those at site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of copper in the stems.

### **5.1.6 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.6.

**November 2004:** Iron concentrations measured in leaves and stems of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. The opposite results were found for roots.

**March 2005:** Comparisons between leaves and between roots from the two sites did not show significant differences ( $P > 0.05$ ). However, iron concentrations in stems from site 3 were significantly higher ( $P < 0.05$ ) than in roots from site 1.

**July 2005:** Iron concentrations measured in leaves, stems and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1.

**September 2005:** Comparisons between leaves, stems and roots from site 1 and site 3 did not show any significant differences ( $P > 0.05$ ).

### **5.1.7 Lead**

Mean ( $\pm$  SD) lead concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.7.

**November 2004:** Lead concentrations measured in leaves and stems of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. The opposite results were found for roots.

**March 2005:** Lead concentrations measured in leaves and stems of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of lead in the roots.

**July 2005:** Lead concentrations measured in leaves and roots of plants from site 3 were significantly higher than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of lead in the stems.

**September 2005:** Lead concentrations measured in leaves and roots of plants from site 3 were significantly higher than those from site 1. Lead was not detected in stems at all.

### **5.1.8 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.8.

**November 2004 and March 2005:** Manganese concentrations measured in leaves, stems and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1.

**July 2005 and September 2005:** Manganese concentrations measured in leaves and stems of plants from site 1 were significantly higher than those from site 3. However, there was

no significant difference ( $P>0.05$ ) between the two sites in terms of manganese in the roots.

### **5.1.9 Nickel**

Mean ( $\pm$  SD) nickel concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.9.

**November 2004:** Nickel concentrations measured in leaves and roots of plants from site 3 were significantly higher than those from site 1. However, there was no significant difference ( $P>0.05$ ) between the two sites in terms of nickel in the stems.

**March 2005:** Nickel concentrations measured in leaves and stems of plants from site 3 were significantly higher than those from site 1. However, no significant differences ( $P>0.05$ ) were found between roots.

**July 2005:** Nickel concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P<0.05$ ) than those from site 1.

**September 2005:** Nickel concentrations measured in leaves of plants from site 1 were significantly higher ( $P<0.05$ ) than those from site 3. However, there was no significant difference ( $P>0.05$ ) between the two sites in terms of manganese in the stems and roots.

### **5.1.10 Zinc**

Mean ( $\pm$  SD) zinc concentration, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.10.

**November 2004:** Zinc concentrations measured in leaves and stems of plants from site 3 were significantly higher ( $P<0.05$ ) than those from site 1. However, there was no significant difference ( $P>0.05$ ) between the two sites in terms of zinc in the roots.

**March 2005:** Zinc concentrations measured in leaves, stems and roots of plants from site 3 were significantly higher than those from site 1.

**July 2005:** Zinc concentrations measured in leaves and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of zinc in the stems.

**September 2005:** Zinc concentrations measured in stems and roots of plants from site 3 were significantly higher ( $P < 0.05$ ) than those from site 1. However, there was no significant difference ( $P > 0.05$ ) between the two sites in terms of zinc in the leaves.

## **5.2 Comparisons of metal concentrations between consecutive sampling occasions, per sampling site**

### **5.2.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in roots, leaves and stems of plants collected from the two sampling sites, over time are shown in Table 5.1.1. These results are graphically portrayed in Figure 5.2.1A-C.

#### **Site 1**

**Roots:** Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Leaves:** Comparisons between November 2004 and March 2005, and between March 2005 and July 2005, showed a statistically significant increase and decrease respectively ( $P < 0.05$ ). Comparisons between July 2005 and September 2005 did not show any significant difference. A comparison between the first sampling occasion (November



2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions did not show significant differences ( $P>0.05$ ). July 2005 vs. September 2005 showed a significant increase ( $P<0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

### Site 3

**Roots:** No comparisons between consecutive sampling occasions showed significant increases or decreases ( $P>0.05$ ), including a comparison between November 2004 and September 2005.

**Leaves:** Comparisons between all consecutive sampling occasions showed significant increases or decreases ( $P<0.05$ ). Concentration peaks were seen in March 2005 and July 2005. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P<0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P<0.05$ ). July 2005 vs. September 2005 did not show any significant difference. A major peak concentration was seen in March 2005 compared to other sampling occasions. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P>0.05$ ).

### 5.2.2 Cadmium

Mean ( $\pm$  SD) cadmium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.2. These results are graphically portrayed in Figure 5.2.2A.

**Site 1:** Cadmium was not detected in leaves, roots or stems for the entire sampling period, therefore statistical comparisons were not done.

**Site 3:** Cadmium was not detected in leaves or stems for the entire sampling period, therefore statistical comparisons were not done.

**Roots:** Cadmium was not detected during November 2004 and March 2005. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **5.2.3 Chromium**

Mean ( $\pm$  SD) chromium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.3. These results are graphically portrayed in Figure 5.2.3A-C.

#### **Site 1**

**Roots:** Most comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ), except the comparison between November 2004 and September 2005.

**Leaves:** All comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### Site 3

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). September 2005 vs. July 2005 did not show any significant difference ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant increase ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### 5.2.4 Cobalt

Mean ( $\pm$  SD) cobalt concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.4. These results are graphically portrayed in Figure 5.2.4A-C.

#### Site 1

**Roots and leaves:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July vs. September 2005 did not show any significant difference ( $P > 0.05$ ). Comparisons between the first sampling occasions (November 2004), and the last sampling occasions (September 2005), showed significant increases for both leaves and roots ( $P < 0.05$ ).

**Stems:** Comparisons between all consecutive sampling occasions showed statistically significant increases ( $P < 0.05$ ), including the comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005).

### Site 3

**Roots:** The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not show a significant difference ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant decrease ( $P < 0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions showed significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not show a significant difference ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

## 5.2.5 Copper

Mean ( $\pm$  SD) copper concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.5. These results are graphically portrayed in Figure 5.2.5A-C.

### Site 1

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did

not differ significantly ( $P>0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P<0.05$ ).

**Leaves:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P<0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P>0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P<0.05$ ).

**Stems:** Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P<0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P<0.05$ ).

### Site 3

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P<0.05$ ). July 2005 vs. September 2005 and did not differ significantly ( $P>0.05$ ). Major concentration peaks were seen in July 2005 and September 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P<0.05$ ).

**Leaves:** Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P<0.05$ ). A major concentration peak was seen in July 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P<0.05$ ).

**Stems:** No comparisons between consecutive sampling occasions showed significant differences ( $P>0.05$ ). However, a comparison between the first sampling occasion

(November 2004) and the last sampling occasion (September 2005) showed a significant decrease ( $P < 0.05$ ).

### **5.2.6 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.6. These results are graphically portrayed in Figure 5.2.6A-C.

#### **Site 1**

**Roots:** Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P < 0.05$ ).

**Leaves:** Comparisons between all consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), did not show a significant difference ( $P < 0.05$ ).

**Stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

#### **Site 3**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

### **5.2.7 Lead**

Mean ( $\pm$  SD) lead concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.7. These results are graphically portrayed in Figure 5.2.7A-C.

#### **Site 1**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant decrease ( $P < 0.05$ ).

**Leaves:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Stems:** Lead was not detected in November 2004, July 2005 and September 2005, therefore, no comparisons could be made.

### **Site 3**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). Major concentration peaks were seen in July 2005 and September 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant increase ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). Concentration peaks were seen in March 2005 and July 2005 compared to the other sampling occasions. A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) did not show a significant difference ( $P < 0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant decrease ( $P < 0.05$ ).

### **5.2.8 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.8. These results are graphically portrayed in Figure 5.2.8A-C.



### **Site 1**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). Major concentration peaks were seen in July 2005 and September 2005. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Leaves and stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). Major concentrations peaks were seen in July 2005 and September 2005. A comparison between the first sampling occasion (November 2004), and the last sampling occasions (September 2005), showed significant increases for both leaves and stems ( $P < 0.05$ ).

### **Site 3**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 did not differ significantly ( $P > 0.05$ ). A major concentration peak was seen in November 2004. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

**Leaves and Stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). Major concentrations peaks were seen in November 2004. A comparison between the first sampling occasions (November 2004), and the last sampling occasions (September 2005), showed significant decreases for both leaves and stems ( $P < 0.05$ ).

## **5.2.9 Nickel**

Mean ( $\pm$  SD) nickel concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005 are shown in Table 5.1.9. These results are graphically portrayed in Figure 5.2.9A-C.

### **Site 1**

**Roots:** All comparisons between consecutive sampling occasions showed a statistically significant difference ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Leaves:** Comparisons between all consecutive sampling occasions showed a statistically significant difference ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Stems:** All comparisons between consecutive sampling occasions showed a statistically significant difference ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

**Roots:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). July 2005 vs. September 2005 and did not differ significantly ( $P > 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

**Leaves and stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). Comparisons between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), did not show significant differences ( $P < 0.05$ ).

### **5.2.10 Zinc**

Mean ( $\pm$  SD) zinc concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2004, July 2004 and September

2005, are shown in Table 5.1.10. These results are graphically portrayed in Figure 5.2.10A-C.

### **Site 1**

**Roots and stems:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). Particularly low mean concentration peaks were found in March 2005 for both roots and stems compared to the other sampling occasions. Comparisons between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease for roots and a significant increase for stems ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant increase ( $P < 0.05$ ).

### **Site 3**

**Roots:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A particularly low mean concentration was found in March 2005 compared to the other sampling occasions, and concentration peaks in July 2005 and September 2005. A comparison between the first sampling occasion (November 2004) and the last sampling occasion (September 2005) showed a significant increase ( $P < 0.05$ ).

**Leaves:** All comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P < 0.05$ ).

**Stems:** The majority of the comparisons between consecutive sampling occasions showed statistically significant increases or decreases ( $P < 0.05$ ). A comparison between July 2005

vs. September 2005 did not differ significantly ( $P>0.05$ ). A concentration peak was seen in November 2004 compared to the other sampling occasions. A comparison between the first sampling occasion (November 2004), and the last sampling occasion (September 2005), showed a significant decrease ( $P<0.05$ ).

### **5.3 Comparisons of metal concentrations between plant components (roots, leaves and stems), at site 1 and site 3 during November 2004, March 2005, July 2005 and September 2005**

#### **5.3.1 Aluminium**

Mean ( $\pm$  SD) aluminium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3 during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.1. Statistically significant differences are indicated by numbers.

**Site 1:** Aluminium root concentrations were significantly higher ( $P<0.05$ ) than leaf and stem concentrations during all sampling occasions. Leaf concentrations were significantly higher ( $P<0.05$ ) than stem concentrations in July 2005. In November 2004, March 2005 and September 2005, there were no significant differences ( $P>0.05$ ) between leaves and stems.

**Site 3:** Root concentrations were significantly higher ( $P<0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004, there were no differences ( $P>0.05$ ) between leaves and stems. In March 2005 stem concentrations were significantly higher ( $P<0.05$ ) than those of leaves, whereas in July 2005 and September 2005 the opposite was found.

#### **5.3.2 Cadmium**

Mean ( $\pm$  SD) cadmium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3 during November 2004, March 2005, July 2005 and

September 2005, are shown in Table 5.1.2. Statistically significant differences are indicated by numbers.

Cadmium was only detected in roots at site 3 during July 2005 and September 2005. The rest of the times it was not detected. Therefore statistical comparisons were not done.

### **5.3.3 Chromium**

Mean ( $\pm$  SD) chromium concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.3. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. During November 2004, March 2005 and September 2005, there were no differences ( $P > 0.05$ ) between leaves and stems, whereas in July 2005, leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than the leaf and stem concentrations in March 2005, July 2005 and September 2005. In November 2004, root concentrations were significantly higher ( $P < 0.05$ ) than those in leaves, but there were no differences ( $P > 0.05$ ) between roots and stems, or between leaves and stems. In March 2005 stem concentrations were significantly higher ( $P < 0.05$ ) than those of leaves, whereas in July 2005 the opposite was found. In September 2005 there were no differences ( $P > 0.05$ ) between leaves and stems.

### **5.3.4 Cobalt**

Mean ( $\pm$  SD) cobalt concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.4. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004 and March 2005 there were no differences ( $P > 0.05$ ) between leaf and stem concentrations. In July 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than those of stems, whereas in September 2005 the opposite was found.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions, except in November 2004, when stem concentrations were significantly higher ( $P < 0.05$ ) than those of roots and leaves. In March 2005 stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations, whereas in July 2005 the opposite was found. In September 2005 there were no differences ( $P > 0.05$ ) between leaves and stems.

### **5.3.5 Copper**

Mean ( $\pm$  SD) copper concentrations measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.5. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions, except in March 2005, when there were no differences ( $P > 0.05$ ) between any of the plant components. No differences ( $P > 0.05$ ) were found between leaves and stems in November 2004. In July 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than those of stems, whereas in September 2005 the opposite was found.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations, except in November 2004, when there were no differences ( $P > 0.05$ ) between any of the plant components. In March 2005 root concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations, but there were no differences ( $P > 0.05$ ) between roots and leaves, or between leaves and stems. In July 2005 leaf

concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations. In September 2005 no differences ( $P > 0.05$ ) were found between leaves and stems.

### **5.3.6 Iron**

Mean ( $\pm$  SD) iron concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.6. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004, March 2005 and September 2005 there were no differences ( $P > 0.05$ ) between leaves and stems but in July 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004 and March stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations, whereas in July 2005 the opposite was found. In September 2005 there were no differences ( $P > 0.05$ ) between leaves and stems.

### **5.3.7 Lead**

Mean ( $\pm$  SD) lead concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.7. Statistical significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004 no differences ( $P > 0.05$ ) were found between leaves and stems however, in March 2005, July 2005 and September 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations in March 2005, July 2005 and September 2005. In November 2004 no differences ( $P > 0.05$ ) were found between roots and stems, or between roots and leaves, however, stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations. In March 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations, but there were no differences ( $P > 0.05$ ) between leaves and roots. In July 2005 and September 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations.

### **5.3.8 Manganese**

Mean ( $\pm$  SD) manganese concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.8. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations, except in March 2005, when there were no differences ( $P > 0.05$ ) between leaves and roots. In November 2004, March 2005 and September 2005 stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations, whereas in July 2005 the opposite was found.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations in July 2005 and September 2005. In November 2004 and March 2005 stem concentrations were significantly higher ( $P < 0.05$ ) than root, and in November 2004, March 2005 and September 2005 stem concentrations were also significantly higher ( $P < 0.05$ ) than leaf concentrations. In July there were no differences ( $P > 0.05$ ) found between leaves and stems.



### 5.3.9 Nickel

Mean ( $\pm$  SD) nickel concentrations, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.9. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during all sampling occasions. In November 2004 stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations, however, in March 2005, July 2005 and September 2005 no differences ( $P > 0.05$ ) were found between leaves and stems.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations during most sampling occasions, except November 2004, when there were no differences ( $P > 0.05$ ) between any of the plant components. In March 2005 and September 2005 no differences ( $P > 0.05$ ) were found between leaf concentrations and stem concentrations but, in July 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentrations.

### 5.3.10 Zinc

Mean ( $\pm$  SD) zinc concentration, measured in roots, leaves and stems of plants collected from site 1 and site 3, during November 2004, March 2005, July 2005 and September 2005, are shown in Table 5.1.10. Statistically significant differences are indicated by numbers.

**Site 1:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations in November 2004, July 2005 and September 2005. In March 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than those of roots and stems. In November 2004 no differences ( $P > 0.05$ ) were found between stem and leaf

concentrations but, in July 2005 and September 2005 stem concentrations were significantly higher ( $P < 0.05$ ) than leaf concentrations.

**Site 3:** Root concentrations were significantly higher ( $P < 0.05$ ) than leaf and stem concentrations in July 2005 and September 2005. In November 2004 there were no differences ( $P > 0.05$ ) between any of the plant components. In March 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than those of roots and stems. In July 2005 leaf concentrations were significantly higher ( $P < 0.05$ ) than stem concentration, whereas no differences ( $P > 0.05$ ) were found between stems and leaves in September 2005.

**Table 5.1.1:** Mean ( $\pm$  SD) aluminium concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	2969.26 $\pm$ 677.78 <sup>a1</sup>	1166.48 $\pm$ 78.97 <sup>a2</sup>	1818.12 $\pm$ 552.63 <sup>a2</sup>	9534.52 $\pm$ 787.48 <sup>b1</sup>	401.54 $\pm$ 90.75 <sup>b2</sup>	461.02 $\pm$ 90.75 <sup>b2</sup>
Mar. 05	*10021.17 $\pm$ 761.75 <sup>a1</sup>	*1556.86 $\pm$ 713.86 <sup>a2</sup>	1003.83 $\pm$ 508.52 <sup>a2</sup>	7588.99 $\pm$ 614.05 <sup>b1</sup>	*3390.36 $\pm$ 849.38 <sup>b2</sup>	*2442.44 $\pm$ 196.95 <sup>b3</sup>
Jul. 05	*6434.47 $\pm$ 961.04 <sup>a1</sup>	*1147.49 $\pm$ 93.55 <sup>a2</sup>	489.01 $\pm$ 98.98 <sup>a3</sup>	9571.70 $\pm$ 1546.34 <sup>b1</sup>	*4308.98 $\pm$ 1389.7 <sup>b2</sup>	*657.71 $\pm$ 275.78 <sup>b3</sup>
Sep. 05	*10125.97 $\pm$ 1553.63 <sup>a1</sup>	704.99 $\pm$ 138.16 <sup>a2</sup>	780.05 $\pm$ 146.23 <sup>a2</sup>	8378.58 $\pm$ 1607.89 <sup>a1</sup>	*820.22 $\pm$ 60.43 <sup>a2</sup>	536.55 $\pm$ 89.91 <sup>b3</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.2:** Mean ( $\pm$  SD) cadmium concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>
Mar. 05	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>
Jul. 05	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	0.62 $\pm$ 0.44 <sup>b1</sup>	N.D. <sup>a2</sup>	N.D. <sup>a2</sup>
Sep. 05	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	N.D. <sup>a1</sup>	*0.49 $\pm$ 0.08 <sup>b1</sup>	N.D. <sup>a2</sup>	N.D. <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.3:** Mean ( $\pm$  SD) chromium concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	12.30 $\pm$ 1.44 <sup>a1</sup>	1.34 $\pm$ 0.44 <sup>a2</sup>	1.27 $\pm$ 0.65 <sup>a2</sup>	3.33 $\pm$ 1.01 <sup>b1</sup>	1.04 $\pm$ 0.53 <sup>b2</sup>	2.08 $\pm$ 1.26 <sup>a1</sup>
Mar. 05	*13.38 $\pm$ 1.37 <sup>a1</sup>	*3.81 $\pm$ 1.76 <sup>a2</sup>	*2.11 $\pm$ 1.21 <sup>a2</sup>	*12.57 $\pm$ 1.54 <sup>a1</sup>	*5.28 $\pm$ 0.52 <sup>a2</sup>	*7.08 $\pm$ 1.69 <sup>b3</sup>
Jul. 05	*9.89 $\pm$ 1.58 <sup>b1</sup>	*1.82 $\pm$ 0.21 <sup>a2</sup>	*0.85 $\pm$ 0.22 <sup>a2</sup>	*18.72 $\pm$ 3.22 <sup>b1</sup>	*8.87 $\pm$ 2.52 <sup>b2</sup>	*1.46 $\pm$ 0.68 <sup>a3</sup>
Sep. 05	*15.94 $\pm$ 4.05 <sup>a1</sup>	*4.75 $\pm$ 0.55 <sup>a2</sup>	*4.43 $\pm$ 0.92 <sup>a2</sup>	20.18 $\pm$ 3.68 <sup>a1</sup>	*4.49 $\pm$ 0.59 <sup>a2</sup>	*4.50 $\pm$ 0.76 <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.4:** Mean ( $\pm$  SD) cobalt concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	3.96 $\pm$ 0.27 <sup>a1</sup>	N.D. <sup>a2</sup>	N.D. <sup>a2</sup>	18.89 $\pm$ 4.26 <sup>a1</sup>	5.59 $\pm$ 0.25 <sup>b2</sup>	31.67 $\pm$ 9.31 <sup>b3</sup>
Mar. 05	*3.30 $\pm$ 0.23 <sup>a1</sup>	*0.45 $\pm$ 0.21 <sup>a2</sup>	*0.22 $\pm$ 0.30 <sup>a2</sup>	*6.79 $\pm$ 0.46 <sup>b1</sup>	*2.12 $\pm$ 0.15 <sup>b2</sup>	*3.87 $\pm$ 0.72 <sup>b3</sup>
Jul. 05	*7.32 $\pm$ 1.10 <sup>a1</sup>	*0.66 $\pm$ 0.08 <sup>a2</sup>	*0.48 $\pm$ 0.09 <sup>a3</sup>	*6.19 $\pm$ 0.83 <sup>a1</sup>	*1.97 $\pm$ 0.49 <sup>b2</sup>	*0.45 $\pm$ 0.28 <sup>a3</sup>
Sep. 05	8.29 $\pm$ 1.50 <sup>a1</sup>	0.71 $\pm$ 0.18 <sup>a2</sup>	*1.26 $\pm$ 0.33 <sup>a3</sup>	5.14 $\pm$ 0.81 <sup>a1</sup>	*0.32 $\pm$ 0.18 <sup>a2</sup>	0.32 $\pm$ 0.18 <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.5:** Mean ( $\pm$  SD) copper concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	10.29 $\pm$ 1.19 <sup>a1</sup>	1.19 $\pm$ 0.38 <sup>a2</sup>	1.27 $\pm$ 1.53 <sup>a2</sup>	20.69 $\pm$ 2.79 <sup>b1</sup>	14.02 $\pm$ 1.11 <sup>b1</sup>	17.79 $\pm$ 6.19 <sup>b1</sup>
Mar. 05	*13.12 $\pm$ 5.56 <sup>a1</sup>	*6.45 $\pm$ 3.91 <sup>a1</sup>	*5.33 $\pm$ 4.44 <sup>a1</sup>	*16.79 $\pm$ 4.08 <sup>a1</sup>	*12.99 $\pm$ 2.29 <sup>b2</sup>	11.63 $\pm$ 2.12 <sup>b2</sup>
Jul. 05	*19.85 $\pm$ 1.99 <sup>a1</sup>	*8.16 $\pm$ 1.17 <sup>a2</sup>	*12.82 $\pm$ 1.10 <sup>a3</sup>	*43.21 $\pm$ 7.63 <sup>b1</sup>	*30.42 $\pm$ 10.48 <sup>b2</sup>	7.37 $\pm$ 4.61 <sup>b3</sup>
Sep. 05	20.83 $\pm$ 2.23 <sup>a1</sup>	7.67 $\pm$ 0.62 <sup>a2</sup>	*9.33 $\pm$ 0.74 <sup>a3</sup>	41.29 $\pm$ 6.55 <sup>b1</sup>	*9.13 $\pm$ 1.07 <sup>b2</sup>	8.22 $\pm$ 0.89 <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.6:** Mean ( $\pm$  SD) iron concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	14476.4 $\pm$ 1130.12 <sup>a1</sup>	736.67 $\pm$ 75.99 <sup>a2</sup>	734.95 $\pm$ 151.64 <sup>a2</sup>	7736.92 $\pm$ 1703.72 <sup>a1</sup>	2064.02 $\pm$ 142.19 <sup>a2</sup>	5343.66 $\pm$ 1591.94 <sup>a3</sup>
Mar. 05	*11469.79 $\pm$ 929.84 <sup>a1</sup>	*2425.43 $\pm$ 1100.01 <sup>a2</sup>	*1549.07 $\pm$ 864.48 <sup>a2</sup>	*11191.04 $\pm$ 899.27 <sup>a1</sup>	*3043.06 $\pm$ 409.20 <sup>a2</sup>	*4520.66 $\pm$ 1197.75 <sup>b3</sup>
Jul. 05	*8891.79 $\pm$ 1409.28 <sup>a1</sup>	*1462.69 $\pm$ 153.43 <sup>a2</sup>	*626.32 $\pm$ 96.66 <sup>a3</sup>	*12971.12 $\pm$ 2401.99 <sup>b1</sup>	*5894.75 $\pm$ 1621.42 <sup>b2</sup>	*1011.95 $\pm$ 474.82 <sup>b3</sup>
Sep. 05	*13391.09 $\pm$ 2573.87 <sup>a1</sup>	*997.13 $\pm$ 192.18 <sup>a2</sup>	*1041.11 $\pm$ 230.06 <sup>a2</sup>	14168.74 $\pm$ 1406.46 <sup>a1</sup>	*1015.83 $\pm$ 570.43 <sup>a2</sup>	842.65 $\pm$ 187.59 <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.7:** Mean ( $\pm$  SD) lead concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	19.94 $\pm$ 1.58 <sup>a1</sup>	N.D. <sup>a2</sup>	N.D. <sup>a2</sup>	5.09 $\pm$ 1.17 <sup>b1</sup>	3.72 $\pm$ 0.44 <sup>b2</sup>	5.55 $\pm$ 1.38 <sup>b1</sup>
Mar. 05	*9.68 $\pm$ 0.88 <sup>a1</sup>	*6.14 $\pm$ 2.88 <sup>a2</sup>	1.72 $\pm$ 2.39 <sup>a3</sup>	*9.65 $\pm$ 0.39 <sup>a1</sup>	*11.00 $\pm$ 1.02 <sup>b1</sup>	*7.41 $\pm$ 1.67 <sup>b2</sup>
Jul. 05	*9.33 $\pm$ 1.31 <sup>a1</sup>	*2.77 $\pm$ 0.62 <sup>a2</sup>	N.D. <sup>a3</sup>	*40.68 $\pm$ 7.44 <sup>b1</sup>	*17.42 $\pm$ 4.85 <sup>b2</sup>	*2.38 $\pm$ 2.61 <sup>a3</sup>
Sep. 05	13.09 $\pm$ 2.73 <sup>a1</sup>	3.32 $\pm$ 0.52 <sup>a2</sup>	N.D. <sup>a3</sup>	44.47 $\pm$ 8.19 <sup>b1</sup>	*4.41 $\pm$ 0.58 <sup>b2</sup>	N.D. <sup>a3</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.8:** Mean ( $\pm$  SD) manganese concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	151.86 $\pm$ 12.79 <sup>a1</sup>	61.07 $\pm$ 2.00 <sup>a2</sup>	100.74 $\pm$ 14.44 <sup>a3</sup>	6322.94 $\pm$ 1559.84 <sup>b1</sup>	1933.09 $\pm$ 81.22 <sup>b2</sup>	12263.58 $\pm$ 3499.95 <sup>b3</sup>
Mar. 05	*56.19 $\pm$ 4.44 <sup>a1</sup>	*60.05 $\pm$ 9.12 <sup>a1</sup>	*78.94 $\pm$ 14.63 <sup>a2</sup>	*391.23 $\pm$ 15.23 <sup>b1</sup>	*281.00 $\pm$ 24.23 <sup>b2</sup>	*754.03 $\pm$ 186.01 <sup>b3</sup>
Jul. 05	*575.78 $\pm$ 102.07 <sup>a1</sup>	*174.29 $\pm$ 5.86 <sup>a2</sup>	*156.16 $\pm$ 11.13 <sup>a3</sup>	*508.48 $\pm$ 56.50 <sup>a1</sup>	*144.96 $\pm$ 15.29 <sup>b2</sup>	*123.13 $\pm$ 22.19 <sup>b2</sup>
Sep. 05	457.12 $\pm$ 75.29 <sup>a1</sup>	*145.70 $\pm$ 17.16 <sup>a2</sup>	*210.32 $\pm$ 35.19 <sup>a3</sup>	531.85 $\pm$ 75.93 <sup>a1</sup>	*97.95 $\pm$ 6.30 <sup>b2</sup>	*140.84 $\pm$ 12.26 <sup>b3</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

**Table 5.1.9:** Mean ( $\pm$  SD) nickel concentrations (mg/kg), measured in plant components from Diep River sampling sites 1 and 3, per sampling occasion. N.D. = not detected. Sample size (n) =5.

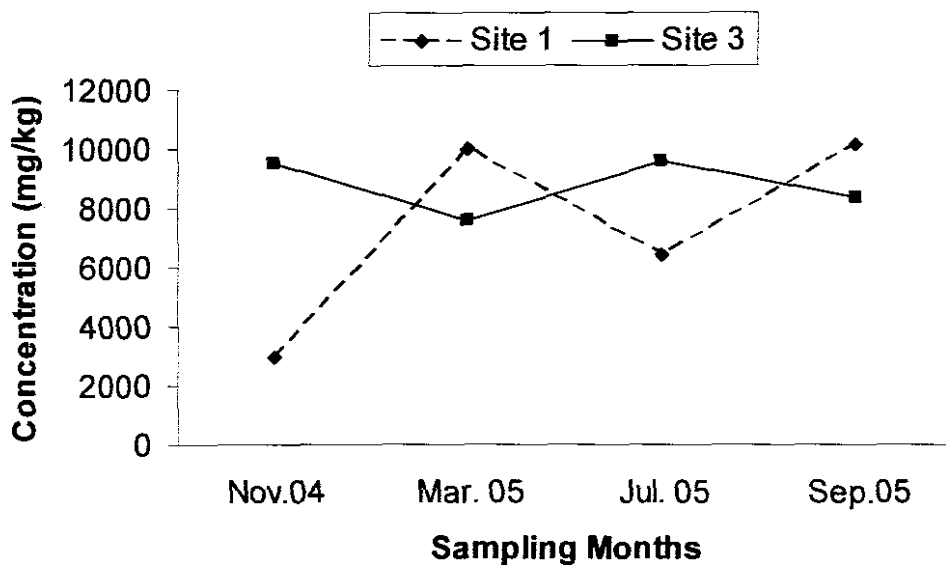
Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	7.54 $\pm$ 0.90 <sup>a1</sup>	0.76 $\pm$ 0.57 <sup>a2</sup>	2.69 $\pm$ 0.51 <sup>a3</sup>	4.71 $\pm$ 0.79 <sup>b1</sup>	3.48 $\pm$ 0.55 <sup>b1</sup>	4.08 $\pm$ 2.44 <sup>a1</sup>
Mar. 05	*9.14 $\pm$ 0.98 <sup>a1</sup>	*2.93 $\pm$ 1.71 <sup>a2</sup>	*1.81 $\pm$ 1.66 <sup>a2</sup>	*8.65 $\pm$ 0.69 <sup>a1</sup>	*5.22 $\pm$ 1.02 <sup>b2</sup>	*5.82 $\pm$ 0.65 <sup>b2</sup>
Jul. 05	*7.43 $\pm$ 1.02 <sup>a1</sup>	*N.D. <sup>a2</sup>	*N.D. <sup>a2</sup>	*10.56 $\pm$ 1.99 <sup>b1</sup>	*4.59 $\pm$ 1.44 <sup>b2</sup>	*N.D. <sup>a3</sup>
Sep. 05	*12.63 $\pm$ 2.08 <sup>a1</sup>	*4.43 $\pm$ 0.32 <sup>a2</sup>	*4.43 $\pm$ 0.71 <sup>a2</sup>	10.92 $\pm$ 1.12 <sup>a1</sup>	*2.99 $\pm$ 1.71 <sup>b2</sup>	*3.79 $\pm$ 0.91 <sup>a2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

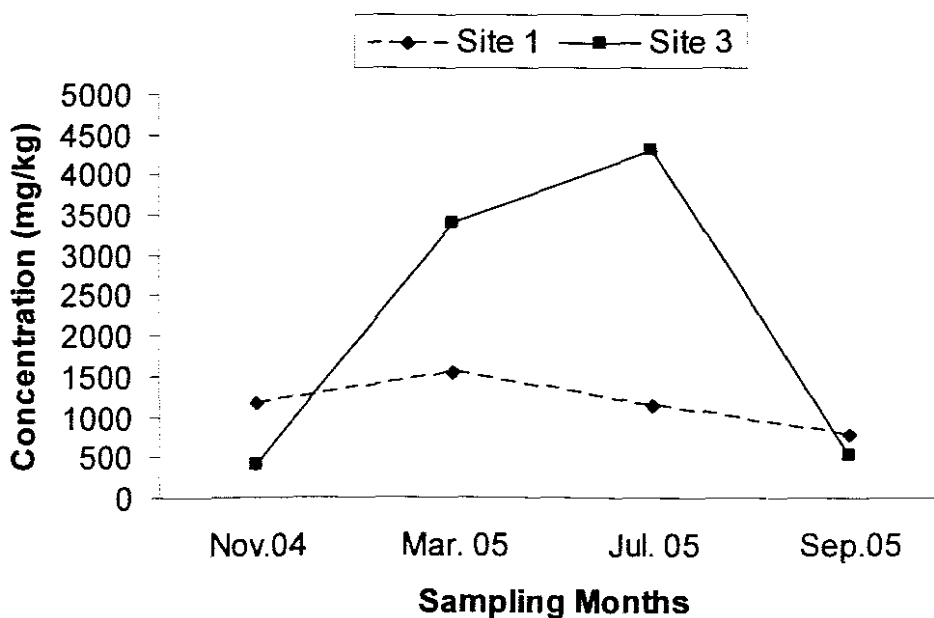
**Table 5.1.10:** Mean ( $\pm$  SD) zinc concentrations (mg/kg), measured in plant components from the Diep River sampling sites, site 1 and 3, per sampling occasion. N.D. = not detected. Sample size (n) =5.

Sampling Period	Site 1			Site 3		
	Roots	Leaves	Stems	Roots	Leaves	Stems
Nov. 04	53.15 $\pm$ 5.19 <sup>a1</sup>	18.41 $\pm$ 2.33 <sup>a2</sup>	23.38 $\pm$ 9.06 <sup>a2</sup>	49.17 $\pm$ 6.23 <sup>a1</sup>	66.63 $\pm$ 9.5 <sup>b1</sup>	64.12 $\pm$ 19.67 <sup>b1</sup>
Mar. 05	*1.96 $\pm$ 0.17 <sup>a1</sup>	*38.03 $\pm$ 1.57 <sup>a2</sup>	*9.62 $\pm$ 5.05 <sup>a3</sup>	*3.02 $\pm$ 0.41 <sup>b1</sup>	*42.26 $\pm$ 1.27 <sup>b2</sup>	*20.04 $\pm$ 0.91 <sup>b3</sup>
Jul. 05	*68.23 $\pm$ 7.22 <sup>a1</sup>	*28.58 $\pm$ 0.66 <sup>a2</sup>	*38.41 $\pm$ 2.09 <sup>a3</sup>	*130.61 $\pm$ 19.85 <sup>b1</sup>	*73.25 $\pm$ 15.11 <sup>b2</sup>	*35.25 $\pm$ 6.91 <sup>a3</sup>
Sep. 05	*51.45 $\pm$ 6.67 <sup>a1</sup>	*23.58 $\pm$ 2.11 <sup>a2</sup>	*31.70 $\pm$ 3.03 <sup>a3</sup>	*152.51 $\pm$ 14.79 <sup>b1</sup>	*24.18 $\pm$ 2.05 <sup>a2</sup>	34.62 $\pm$ 5.99 <sup>b2</sup>

Different letters indicate statistical significant differences of plant components between the two sites. Statistical differences between consecutive sampling occasions are illustrated by an asterisk (\*). Different numbers indicate statistical significant differences between plant components per sampling occasion, per site.

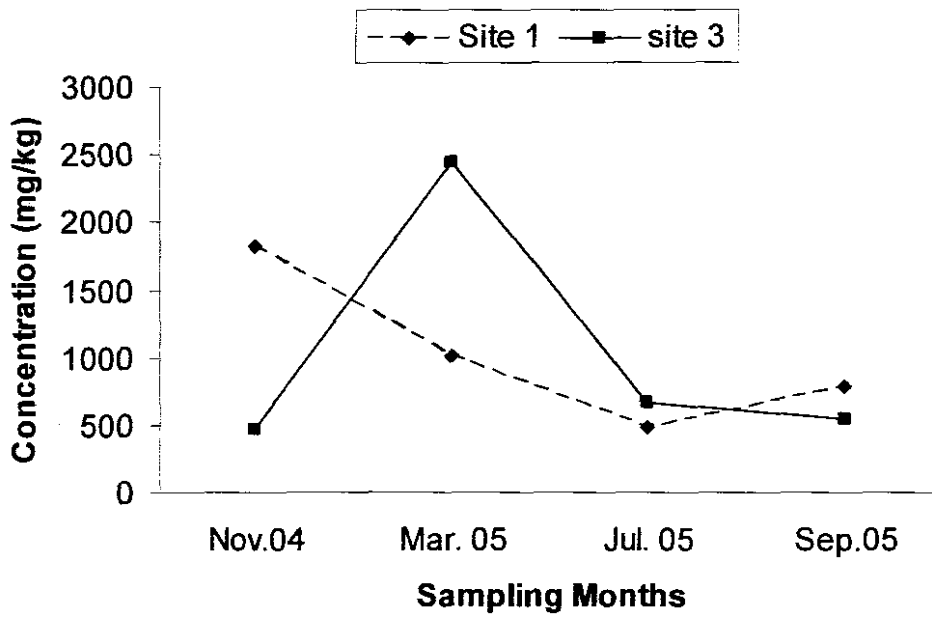


**Figure 5.2.1A:** Mean aluminium concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

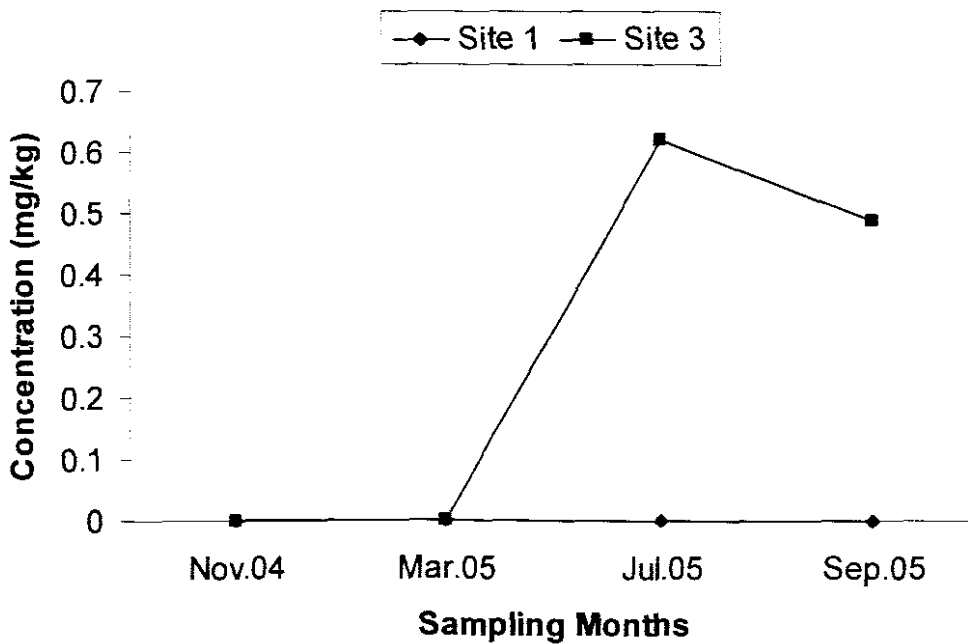


**Figure 5.2.1B:** Mean aluminium concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

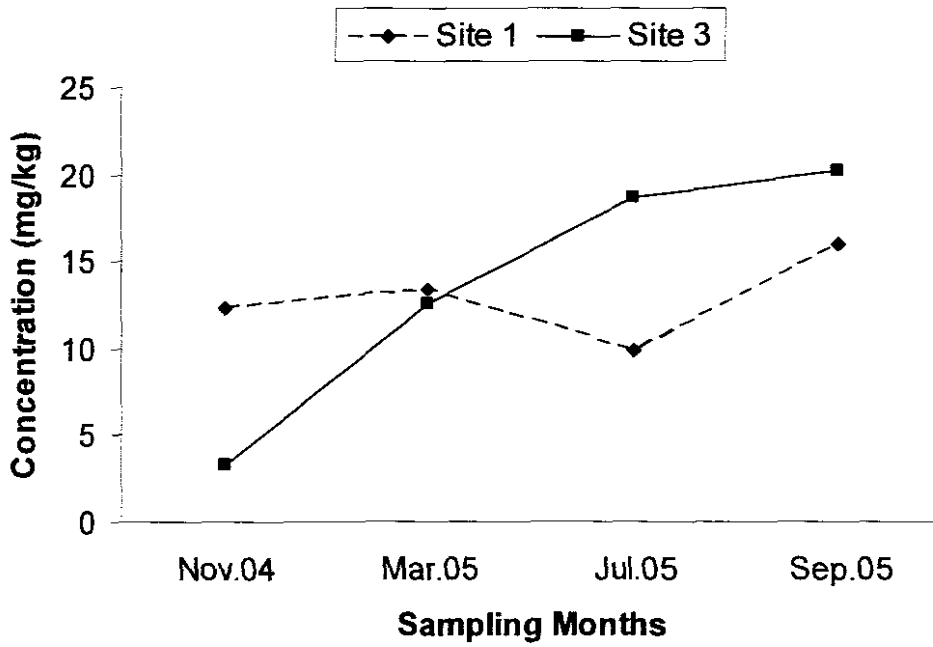




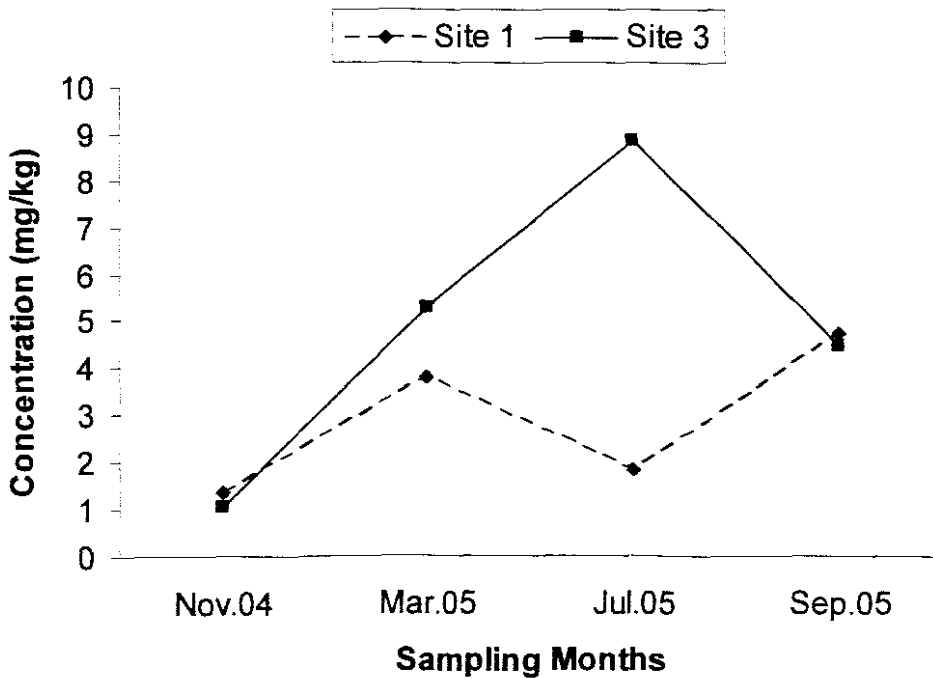
**Figure 5.2.1C:** Mean aluminium concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



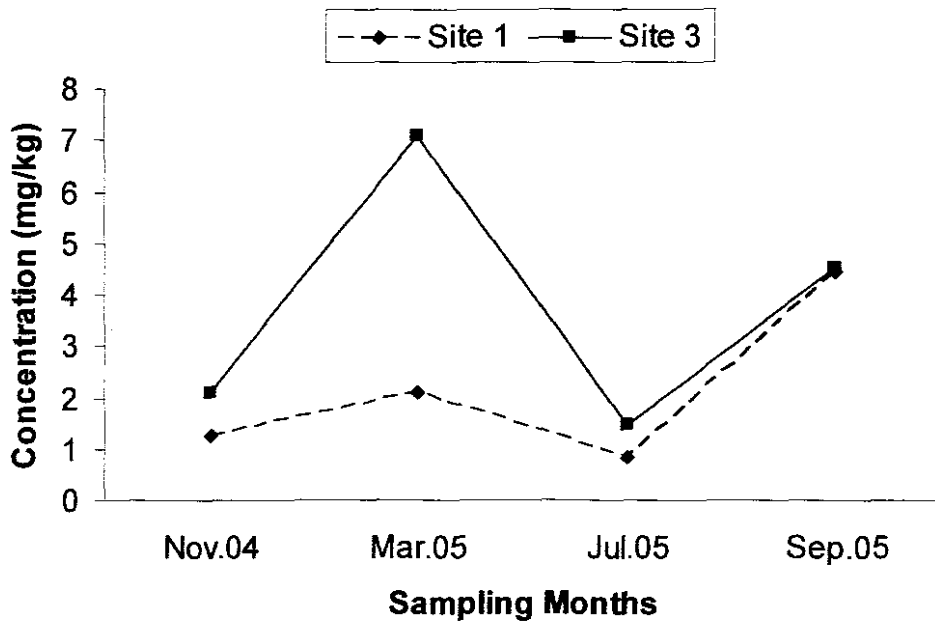
**Figure 5.2.2A:** Mean cadmium concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



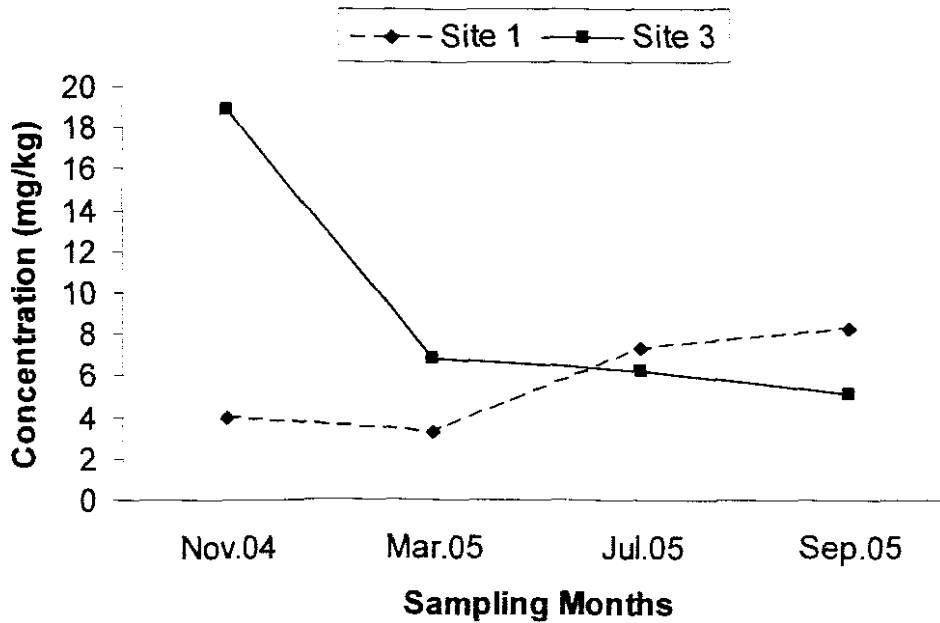
**Figure 5.2.3A:** Mean chromium concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



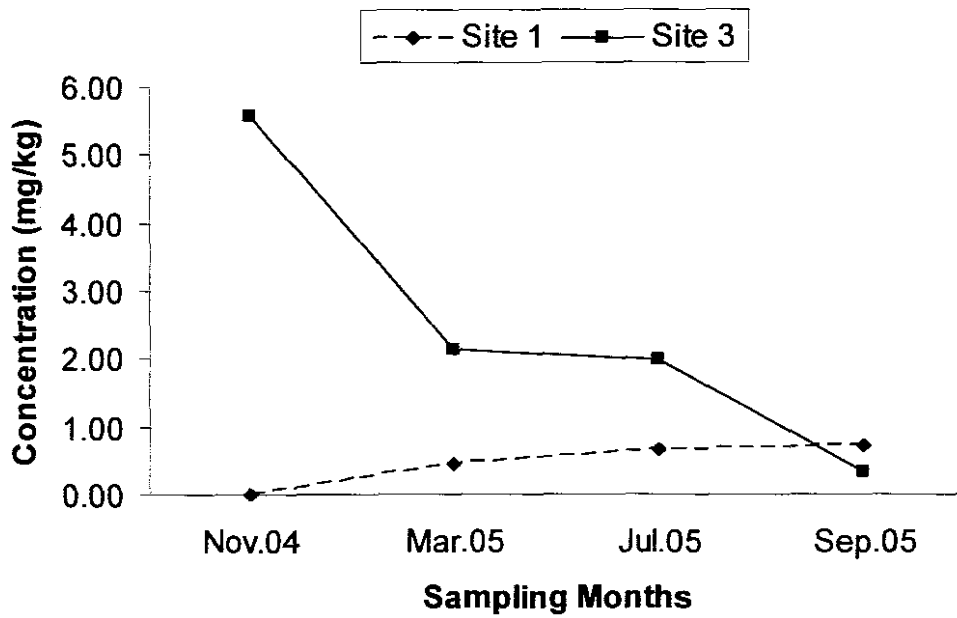
**Figure 5.2.3B:** Mean chromium concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



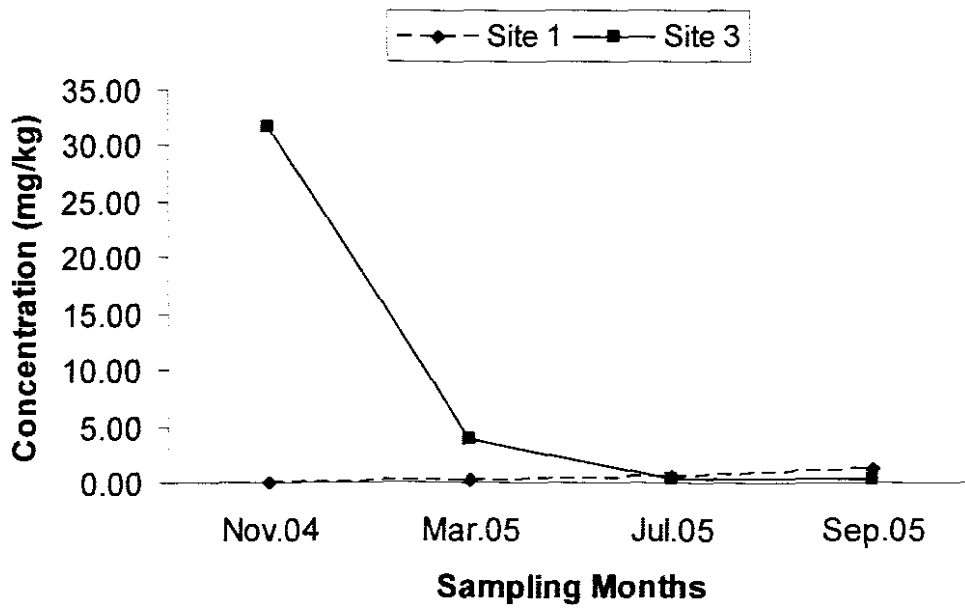
**Figure 5.2.3C:** Mean chromium concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



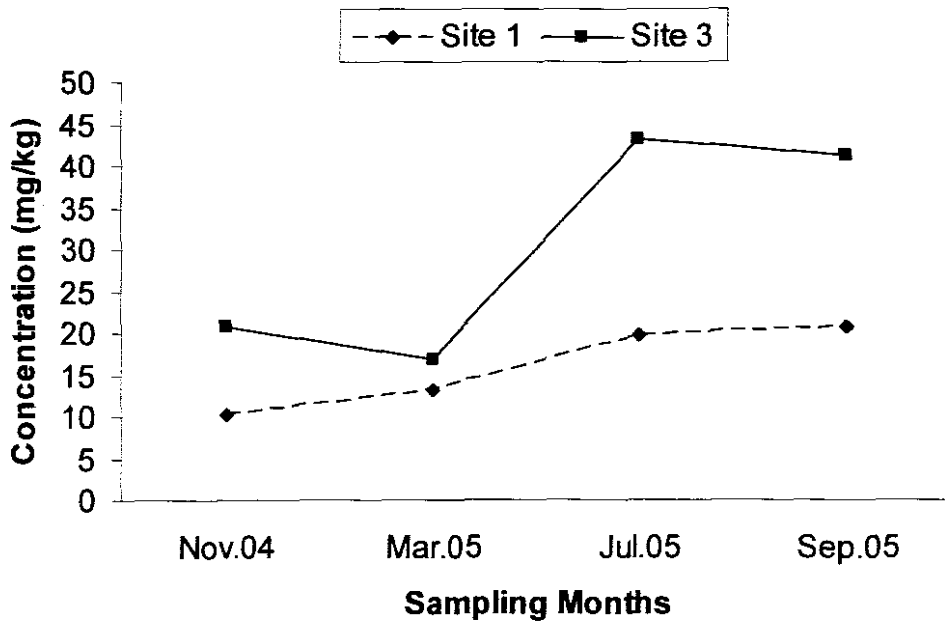
**Figure 5.2.4A:** Mean cobalt concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



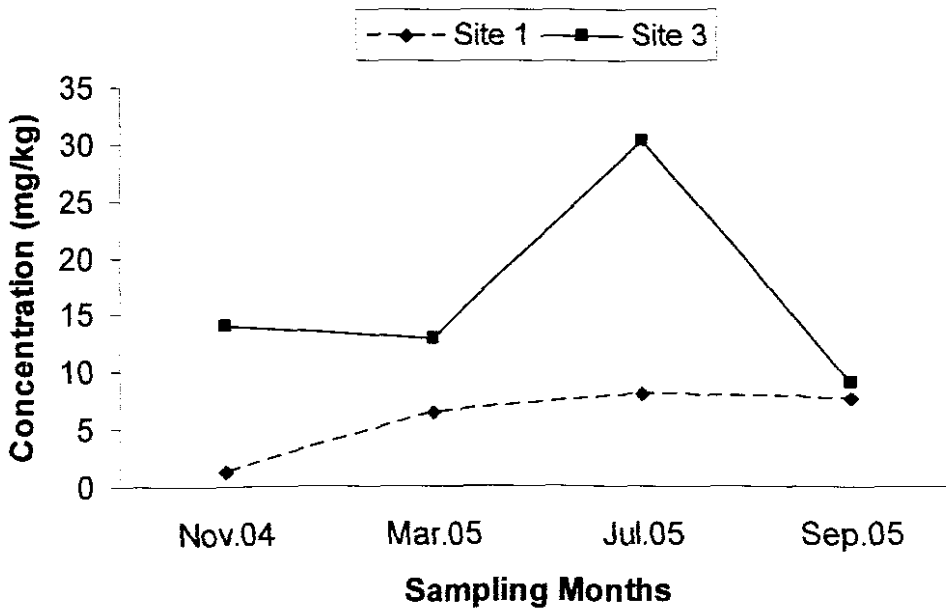
**Figure 5.2.4B:** Mean cobalt concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



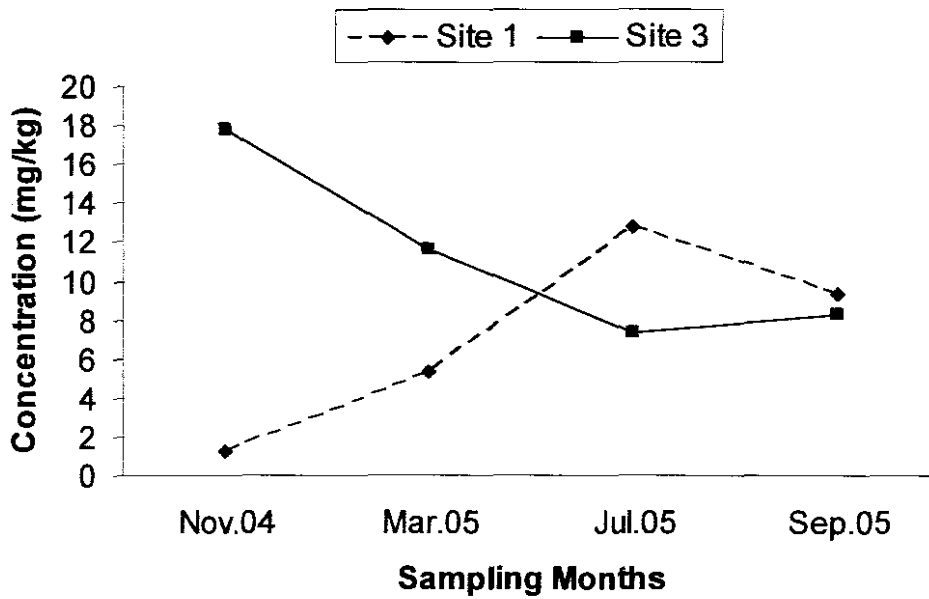
**Figure 5.2.4C:** Mean cobalt concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



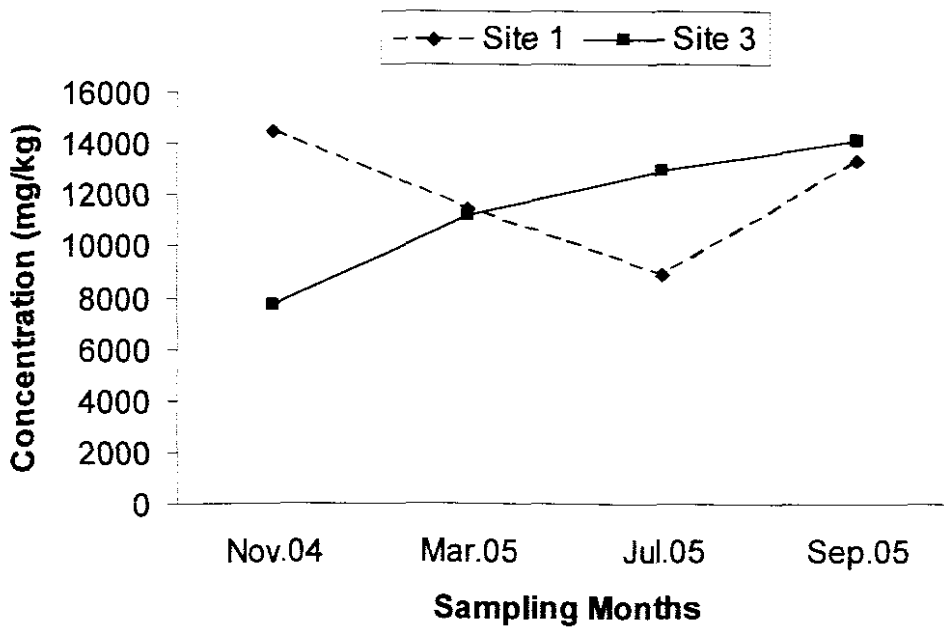
**Figure 5.2.5A:** Mean copper concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



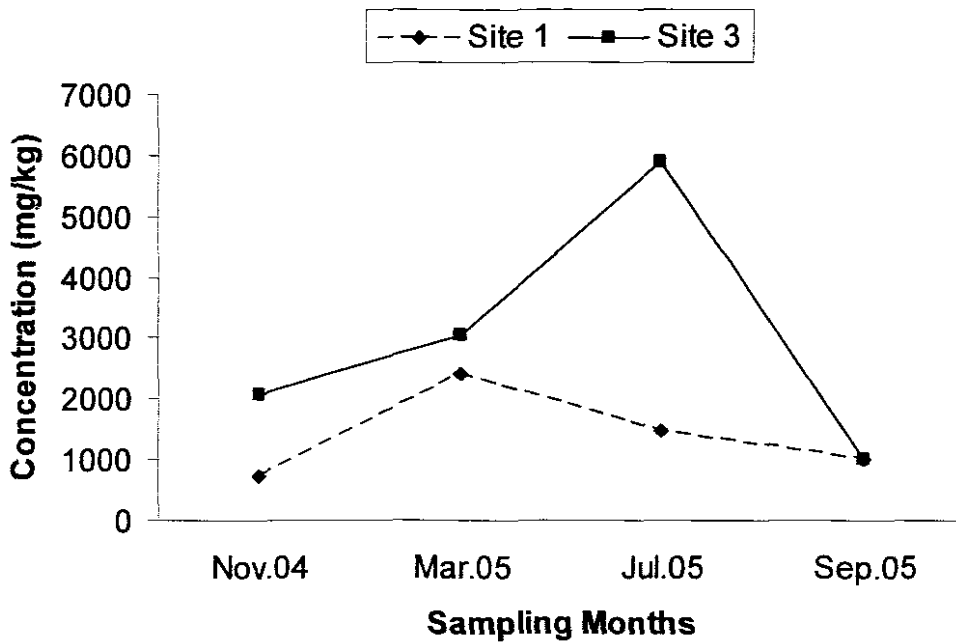
**Figure 5.2.5B:** Mean copper concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



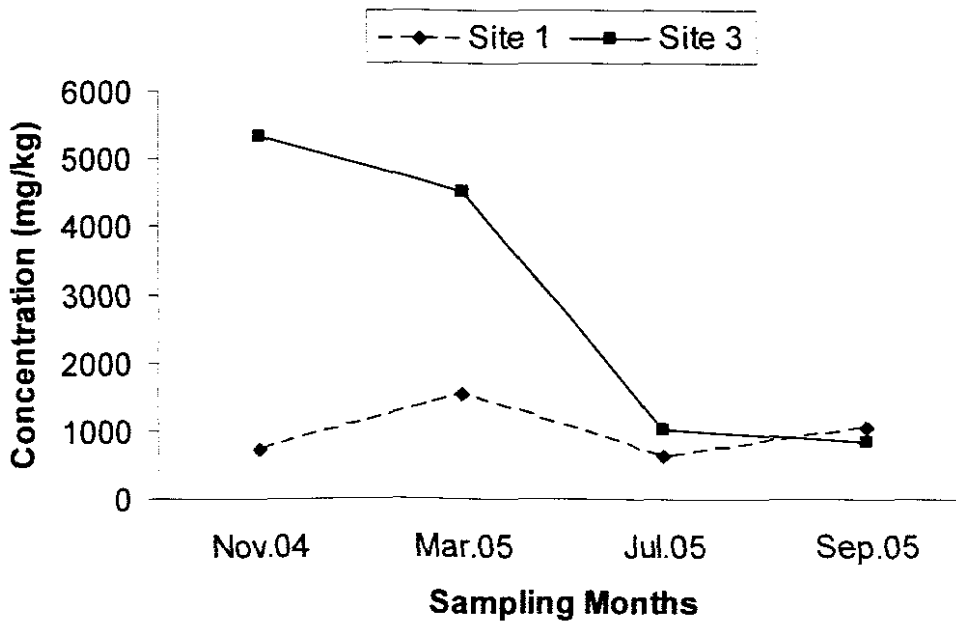
**Figure 5.2.5C:** Mean copper concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



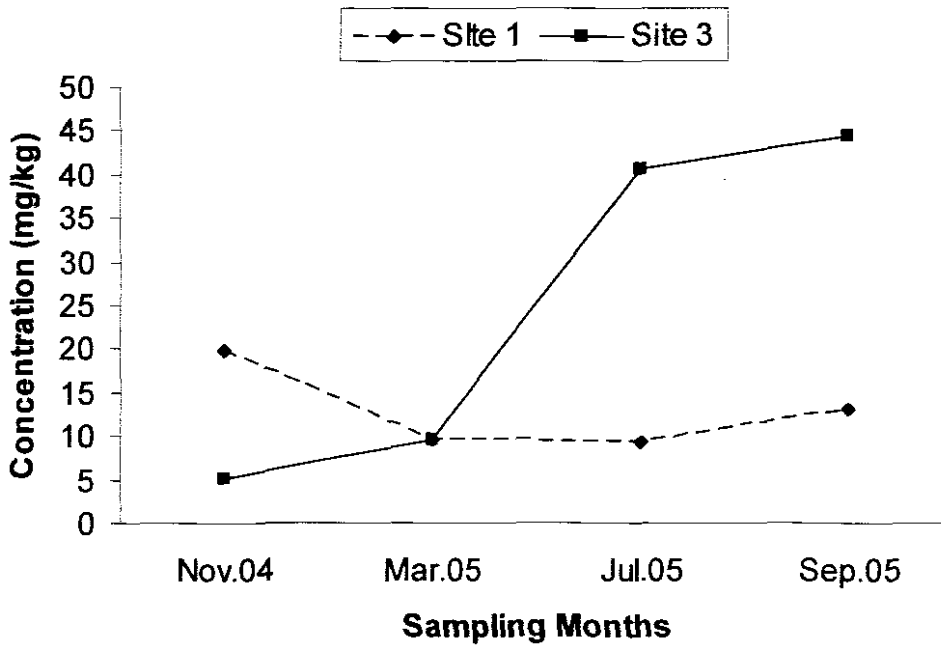
**Figure 5.2.6A:** Mean iron concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



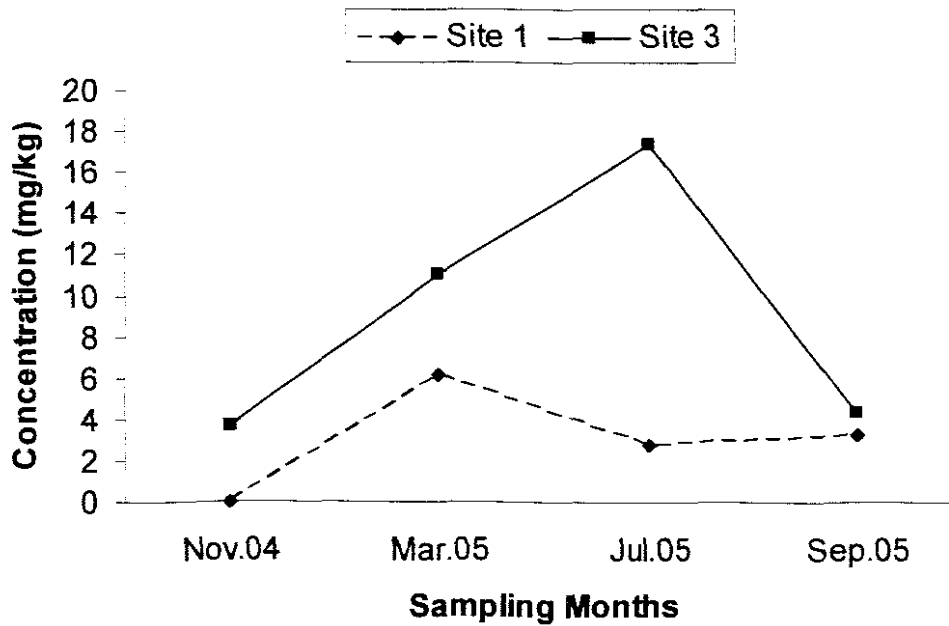
**Figure 5.2.6B:** Mean iron concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



**Figure 5.2.6C:** Mean iron concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

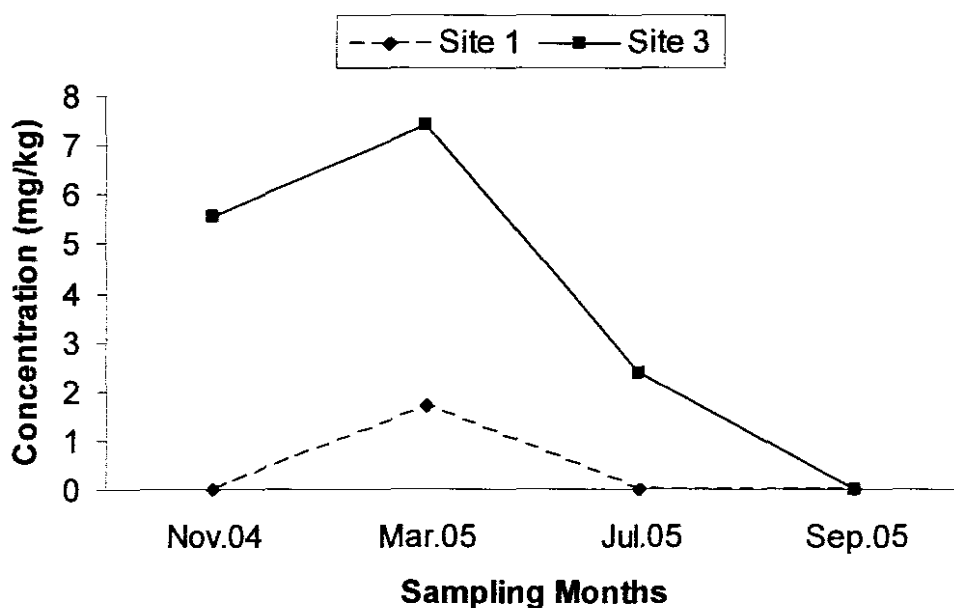


**Figure 5.2.7A:** Mean lead concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

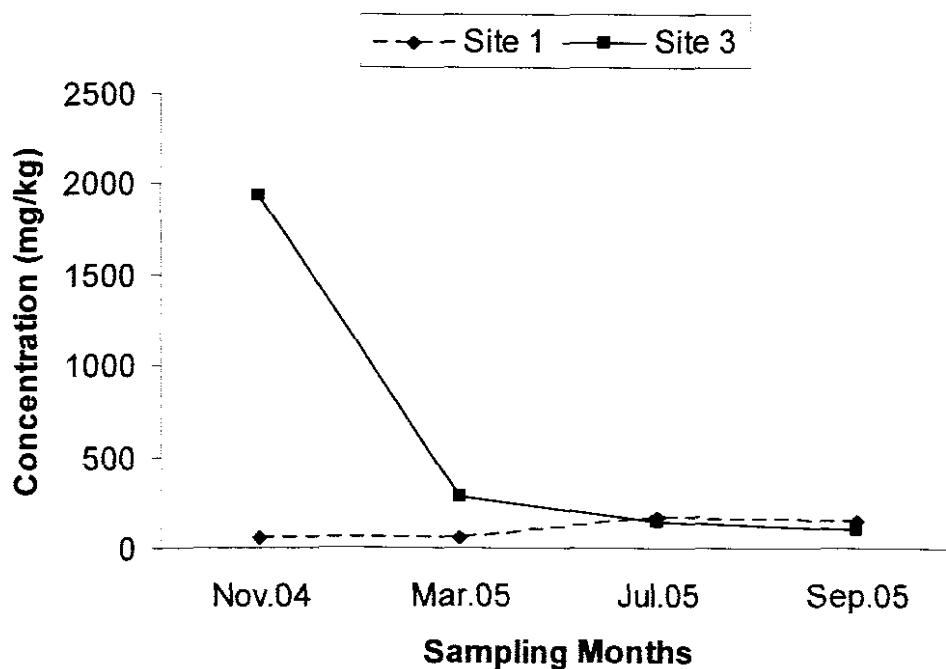


**Figure 5.2.7B:** Mean lead concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

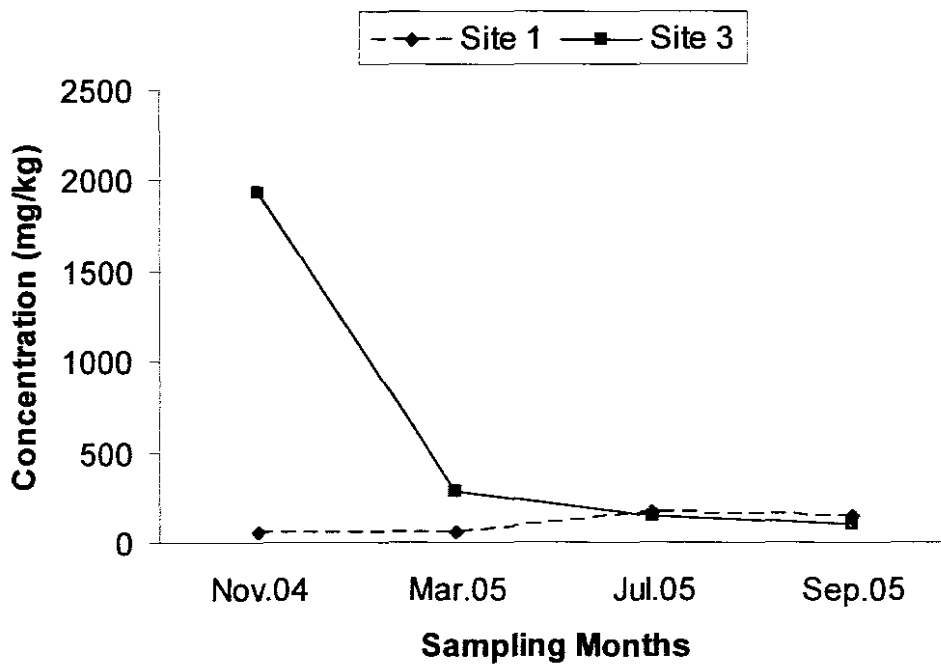




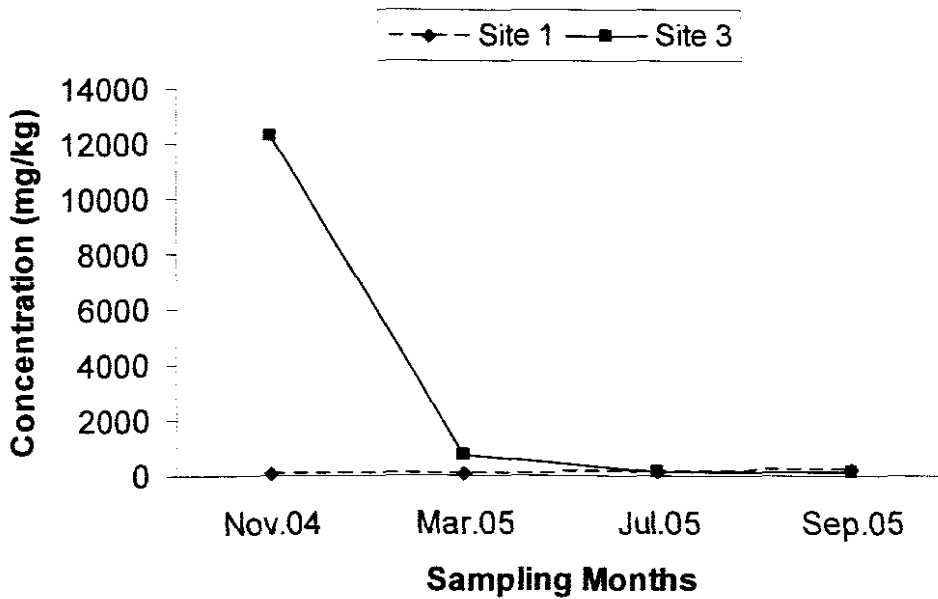
**Figure 5.2.7C:** Mean lead concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



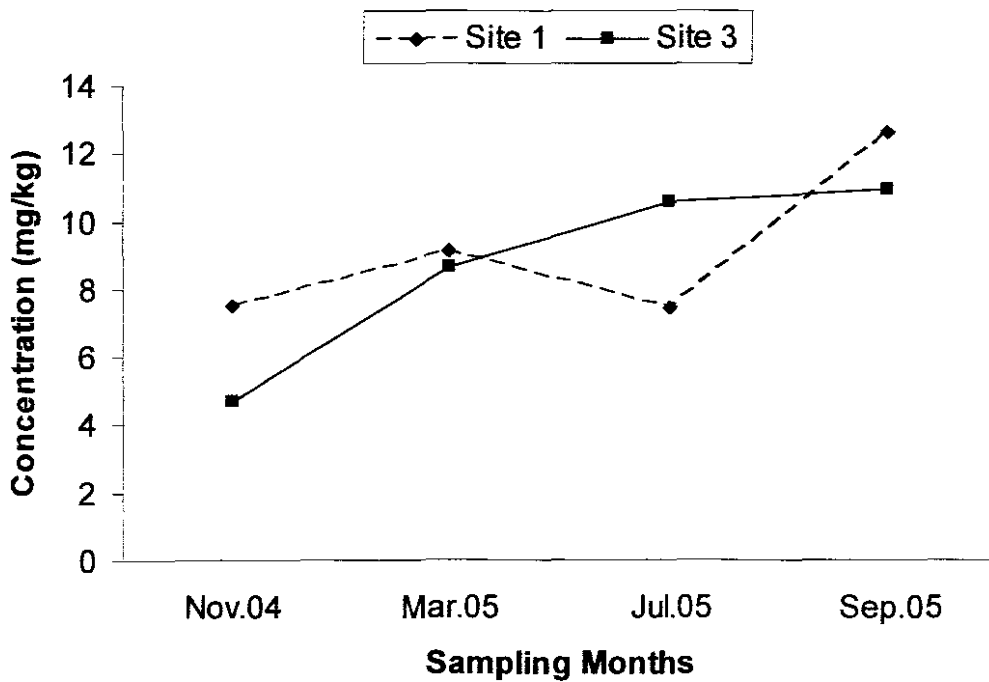
**Figure 5.2.8A:** Mean manganese concentrations (mg/kg), measured in roots Diep River sampling sites 1 and 3 between November 2004 and September 2005.



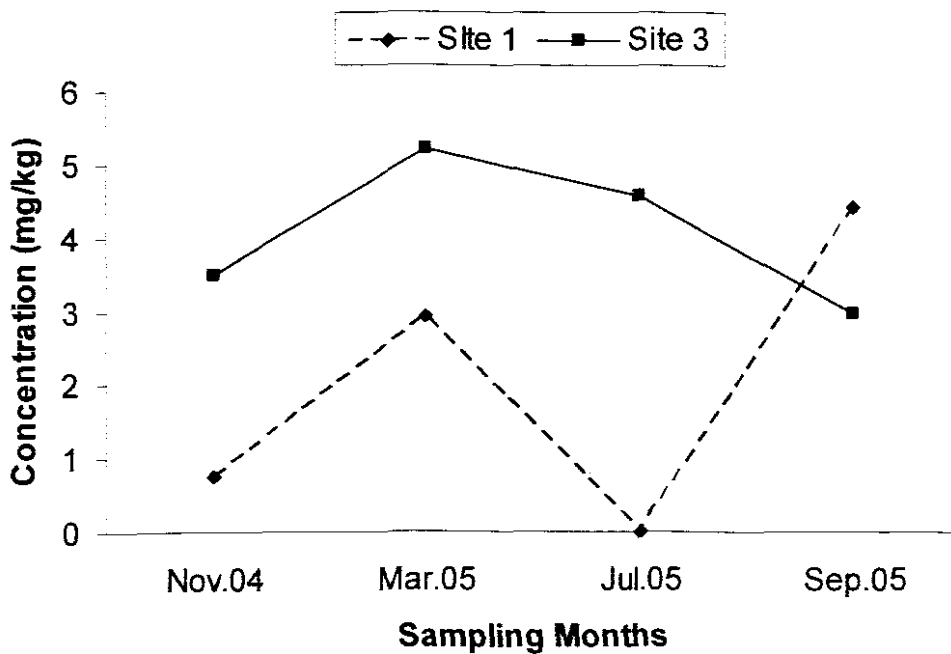
**Figure 5.2.8B:** Mean manganese concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



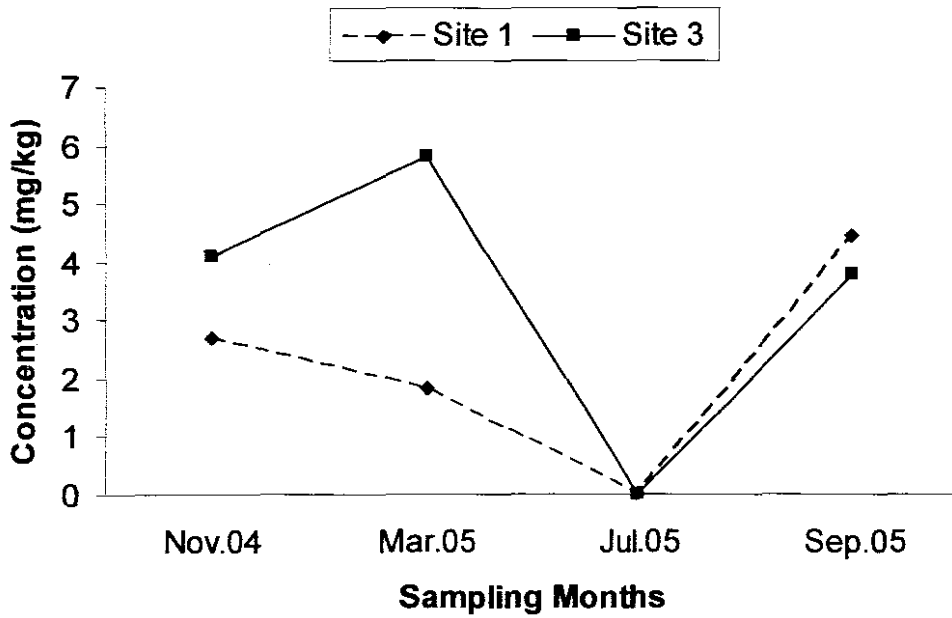
**Figure 5.2.8C:** Mean manganese concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3, between November 2004 and September 2005.



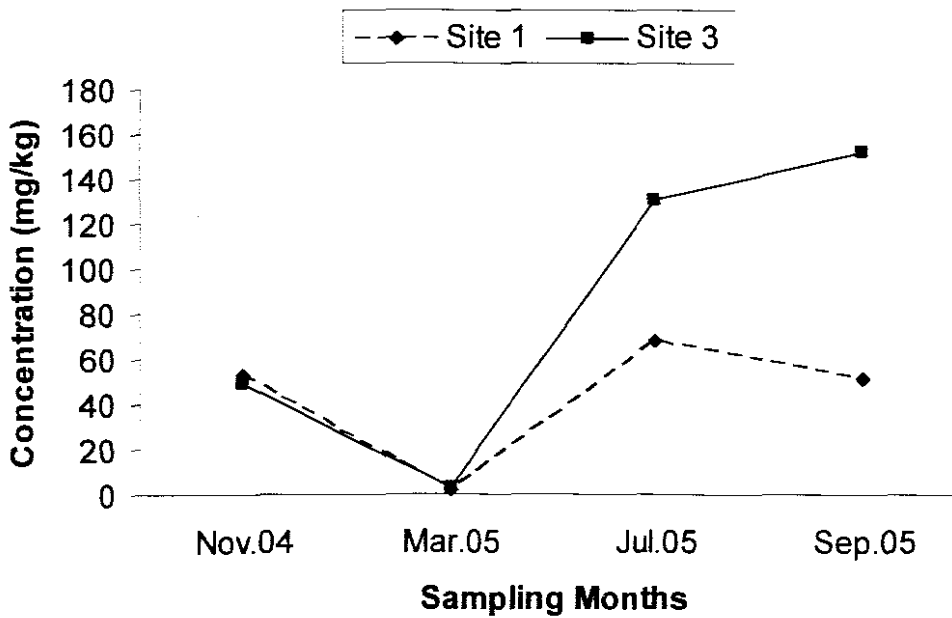
**Figure 5.2.9A:** Mean nickel concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



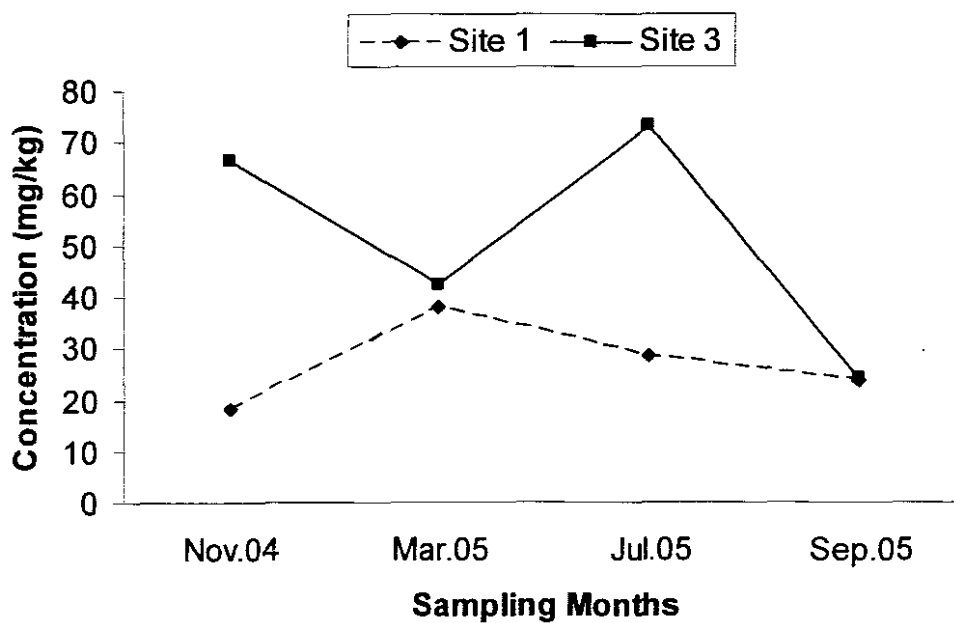
**Figure 5.2.9B:** Mean nickel concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



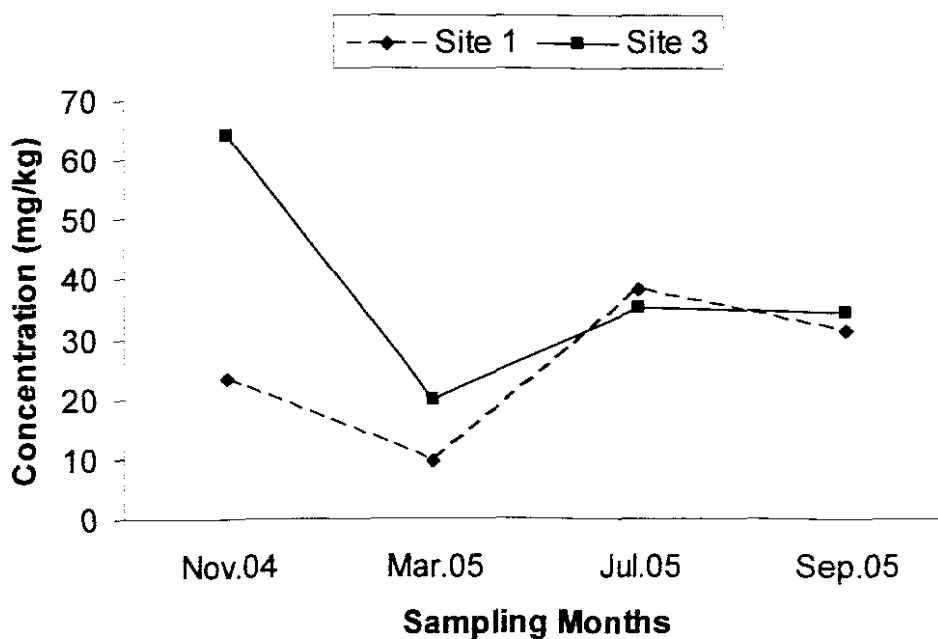
**Figure 5.2.9C:** Mean nickel concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



**Figure 5.2.10A:** Mean zinc concentrations (mg/kg), measured in roots from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



**Figure 5.2.10B:** Mean zinc concentrations (mg/kg), measured in leaves from Diep River sampling sites 1 and 3 between November 2004 and September 2005.



**Figure 5.2.10C:** Mean zinc concentrations (mg/kg), measured in stems from Diep River sampling sites 1 and 3 between November 2004 and September 2005.

## DISCUSSION

When the two sites were compared in terms of metals in the various plant components, it was often found that there were no significant differences (Tables 5.1.1-5.1.10). However, wherever significant differences were found, plants from site 3 overwhelmingly had the highest metal concentrations. On the other hand, this study has already shown (chapter 4) that sediment metal concentrations were mostly significantly higher at site 1, compared to site 3. It therefore seems that there was greater bioaccumulation by the plants from site 3. The most likely explanation for this is an increased bioavailability of metals at site 3. Bioavailability is influenced by various factors such as pH, temperature, redox potential, chemical speciation, seasonal changes, sediment type, salinity and organic matter (Otte et al., 1993).

Bioavailability in this study may have been influenced by several of the above-mentioned factors. Salinity could be a possible reason for the higher metal bioavailability at site 3 because during high tide, the seawater mixes with the riverwater, which increases the salinity (Grindley and Dudley, 1988). An increase in salinity is known to increase metal bioavailability to plants (Fitzgerald et al., 2003). Otte et al. (1991) also found such an increase in metal concentrations in *Aster tripolium* under saline conditions.

The lower metal bioavailability at site 1, on the other hand, may have been due to the fact that sediment at this site has a high clay content (Table 4.1), which could lead to metals binding to sediment and not being readily available for plants. Clay minerals are well known for their adsorbing functions and immobilization of metals (Salomons, 1995; Dassenakis et al., 1995; Usman et al., 2005).

Plant components (roots, leaves and stems) were compared with one another, per site, to determine the distribution of metals in *Bolboschoenus maritimus* (Tables 5.1.1-5.1.10). In general, root metal concentrations were significantly higher than in any other plant component. Higher metal content in the roots is to be expected, according to Almeida et al. (2006), since the root system is the main uptake pathway of metals from the sediment. However, several authors (Otte et al., 1991; Peverly et al., 1995; Weis and Weis, 2004; Almeida et al., 2006; Demirezen and Aksoy 2006; Madejón et

al., 2006a) found that various wetland plants actually accumulate metals in their root tissues and therefore concluded that these plants are root accumulators. Otte et al. (1991), Almeida et al. (2006) and Madejón et al. (2006a), in particular, concluded that *B. maritimus* accumulates metals in its roots. The results of the present study are generally in agreement with the results of these latter authors.

Bioaccumulation of metals in below-ground tissues is a strategy that plants use to restrict distribution of metals to above-ground tissues, to avoid contamination of their photosynthetic tissues by high metal concentrations (Deng et al., 2004; Bragato et al., 2006). Metals are stored in the inner root tissues, within cells of the stele, or within cell walls and vacuoles (Weis and Weis, 2004). Metals may also be immobilised through the production of metallothioneins and phytochelatins (MacFarlane and Burchett, 2000).

It must be noted that iron plaques on root surfaces may affect concentrations measured in roots. Iron plaques are composed mostly of iron hydroxides and other metals such as manganese that are mobilised and precipitated on the root surface (Weis and Weis, 2004). Apart from the fact that they could give a false impression about metal concentrations contained inside roots, they could also increase or decrease the uptake of metals by plants. Iron plaques are known to adsorb large amounts of cations and on roots may, for example, form a barrier to the uptake of cationic nutrients and metals and may immobilise metals (Salomons and Förstner, 1984). It is possible that iron plaques may have, to some extent, influenced metal concentrations measured for the roots in the present study. However, the author assumes that the largest part of the metals measured, were in fact contained inside the roots. This assumption is based on a large body of literature on *B. maritimus* and root accumulation (as discussed previously).

Metals were not only detected in the roots of *B. maritimus* in the present study, but were also detected in the above-ground tissues (with the exception of cadmium). This is easily explained for metals such as Cu, Zn, Mn, and Fe as they are essential micronutrients (Madejón et al., 2006a) and therefore need to be distributed to all parts of the plant. They may even be found in higher concentrations above-ground, as

shown for Zn and Cu by Cacador et al. (2000) for *Spartina maritima* and *Halimione portulacoides*.

The other metals measured in the leaves and stems had probably been translocated from the roots. Translocation occurs due to several factors: (i) The demand for essential micronutrients in above-ground parts, as discussed before. (ii) Storage capacity: excess metals are stored in the roots and if the storage capacity is exceeded, the metals are translocated to the above-ground tissues regardless of whether they are essential or non-essential (Otte et al., 1991). This is a very likely explanation for the detection of non-essential metals in the stems and leaves in the present study. (iii) Senescence of above-ground tissues, especially leaves: Bragato et al. (2006) suggested that when photosynthetic activities are reduced due to aging of leaves, plants translocate metals to the aging parts as a mechanism to reduce metal burden. Luque et al. (1999) also found that old leaves had higher concentrations of various metals than young leaves. In the present study there is a possibility that a certain percentage of the leaves analysed for metals were older because leaves were selected randomly. This may have influenced the results. (iv) Increased transpiration by leaves, leading to increased metal uptake in the process: Otte et al. (1991) found increased concentrations of metals in *Aster tripolium* tissues under saline conditions, which they suggested may have been related to higher water uptake due to increased transpiration, leading to higher flux of metals into the entire plant. This is also a likely explanation for the results of the present study, since EC readings were high at both sites (Table 3.1). (v) Other metals present in the plant: the presence of other metals may increase or decrease the accumulation of metals by plants. Weis et al. (2004) found that Cu distribution was affected by the presence of Zn or Pb in *Phragmites australis*. Fritioff and Greger (2006) found a decrease of Cd in the roots and an increase of Cu in leaves of *Potamogeton natans*, in the presence of other metals in these tissues. In the present study, a wide range of metals were present in the plants and these may have influenced one another in varying degrees.

Seasonal differences were investigated. This was done only for roots, not leaves and stems, since *B. maritimus* was shown to be a root accumulator (as discussed previously). Seasonal variations in metal concentrations in *B. maritimus* roots were observed, but these did not follow similar patterns between the different metals or



between the two sites (Figures 5.2.1A, B, C - 5.2.10A, B, C). These variations also did not correspond with fluctuations in sediment concentrations (Figures 4.3.1 - 4.3.10). Only one exception was observed. This was for Co at site 3 (Figures 4.3.4 and 5.2.4A), where seasonal root concentrations mirrored seasonal sediment fluctuations (Figures 4.3.4 and 5.2.4A). This may simply have been a coincidence.

Particularly high concentration peaks were measured for Cd (Figure 5.2.2A), Cu (Figure 5.2.5A), Pb (Figure 5.2.7A) and Zn (Figure 5.2.10A) at site 3 during July (winter) and September (spring), as well as for Mn (Table 5.2.8A) at site 1 during these months and at site 3 during November (summer). In the cases of Mn and Zn, these peaks corresponded with peaks in sediment concentrations (Figures 4.3.8-4.3.10).

Seasonal fluctuations in plant root concentrations are influenced by many factors such as bioavailability (Larsen and Schierup, 1981), which in turn is affected by for example, pH and temperature, as well as physiological factors of the plant itself (Otte et al., 1993). The fact that seasonal fluctuations in root concentrations of *B. maritimus* mostly did not correspond with fluctuations in sediment concentrations, clearly indicate the important influences of the above-mentioned factors on metal uptake in this plant. The high concentration peaks found for several metals in July (winter) and September (spring), especially at site 3, were probably also caused by a combination of the above-mentioned factors.

Generally, root concentrations were highest in September (spring), followed by July (winter) but in most cases this pattern was not observed for sediment concentrations. Almeida et al. (2006) stated that there is normally a higher plant activity in summer and spring, with higher uptake of elements. Also, it is known that rhizomatous plants translocate metals to the roots in preparation for the growing processes during the growing season (Chapin et al., 1990) and that the interaction between plant roots and sediments increases during the growing season and decreases in winter (Otte et al., 1991). The higher root concentrations found in September (spring) for most metals, may be an indication that *B. maritimus* follows a similar strategy, in preparation for growth, which, according to C. Archer (pers. comm., 2007), is in October in the Western Cape.

In conclusion, comparisons between sites, sediments, plants and seasons, revealed the significance of factors such as bioavailability in the bioaccumulation of metals. The results revealed greater bioaccumulation by plants at site 3, which was probably influenced by several factors, particularly by salinity levels. Sediment clay content at site 1 probably played a major role in making metals less available to plants. Seasonal variations in metal concentrations in *B. maritimus* roots were observed, as well as some concentration peaks, but these did not follow similar patterns between the different metals or between the two sites. Neither did the results correspond with seasonal sediment concentrations. Again, the significance of bioavailability is highlighted.

The results also confirmed *B. maritimus* as a root accumulator, as higher concentrations of metals were found in roots than in above-ground tissues. The distribution of metals from the roots to other plant parts was probably mainly influenced by factors such as seasonality and translocation of metals, as a result of a demand for essential micronutrients in the above-ground parts, limited storage capacity of the roots, saline river conditions and the presence of other metals in the plant.

Finally, there is some doubt as to whether *B. maritimus* can be effectively used as biomonitor species in an environment such as the lower Diep River, particularly since root concentrations mostly did not indicate the actual level of contamination in the environment (sediment), or changes in contamination levels over time. On the other hand, *B. maritimus* did provide additional information that soil analyses alone would not have provided, namely the bioavailability of the metals in the sediment and water. According to Madejón et al. (2006b), and Mertens et al. (2006), such additional information is necessary, for a species to qualify as a biomonitor species. However, Mertens et al. (2006) also stated that the information provided by a biomonitor species should ideally also include information on plant or ecosystem functioning. In the present study this aspect, e.g. with the use of biomarkers, has not been investigated, therefore final conclusions about the use of *B. maritimus* as biomonitor species cannot be drawn.

The water of the lower Diep River is contaminated in terms of aluminium, copper, manganese, zinc and iron, as they were higher than DWAF guidelines. Zinc, aluminium and iron concentrations were higher than some of the South African studies compared with. This indicates that, at times, the lower Diep River may be more contaminated with these metals, than the other river systems that have been investigated. Several point sources of pollution, such as agricultural runoff and landfill sites near site 1, industries at site 2, and a sewage treatment plant before site 3, may contribute to this contamination. Undetected metals, particularly the non-essential metals, might, due to several factors, actually be available to freshwater organisms of the lower Diep River and could lead to toxic effects at various levels of biological organisation.

Sediment metal analysis revealed that the lower Diep River is in fact highly contaminated with metals and also confirmed that analysing water samples only, does not give any true indication of the level of metal contamination in a river. This was deduced from the high metal concentrations measured in the sediments, particularly in the vicinity of the sensitive Rietvlei reserve (close to site 2). The metals, originating from various sources in the area, settle into the sediments at a faster rate than they are washed downstream. Closer to the mouth of the river, large concentrations of metals have already been accumulated by plants such as *Bolboschoenus maritimus*, lessening the threat to the estuary. However, these plants do not remove the accumulated metals out of the ecosystem and, through decomposition, and via food chains, these metals are again made available to the rest of the ecosystem, where they remain a threat.

Results showed that *B. maritimus* accumulates metals to high concentrations, particularly in the roots. In fact the species was shown to be a root accumulator. Greater bioaccumulation by plants occurred at site 3, which was probably influenced by several factors, particularly by salinity levels. Sediment clay content at site 1 probably played a major role in making metals less available to plants. Such a deduction could not have been made without sediment characterisation, thus highlighting the importance of this procedure in aquatic biomonitoring.

Metals were not only measured in the roots but also, to a lesser extent, in the above-ground tissues. The distribution of metals from the roots to other plant parts was probably mainly influenced by factors such as seasonality and translocation of metals, as a result of a demand for essential micronutrients in the above-ground parts, limited storage capacity of the roots, saline river conditions and the presence of other metals in the plant.

Seasonal variations in metal concentrations in *B. maritimus* roots were observed, as well as some concentration peaks, but these did not follow similar patterns between the different metals or between the two sites. Neither did the results correspond with seasonal sediment concentrations. Again, the significance of bioavailability is highlighted.

Root concentrations mostly did not indicate the actual level of contamination in the environment (sediment), or changes in contamination levels over time, but using *B. maritimus* as test species in this study did provide additional information that soil analyses alone could not have provided, namely the bioavailability of the metals in the sediment and water. With such mixed results it is therefore not possible to make final conclusions about the effective use of *B. maritimus* as biomonitor species in an environment such as the lower Diep River. More extensive research is needed.

In conclusion, this study has shown the importance of not only using water and sediment to determine the degree of metal pollution in a river, and the impact thereof, on the ecosystem. The use of living organisms needs to be incorporated, as this will reveal whether metals are actually in bioavailable forms and therefore truly pose a threat to the ecosystem or not.

It is clear that the present study can serve as a foundation for future studies in this river. Therefore, further monitoring should be undertaken on metal contamination in the lower Diep River, as the river runs through an area where there is continuous development. Since the possibility exists that *B. maritimus* may not to be a reliable biomonitor of metal contamination, the possibility of using other aquatic plant species, such as *Phragmites australis*, or invertebrates such as crabs and freshwater snails, should be investigated. An important question emanating from this study is

what the actual toxicity of metals is to the aquatic organisms, particularly to *B. maritimus*. Biomarkers may be used for this purpose.

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