AN ASSESSMENT OF THE IMPACT OF INDUSTRIAL EFFLUENT FROM A KWEKWE-BASED IRON AND STEEL COMPANY ON KWEKWE RIVER WATER QUALITY

BY

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To survive, let alone maintain dignified life, requires that we make the best and least use of natural resources. If we do not sustain them, they will not sustain us"

Dr. J.T. Ling

ABSTRACT

The water quality of Kwekwe River, upstream and downstream of the industrial effluent discharge point was examined with the view of determining the effect of the effluent on water quality. Five sampling sites, each 20m long were selected along the river. Water and biological samples were collected between the months of April and June 2005. Both macroinvertebrates and water variable characteristics data were analysed for variations using one-way analysis of variance (ANOVA). Hierarchical method, average linkage cluster analysis was applied to the mean values of the water variables for each site. Two clusters were produced, grouping the reference site and the two sites furthest from the discharge point. Water physico-chemical variables (total dissolved solids, chemical oxygen demand and conductivity), heavy metals (calcium, iron, manganese and chromium), Average Score per Taxon (ASPT) score; metric and diversity indices changed markedly downstream ($p<0.05$). The river had the highest self-purification amounts with respect to total dissolved solids. The results of the study suggested that the effluent discharged into Kwekwe River have an adverse effect on water quality. Macroinvertebrate structure changed markedly downstream with a complete disappearance of taxa at the discharge point.

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DEDICATION

Thesis dedicated to the memory of Mr. C.J. Chinhanga. Father, I solely miss you, may your soul rest in eternal peace.

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1. INTRODUCTION

1.1 Overview

Despite a variety of alternatives available for industrial wastewater management, many industries continue to degrade the most precious but scarce natural resource. Quite a number of industries in developing countries still use either outdated or the least practicable technologies due to economic constrain (Fakayode, 2005). The Dublin Principles, Agenda 21, Vision 21 and the Millennium Development Goals, for example, provide the basis for development, holistic and sustainable approaches (Nhapi, 2005), but project proponents continue degrading the aquatic ecosystems. Pollution of surface and ground water is a global problem and water quality remains a matter of considerable concern in southern Africa. Increase in population and industrial revolution has seen lotic systems becoming the most heavily impacted ecosystem on the planet. Riverine ecosystems have acted as magnets for human settlement and heavily exploited for water supplies and waste disposal

The fundamental importance of freshwater for life on the earth needs little justification. Indeed, freshwater is central to human welfare and economic development in many ways. Water is an essential resource for supporting human and other ecological systems and sustainable economic development in all sectors (Hirji *et al.,* 2002). Studies have shown that water quality in aquatic ecosystems has a strong ecological impact (Harding *et al.,* 1999; Ometo *et al.,* 2000). Freshwater is not only essential to life, it is also clearly a relatively scarce resource and this is likely to become more so with the impacts of climate change (Mason, 1996). Climate change will influence the effects from which chemical pollutants as increased temperature are likely to increase the biochemical rates and biomagnifications of toxicants. According to Matiza *et al.,* (2002 in Hirji *et al.,* 2002), the southern African region is expected to be drier by the year 2025. Predictions are that Lesotho, Mauritius, Tanzania and Zimbabwe will be water stressed, while Malawi and South Africa will face absolute water scarcity. Climate change rainfall scenarios also suggest that annual rainfall will decrease by up to 5% and this will be experienced in Namibia, Mozambique and parts of Zimbabwe and South Africa (Hirji *et al.,* 2002). Sustainable utilisation of the aquatic ecosystems is therefore, of best interest to living organisms, human beings included.

The costs of correcting degraded water and dealing with unforeseen conflicts over water shortages may be very high for future generations to come. There has been concern in Zimbabwe about the health of Kwekwe River due to effluents being discharged into the river by a Kwekwe-based iron and steel company (Magadza, personal communication). The Kwekwe-based iron and steel company is said to discharge high quantities of iron, sulphate, oil and tar into Kwekwe River, making the water unsuitable for irrigation and domestic use (Moyo *et al.*, 1998).

1.2 Project Justification

Zimbabwe's water resources are under increasing threat of pollution due to discharge of partially or an untreated industrial effluent (personal observation), Kwekwe River is not an exception. No studies have been done to assess the ecological health of the river, despite numerous complaints from Kwekwe residents concerning the health of the river due to effluents being discharged into it by the Kwekwe-based steel company.

Fears have been raised that due to the discharges from the Kwekwe-based steel company, the river could be polluted excessively. The need to assess the state and quality of Kwekwe River water becomes imperative given that the water is used for domestic use, irrigation and livestock rearing. The river is of importance not only to people who live, fish and farm in Kwekwe town but also to citizens in faraway towns, who consume fish from the river.

The study describes the current state of the physico-chemical and macroinvertebrates characteristics to assess whether the industrial effluent being discharged in the river has an impact on water quality or not. The study will enable the establishment of baseline biological and water quality data in Kwekwe River. The data will be used to assess any changes in water quality and assist environmental law enforcers and policymakers in coming up with strategic pollution abatement measures.

1.3 Objectives

The general objective of the present study was to investigate the impact of industrial effluent from the Kwekwe-based iron and steel-making company on Kwekwe River water quality.

The specific aims were:

a) to investigate changes in composition, distribution and estimate the abundance of macroinvertebrate communities upstream and downstream of effluent discharge point;

b) to measure changes in the levels of temperature, chemical oxygen demand (COD), conductivity, pH, and dissolved oxygen; and concentrations of iron, manganese, cadmium, calcium, chromium, lead and zinc,

c) to determine relative concentrations, distributions and bioavailability of iron, manganese, cadmium, calcium, chromium, lead and zinc in the most abundant plant species along the river, *Phragmites australis,*

1.4 Hypotheses

a) Effluent has no effect on the water chemistry of Kwekwe River.

b) Effluent has no relation to metal content in *Phragmites australis.*

1.5 Research Questions

a) What are the levels of iron, manganese, zinc, calcium, chromium, cadmium, lead, ammonia, nitrates, sulphates and total phosphates in the water-column phase along Kwekwe River?

b) What are the concentrations of iron, manganese, zinc, calcium, chromium, cadmium and lead in Kwekwe River sediments and bank soils?

c) What are the concentrations of iron, manganese, zinc, calcium, chromium, cadmium and lead in *Phragmites australis* leaves and rhizomes?

d) What is the composition of macroinvertebrate communities along the river?

e) Do metric and diversity indices vary between sites?

2. LITERATURE REVIEW

2.1 Introduction

Most industrial effluents are toxic, discharge of untreated or partially treated effluent could have direct deleterious effects to aquatic life. The ecological status of an aquatic ecosystem can be estimated by assessing water quality variables and biological diversity attributes (Ndaruga *et al.,* 2004). According to Magadza and Masendu (1986), information on the behaviour and ecological impact of various effluent types enables the formulation of national policy on effluent disposal. Once the health status of Kwekwe River is known, the need and priorities for water management intervention can be determined and this may involve the introduction of policies, local and national management strategies.

2.2 Biological Monitoring (Biomonitoring) of Water Quality

Biological monitoring or biomonitoring was defined by Dallas (2000), as the use of biota to determine the quality of the riverine environment. It utilises one or more components of the biota and macroinvertebrates are the most commonly used (Metcalfe-Smith, 1991 cited in Dallas, 2000). Benthic macroinvertebrates are often used as indicators of water quality because of their sedentary, comparatively long lives and varying degrees of sensitivity to pollutants. Macroinvertebrates act as continuous monitors of the water they live in, enabling long-term analysis of both regular and intermittent discharges, different levels of pollutants and synergistic or antagonistic effects (Dallas, 2000). Macrophytes are also good biological indicators and act as buffers to pollutants entering a stream (Madejon *et al.,* 2003 cited in Awofolu *et al.,* 2005).

The South African Scoring System Version 4 (SASS4), now in its 5th iteration (Dickens and Graham, 2002 cited by Harding *et al.,* 2005), is an important biomonitoring tool used to determine the health of a river. Severely impaired lotic ecosystems are characterised by dominance of pollution-tolerant organisms such as, Chironomidae, Simuliidae, Crabs, Oligochaeta, Tipulidae and Corixidae (Winner *et al.,* 1980). Undisturbed or slightly disturbed lotic ecosystems generally consists of a high diversity of benthic fauna which include pollution-sensitive organisms of the orders Ephemeroptera, Plecoptera, Trichoptera and pollution tolerant organisms may also be present.

Biomonitoring has been acclaimed as being a more sensitive and reliable measure of river health and water quality than either physical or chemical measurements (Dallas, 2000). The aquatic invertebrate method does not always reveal the causes of pollution or measure the levels of pollutants in an impacted aquatic ecosystem. Biological monitoring and analytical procedures must therefore be viewed as complementary. The ultimate goal of biomonitoring is to evaluate the impact of anthropogenic activities on aquatic ecosystems (Fore *et al.,* 1996 cited by Dallas, 2000). According to Hawkes (1957), the direct measure of pollution is the determination of the effects of pollutants on macrophytes and aquatic organisms. Assessment and control of adverse impacts of toxic discharges on aquatic communities is therefore incomplete without the use of living organisms as indicators of toxic effects (Wall and Hanmer, 1987). The analysis of biomagnification and bioaccumulation of pollutants in the tissues of organisms may also indicate possible human risks.

The use of biomonitoring in water quality assessment in Zimbabwe is still in its infancy. Only a few studies have attempted to use biomonitoring to assess water quality in Zimbabwe aquatic ecosystems. For example, Phiri (1998) compared the water quality of two rivers in Zimbabwe, Mukuvisi and Gwebi Rivers using presence or absence of benthic fauna as indicators of water quality and found the former river to be more polluted. He noted a decline in the number of macroinvertebrate taxa along Mukuvisi River, suggestive of deteriorating water quality while along Gwebi River the benthic fauna were evenly distributed, indicating no major changes in water quality. In a study by Magadza and Masendu (1986), on the effect of mine in the Yellow Jacket Stream no benthic fauna were collected from one of the sampling sites, suggesting massive pollution. However, a number of organisms including the most pollution sensitive organisms of the order Ephemeroptera were collected from the upstream site, indicating that the stream was undisturbed or slightly disturbed at that point. In a related study on the effects of organic pollution on the Mukuvisi River in Zimbabwe, Moyo and Worster (1997), found the river to be dominated by pollution tolerant organisms, *Chironomidae* and *Branchiura.*

The South African Scoring System (SASS) is a qualitative, multi-habitat, rapid field-based biomonitoring tool that requires macroinvertebrate family level data (Dallas.2004a). SASS like any other analyses is not without its shortcomings. The distribution of benthic fauna is also affected by factors other than water pollution such as season (Gratwicke, 1999; Cowell *et al.,* 2004; Dallas, 2004b), hydrology (McElravy *et al.*, 1989 cited by Dallas, 2004b), current velocity and nature of substratum (Bargos *et al.,* 1990; Sues, 1982; Friedrich *et al.,* 1992), biotope availability (Armitage and Pardo 1995; Armitage *et al.,* 1995 cited by Dallas, 2004). Gratwicke (1999), investigated the effect of season on SASS biotic index using the Yellow Jacket and Mazowe Rivers in Zimbabwe as a case study. He found that SASS scores at and downstream of polluted sites were higher at the end of the rainy season than during the dry season. In a related study on investigating community composition and distribution of macroivertebrates in the Umzimvubu River, South Africa, Madikizela and Dye (2003) found that community composition was more similar in three of the four seasons studied. They found autumn, winter and spring to be more similar than summer.

2.3 Iron and Steel Manufacturing.

The iron and steel industry generates large quantities of residuals from the primary iron making and steelmaking process. Steel is manufactured by the chemical reduction of iron ore and pig iron is manufactured from sintered, palletised, or lump iron ores using coke and limestone in a blast furnace (http//www.epa.gov/ost/ironsteel/pdf/prelim 3.pdf). Steel is manufactured by feeding the molten pig iron into a basic oxygen furnace along with scrap metal, fluxes, alloys and high purity oxygen to manufacture steel. The addition of 10% to 30% chromium creates stainless steel, which is very resistant to rust (http//www.epa.gov/ost/ironsteel/pdf/prelim 3.pdf). Furnace flue dusts and blast furnace gas wash water and wastewater treatment sludge are recovered through sinter plants.

Slags are processed for reuse in a variety of construction such as brick moulding and road building uses. Major pollutants present in untreated wastewaters generated from iron and steel manufacturing include cyanide, limestone, iron, manganese zinc, lead, cadmium, chromium, oils, phenols, ammonia, suspended solids and fluoride. Limestone deposit occurs near the steelworks, about 2km west-north-west of Redcliff (Cheshire, *et al.,* 1980). Manganese orebodies are found in banded ironstones and the metal is a useful additive to the production of steel (Cheshire, *et al.,* 1980).

2.4 Heavy Metal and Non-Metal Pollution

Heavy metal salts in solution constitute a serious form of pollution and are very harmful to aquatic organisms at very low concentrations (Schmitz, 1996). Heavy metals may have detrimental effects to the health of aquatic ecosystem and people who utilises raw river water for drinking and cooking. For example, Cadmium affects normal metabolic function of an organism by replacing zinc in many enzymes (Schmitz, 1996). Borgman (1983 cited by Awofolu *et al.,* 2005) described lead and cadmium as non-essential metals of no benefit to human. Ingestion of toxic levels of cadmium may cause renal dysfunction, hypertension, artriosclerosis, chronic diseases of old age and testicular tumours (Schmitz, 1996). Cadmium is widely distributed in the aquatic environment, its sources include: weathering of rocks and soils (Merian, 1991 cited by Fatoki *et al.,* 2004), atmospheric deposition from non-ferrous metal mines, smelters and refineries, coal combustion, refuse incineration and iron and steel companies (Merian, 1991 cited by Fatoki *et al.,* 2004).

Iron cause water to have an objectionable taste at levels above 1 or 2mg l^{-1} and cause staining of laundry. Manganese like iron has no known ecological effects. It imparts objectionable and tenacious stains to laundry and plumping fixtures (APHA *et al.,* 1980). Lead has been found to cause quite a number of ailments in human beings, such as neurological disorders and large doses of zinc may result in some health complications such as fatigue and dizziness (Awofolu, *et al.,* 2005). Ammonia has immediate adverse effects on aquatic life, a case in point is the massive fish deaths that occurred in Lake Chivero in March/ April 1996 (Moyo, 1997). Thousands of *Oreochromis macrochir* died due to deoxygenation of water in the lake, which was worsened by ammonia toxicity.

2.5 Zimbabwe's Legislation Governing Water Use and Pollution Control

Zimbabwe has got a vast number of environmental laws and policies that need to be saved from dying a natural death due to lack of implementation. Most if not all the pieces of environmental legislation have however, been and up to this day relate primarily to the imposition of control measures, for example the 'Polluter Pays Principle'. It is very important to note that pollution prevention is much cheaper, environmentally friendly, technically and economically sound than corrective measures. Zimbabwe National Water Authority (ZINWA), a parastatal under the ministry of Rural Resources and Water Development, has the mandate to oversee the management of water catchments authorities and their areas. Water quality monitoring in Zimbabwe is intended to control pollution and enforce water protection legislation. Environmental law enforcement agents, which are mainly government ministries and departments, have been described by many Zimbabweans as failures (personal observation).

The failure to effectively enforce environmental legislation by the agents has been attributed to the prevailing economic hardship that has led to brain drain, resulting in staff shortages. The fuel shortages bedevilling the country as a whole, has hampered the activities of the legislation enforcement agents, making it difficult if not impossible for the agents to implement and monitor the various pieces of legislation. The ineffectiveness of the legislation enforcement agents has resulted in serious degradation of water bodies and Kwekwe River is not an exception. According to law, water authorities supplying water for human consumption are under a statutory obligation to supply a pure and wholesome water (Government of Zimbabwe, 1998).

Pieces of legislation that control development and use of water, as well as water pollution include: the Environmental Management Act [Chapter 20:27]; Water Act (Chapter 20:24); Zimbabwe National Water Authority Act [Chapter 20:25] and Water (Waste and Effluent Disposal) Regulations, 2000.

2.5.1 Water Act [Chapter 20:24]

Water Act is the main law that regulates the development and utilisation of water (Government of Zimbabwe, 1998). The Act was amended in 2003 and sections on water pollution control, that is, section 67-71 were incorporated into the new environmental Act, Environmental Management Act, Chapter 20:27.

2.5.2 Environmental Management Act [Chapter 20:27]

The Act provides for the sustainable management of natural resources and protection of the environment, the prevention of pollution and environmental degradation (Government of Zimbabwe, 2003). The Act incorporates Environmental Impact Assessment (EIA) provisions and environmental quality standards are covered in part lX of the Act. EIA studies have to be conducted for all water projects before project implementation. Section 57 (1) regulates water pollution, makes it a punishable offence to discharge pollutants into aquatic ecosystems. Section 61 of the Act gives power to the Environmental Management Agency Board to cancel an effluent discharge licence in case of any violations of the provisions of the Act. The first schedule of the Act contains a list of projects to which EIA studies have to be conducted before project implement The Act also introduces the Polluter Pays Principle, a most effective way of discouraging polluters from degrading the environment. Polluters are ordered to clean up at a cost determined by the nature of pollution.

2.5.3 Zimbabwe National Water Authority Act (ZINWA) [Chapter 20:25]

The Act repeals the Regional Water Authority Act [Chapter 20:16]. ZINWA Act provides for the functions of the national water authority and among other things provides for; the raising of charges for the provision of water and other services by the authority. Furthermore, under this Act, the Minister of Rural Resources and Water Development with approval of the Minister of Finance and through a statutory instrument may impose a water levy on any effluent discharge permit holder.

2.5.4 Water (Waste and Effluent Disposal) Regulations, 2000

The Water (Waste and Effluent Disposal) Regulations, 2000 repeals the Water (Effluent and Waste Water Standards) Regulations, 1977, as amended by the Water (Effluent and Waste Water Standards) (Amendment) Regulations, 1982. The Water (Waste and Effluent Disposal) Regulations, 2000, introduces environmental effluent standards for discharge into water bodies, sampling procedures for most effluents and wastewater.

Table 1. Maximum permissible concentration of certain chemical constituents discharged into water bodies*

Variables	Maximum Concentration (mgl^{-})
PH	6.0-7.5
COD	≤ 30
DO % Saturation	≥ 75
Temperature (O ^{o}C)	< 25
TDS	≤ 100
Conductivity ($\mu S\ cm^{-1)}$	≤ 200
Total phosphate	≤ 0.5
Ammonia	≤ 0.5
Iron	≤ 0.3
Chromium	≤ 0.05
Cadmium	≤ 0.01
Calcium	No prescribed limits currently exists
Lead	≤ 0.05
Manganese	≤ 0.1
Nitrate Nitrogen	≤ 3
Sulphate	≤ 100

*Zimbabwe Water (Waste and Effluent Disposal) Regulations, Statutory Instrument 274 of 2000.

3. MATERIALS AND METHODS

3.1 Description of Study Area

The study area is located within Midlands province of Zimbabwe, covering a 12km stretch of Kwekwe River. It is a perennial river, originating from Whitewaters Dam in Chiwundura and flows through the town of Kwekwe. The town lies 18^0 92^1 S, 29^0 81^1E and 1 200m above sea level. The town is located 213km south-west of the capital city of Zimbabwe, Harare (Figure 1). Kwekwe town receives mean annual rainfall of between 600 and 699mm (Chenje, 2000). Redcliff, located in the town of Kwekwe, is the iron and steel-producing centre of Zimbabwe.

Kwekwe River stretches for about 78km into Sebakwe River, which connects it into Munyati River. Munyati River flows into Lake Kariba, which subsequently drains into Zambezi River. Kwekwe River channel is protected from erosion by riparian vegetation consisting mainly of dense stands of *Phragmites australis*. No floating macrophytes were observed during the study period. The vegetation in the catchment area mainly consists of miombo woodland, dominated by *Brachystegia* species and *Julbernardia globiflora*. The fauna found in the area mainly consists of *Tragelaphus strapsiceros* (kudu), *Hippotragus niger* (sable antelope) and *Aepyceros melampus* (impala). Fish in Cactus Poort Dam, about 1km upstream of sampling site Kwe1 (Figure1), include Tilapia species.

The geology of the catchment is mainly limestone, basaltic and peridotitic, metavolcanics and metasediments (Cheshire *et al.,* 1980). The oldest rocks in the study area belong to the Sebakwian group, occurring as inclusions, composed of ironstones and various ultramafic rocks within the granite batholiths along the western margin of the greenstone belt (Cheshire *et al.,* 1980). Kwekwe River flows for the greater part along direct courses over granitic rock, but forms meanders on approaching the belt and subsequently breaks through jaspilite ridge in the gorge at Cactus Poort (Cheshire *et al.,* 1980). Kwekwe River serves not only as one of the drainage for Midlands region, but also provides water for domestic and industrial use, irrigation and a conduit for effluent disposal in Kwekwe town.

Sampling sites are as shown in Figure 1 and Table 2 gives a description for each site. The five sites were chosen because of their easy accessibility and are a true representative of the affected stretch of the river channel. Point and non-point sources of pollution exist further downstream of the study area, but due to financial constrains these were left out in the study. The pollution sources include: sewage works at Redcliff, sewage effluent from Kwekwe town, waste and wash water from companies downstream and alluvial gold panning.

Table 1. Description of the sampling sites and their location as given by the Geographical Positioning System (GPS)

Site	Width (m)	Depth (m)	Velocity (m s^{-1})	Marginal Vegetation	GPS (UTMs) latitude	GPS (UTMs) longitude	Distance (km) from point source	Turbidity
Kwe1	3.0	0.95	0.37	*Gardenia volkensi, Peltoforum africanum, Phragmites australis, Pseudolachynostilis maphroneofolia, Rhus quartiana, Syzigium guiniense, Terminia serisceria*	792857	7891779	6.73	low
Kwe2	4.0	0.73	0.29	*Lantana camara, P. australis, Rhus quartiana*	788669	7895936	0	high
Kwe3	7.0	0.45	0.29	*Lantana camara, Phragmites australis, Rhus quartiana*	788753	7896375	0.46	high
Kwe4	10	0.55	0.20	*Phragmites australis, Rhus quartiana*	787780	7901726	6.53	medium
Kwe5	13	0.55	0.12	*Phragmites australis, Rhus quartiana*	787774	7905945	11.46	medium

3.2 Sampling Procedure

Guided by a geographical positioning system (GPS), sampling sites were systematically located. A 20m stretch of the river channel was examined for each site on each occasion to evaluate the environmental impact of the effluent from the Kwekwe-based steel company on Kwekwe River. The sampling sites are shown in Figure 1 and were chosen due to their easy accessibility and are a true representative of the affected part of the river. Only one sampling site, Kwe1, was located as a reference point.

The study was conducted when the country as a whole had received low rainfall in the preceding rainy season, for the period April through June 2005. Sampling followed standard cleaning protocols, which involved cleaning of sampling equipment between sampling sites to avoid cross-contamination of samples with heavy metals. Water, soil and sediments samples were collected from the river following standard procedures described in the sampling guide (DWAF, 1999; 1992). Water, bank soils and river sediment samples were collected prior to benthic fauna sampling at each site. Three sample points were randomly chosen on each occasion at each site. *Phragmites australis* leaves and rhizomes were collected for heavy metal determination in the laboratory using atom absorption spectrometry finish. *Phragmites australis* was chosen for the study because it was most common at all sampling sites.

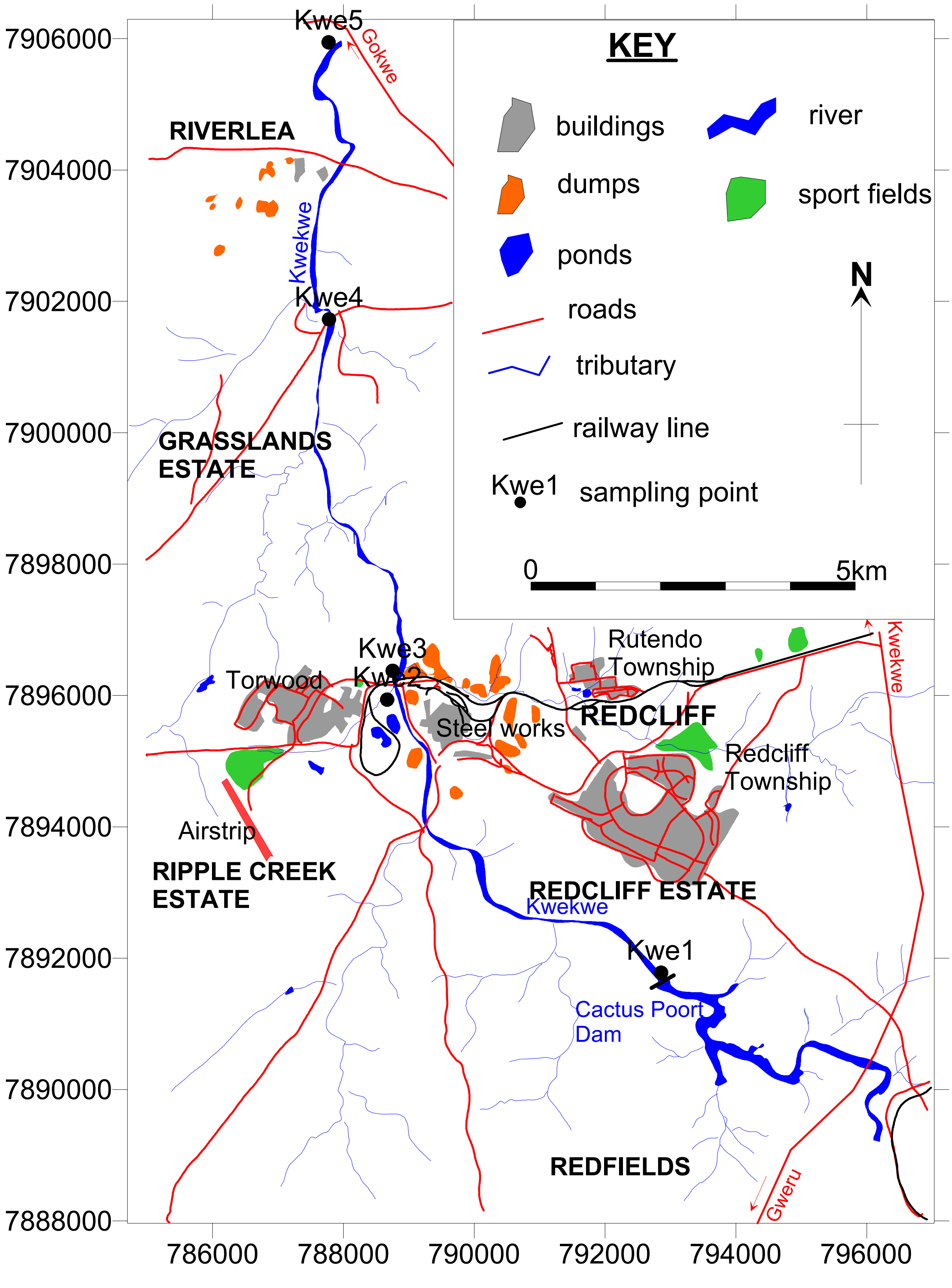

Figure 1. Study area map showing sampling sites along Kwekwe River

3.2.1 Physico-chemical Variables

Physico-chemical variables were examined at 3 occasions for the period April through June 2005. Dissolved oxygen, pH, conductivity and temperature of the water were measured electrometrically on site using WTW Oxi 330 meter, WTW pH 330 meter and WTW LF 330 meter, respectively. Turbidity was subjectively assessed as high, medium or low. Total dissolved salts (TDS), were determined by filtering 100ml of water and then evaporating it gradually in pre-weighed crucibles. The change in weight was used to determine the dissolved salts. Chemical oxygen demand (COD) was determined by titration method, using ferrous ammonia sulphate and ferroin as indicator (APHA, *et al., 1992).*

Velocity at each sampling site was estimated by measuring the time taken by a leaf to float to a distance of 10m. According to Allan (1995), a float gives a rough measure of surface velocity. The average river depth at each site was determined by taking 5 measurements at 1m intervals across the river channel. Average river discharge (r) at each site was calculated using the following formula;

r=Wdva (Welch, 1948, cited by Machena, 1997)

Where; r is average rate of flow in $m^3 s^{-1}$; W is average width of the river channel at the sampling site in meters; v is average velocity in $m s^{-1}$ at the sampling site; d is average depth of the river channel at the sampling site; a is a constant and is 0.9 when the river bed is smooth and composed of such material as sand, mud or hard pan; and a=0.8 when the river bed is composed of loose rocks and coarse gravel (Welch, 1948 cited by Machena, 1997).

3.2.2 Water Chemistry.

Water samples were collected at random in triplicate within a distance of 15m, at the centre of the river channel at each site on 3 occasions for the period April through June 2005. The samples were collected using 500ml polythene bottles. The bottles were thoroughly cleaned in soap solution first, soaked in 10% hydrochloric acid (HCl) for 24hrs, and then rinsed with deionised water. The bottles were further rinsed three times with sample water, immersed about 20cm (Downson *et al.,* 1996) below the water surface and filled to the brim. Care was taken not to disturb the sediments and the benthic fauna on the riverbed. All samples were tightly sealed and kept cool using ordinary dry ice in the field and while on transit to the laboratory. Immediately upon arrival at the laboratory, all water samples for heavy metal and anion analysis were filtered through 0.45 micron-pore-diameter filter and preserved by adding 0.3ml 65% nitric acid (HNO_3) to a pH below 2 and stored at 4 ^{0}C until analysis. The samples were analysed for iron, manganese, calcium, cadmium, chromium, lead, zinc, sulphates, phosphates, nitrates and ammonia.

The concentrations of the heavy metals and anions in the samples were determined according to standard procedures (APHA *et al.,* 1989). The concentrations of the heavy metals were determined by using atomic absorption spectrophotometer (AAS). Ammonia, phosphate and nitrate ions were determined by the methods of Madêra *et al.,* (1982). Ammonia was determined calorimetrically by measuring the intensity of the blue colour produced by the reaction of dissolved ammonia in the samples with the hypochlorite in the presence of phenol. Nitrates (NO_3^{-2}) were determined by using the chromotropic acid method based on measuring the intensity of the yellow colour produced by the reaction of NO_3^{-2} ions with phenoldilsulphonic acid. Total phosphate (PO_4^{-3}) was determined spectrophotometrically by measuring the intensity of the blue colour produced in the reaction between phosphate and ammonia molybdate in the presence of amonoaphtholsulphonic acid, a reducing agent. The concentration of sulphates (SO_4^{-2}) in water samples was determined by using the turbidimetric procedures based on the precipitation of sulphate from the water using a conditioning reagent and barium chloride dihydrate.

3.2.3 Soil (river bank sediments) and Sediment (river bed) Chemistry

Soil and sediment samples were randomly collected on two different occasions in April and June 2005. Triplicate samples were taken at each site and then pooled in a polythene bag. Soil samples were taken from the surface of riverbanks at each site using a garden trowel. A core sampler was used to collect sediments from the riverbed at each site to a depth of 5cm. The samples were kept cool in the field and en route to the laboratory using dry ice. The samples were kept frozen in the laboratory until analysis. The sediment and soil samples were allowed to defrost then air-dried at 30^0C and thereafter sieved mechanically using a 2mm sieve. The samples were subjected to a total digestion method to determine the concentrations of Fe, Mn, Cr, Cd, Ca, Zn and Pb using atomic absorption spectrophotometer (APHA *et al.,* 1989). All determinations were based on the fine sediment and soil obtained from sieving since metals adhere to these fine particles (Awofolu *et al.,* 2005).

3.2. 4 Biological Sample Collection

Leaves and rhizomes of *Phragmites australis* stems and leaves were hand collected at two different occasions in April and June 2005. Samples were thoroughly rinsed with water and then rinsed with distilled water to remove any attached soil particles and then packaged in polythene bags and kept cool using dry ice in the field and in transit to the laboratory. The samples were stored frozen in the laboratory until analysis. The selected heavy metals in the plant samples were determined according to standard methods (APHA *et al.,* 1989). The samples were allowed to defrost, oven-dried at 60^{0}C and then ground using pestle and mortar. The ground samples were dried to constant weight at 80^{0}C and analysed for Fe, Mn, Zn, Ca, Cd, Cr and Pb content by acid digestion with atomic absorption spectrometry finish.

A stretch of 20m was examined for benthic fauna at each site and the biotopes (Table 2) were noted as defined by Thirion *et al.,* (1995). Three (3) samples of benthic fauna were randomly collected at each site on each occasion in April, May and June 2005. The presence or absence of benthic macroinvertebrates was noted by sampling at each of the sampling sites, using kick-net sampling method. A 50cm multifilament polyester hand net with 0.05 pore size, secured to a 30cm x 30cm square frame was used. Materials trapped in the net were removed; large stones were cleaned and discarded then poured into bucket from which the debris was poured into white tray. The sampling net was also washed before moving to the next sampling site. Forceps and suckers were used to collect the macroinvertebrates from the tray into preservation bottles containing 70% ethanol. Samples were transported to laboratory for sorting and identification. The benthic fauna were counted and identified in the laboratory up to the family level using taxanomic keys from Thirion *et al.,* (1995); Gerber and Gabriel (2002). No attempt was made to identify the organisms up to the species level as SASS4 uses family level data to assess the degree of water quality degradation in lotic ecosystems (Dallas, 1995 cited in Dallas, 2000).

3.3 Data Analyses

3.3.1 Benthic Macroinvertebrates Structure and Distribution among Sites

The degree of river water impairment was assessed by calculating the following widely-used metrics; a) taxa richness; b) % dominant taxa; c) % intolerant taxa; d) % tolerant taxa; e) % ephemoptera, plecoptera and trichoptera (EPT), (Lenat and Crawford, 1994); f) ratio of EPT/ Chironomidae (Klemn *et al.,* 1990). Percent EPT taxa, measures richness in 3 insect orders (Ephemeroptera, Plecoptera and Trichoptera) known to be generally sensitive to disturbance. Percent tolerant individuals indicate the abundance of organisms considered to be tolerant of various types of perturbation.

3.3.2 Diversity Indices

Two (2) diversity indices were used, namely; Shannon's index (H^1) the most commonly used index in community ecology and Simpson's index of diversity (1-D) (Ludwig and Reynolds, 1988). H^1 normally ranges between 1.5 and 3.5, with values greater than 3 being very good, while those below 2 are bad. Simpson's index of diversity ranges from 1-0, the greater the value the greater the sample diversity.

$D=\Sigma n_i (n_i-1)/n(n-1)$ (Simpson, 1949 cited by Ludwig and Reynolds, 1988)

$H^1= -\Sigma\ n_i /n \ In\ n_i /n$ (Shannon and Weaver, 1949 cited by Ludwig and Reynolds, 1988)

Where; D is Simpson index; H^1 is Shannon index; n_i is the number of individuals of the i^{th} family and i= 1,2,3,…,S.

n is the total number of individuals for all S families in the population at each site.

Evenness (modified Hill's ratio) was then calculated as shown below:

$E=[(1/\lambda)-1]/(e^{H1}-1)$ (Hill, 1973 cited by Ludwig and Reynolds, 1988).

H^1= Shannon index

Diversity indices were compared between sites using ANOVA and differences between sites were considered statistically significant at $p<0.05$. All data were tested for normality using Kolmogorov-Smirnov test and were appropriate log transformed, $\log_{10}(x+1)$ prior to analysis to meet the criteria of normality. According to Ludwig and Reynolds, (1988), the modified Hill's ratio is the least ambiguous and most interpretable as it does not require an estimate of the number of families in the community which depend on sample size. The application of diversity indices in water quality assessment is based on the assumption that unimpacted aquatic ecosystem has more taxa than impacted aquatic ecosystem. The pollution intolerant taxa in the unimpacted site are gradually replaced by an increase in the number of pollution tolerant, as the conditions become more adverse (Wilhm and Dorris, 1968). A community is said to have high diversity if it has many taxa and their abundances are fairly even. However, diversity indices are not without their weaknesses, for example, the same diversity index value can be obtained for a community with high richness and low evenness as for a community with low richness and high evenness (Ludwig and Reynolds, 1988).

3.3.3 The South African Scoring System Version 4 (SASS4)

SASS4 is a quick and cost-effective biological water quality analytical tool (Chutter, 1999: 1994). SASS has proved to be an extremely useful tool for assessing river health (Dallas, 1997; Dallas *et al.,* 1998). It is a scoring system based on riverine macroinvertebrates' diversity and abundance (Dallas, 1995 cited in Dallas, 2000). Each taxon is allocated a water pollution tolerance score, the higher the score the greater the organisms sensitivity and the lower its tolerance (Dallas, 1995 cited in Dallas, 2000).

Interpretation of SASS scores is based on two calculated values; SASS4 score and the average score per taxon (ASPT). SASS4 score is the sum of the taxon scores for the families present at a site and ASPT is obtained by dividing SASS4 score by number of families present at a site. A sampling site is considered impacted if the SASS4 scores are lower than those at the reference site. SASS4 incorporates habitat quality assessment as shown in Table 3.

Table 3: Categories used to classify river water using Habitat, SASS4 and ASPT scores, adapted from Thirion *et al.,* (1995).

Habitat	SASS4	ASPT	Condition
>100	>140	>7	Excellent
80-100	100-140	5-7	Good
60-80	60-100	3-5	Fair
40-60	30-60	2-3	Poor
<40	<30	<2	Very Poor.

4. RESULTS

4.1 Water Chemistry of Kwekwe River

The mean concentrations of ammonia-nitrogen and nitrate-nitrogen in the water column phase decreases with increase in distance from effluent discharge point, Kwe 2 (Figure 2). There was a sharp increase of ammonia-nitrogen and nitrate-nitrogen upstream of Kwe 2. The mean concentrations of ammonia-nitrogen and nitrate-nitrogen were high in the industrial effluent, Kwe X.

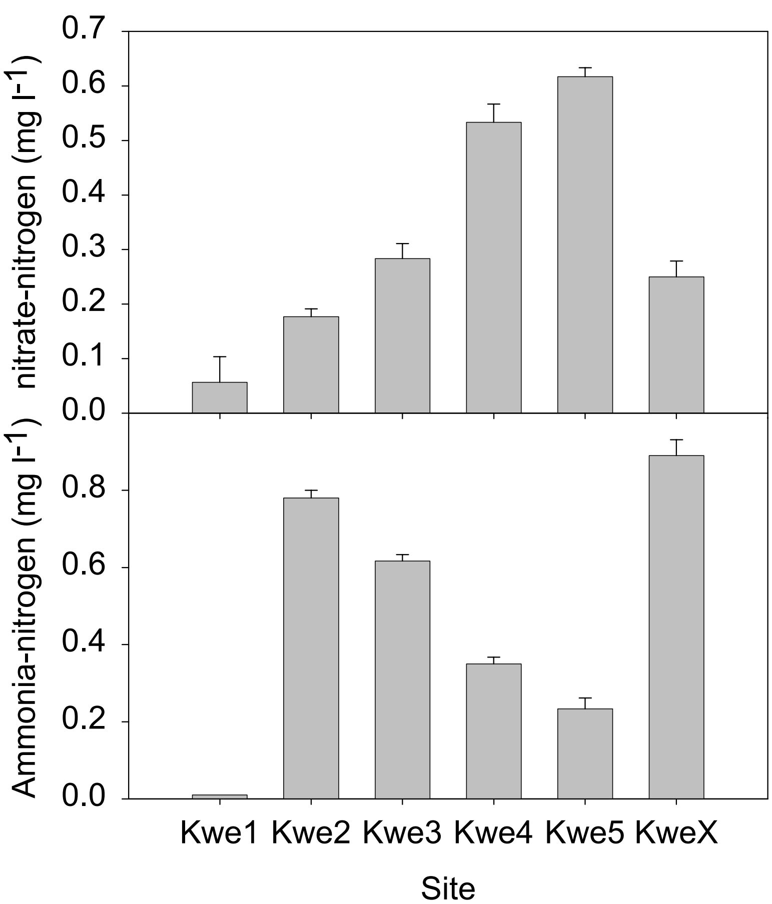

Figure 2. Mean ± (SE) concentrations of ammonia-nitrogen and nitrate-nitrogen in Kwekwe River and effluent (KweX)

The mean TDS and conductivity decreases with increase in distance from Kwe 2 (Figure 3). The mean pH varied slightly downstream of the effluent discharge point.

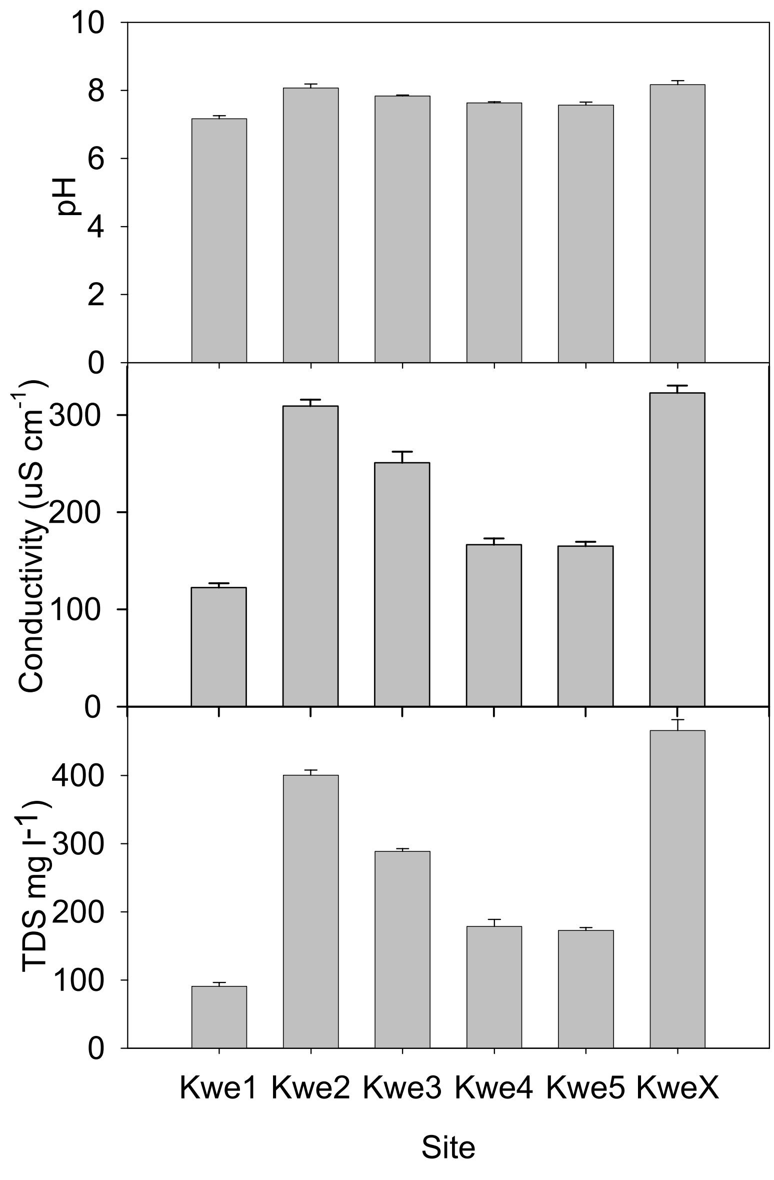

Figure 3. Mean ± (SE) concentrations of ammonia-nitrogen and nitrate-nitrogen

The mean concentrations of sulphate were very low and decreases downstream of Kwe2. The mean concentrations of total phosphorus decrease with increase in distance from Kwe 2 (Figure 4). Highest mean levels of sulphate and total phosphorus were recorded for the industrial effluent, Kwe X.

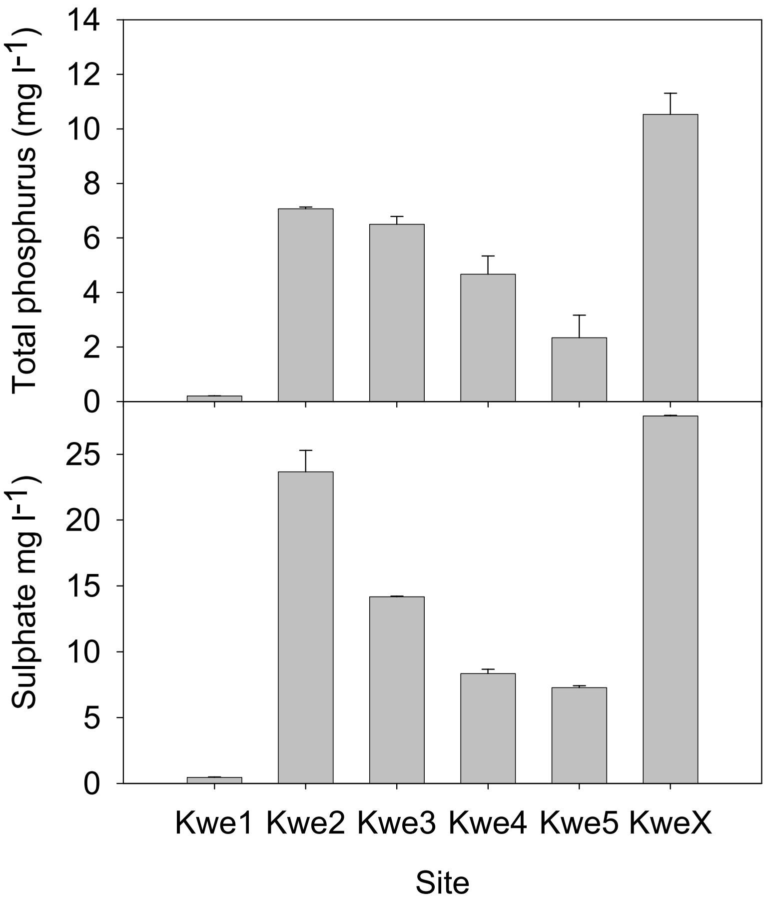

Figure 4. Mean ± (SE) concentrations of sulphates and total phosphorus in Kwekwe River and industrial effluent (KweX)

The mean concentrations of calcium and chromium ions decreases upstream of Kwe 2 and increases sharply at Kwe3. However, the concentrations decreases with increase in distance from Kwe2 (Figure 5).

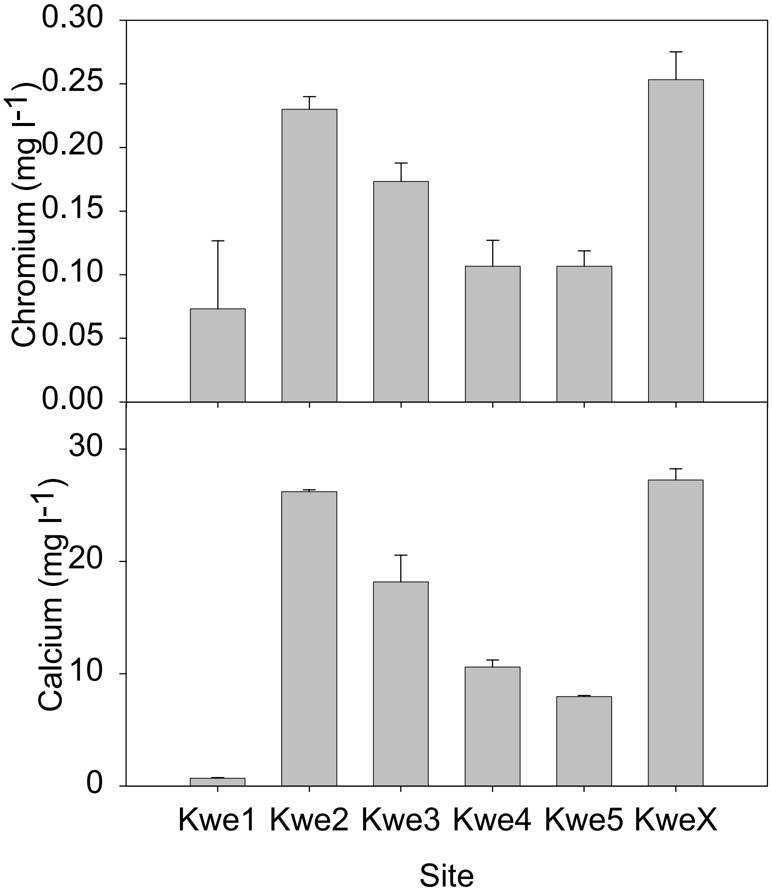

Figure 5. Mean ± (SE) concentrations of calcium and chromium in Kwekwe River, also shown is the level of these heavy metals in the effluent (KweX)

The mean levels of iron and manganese decreased gradually downstream of Kwe 2 (Figure 6). Low levels of iron and manganese were detected upstream of Kwe 2.

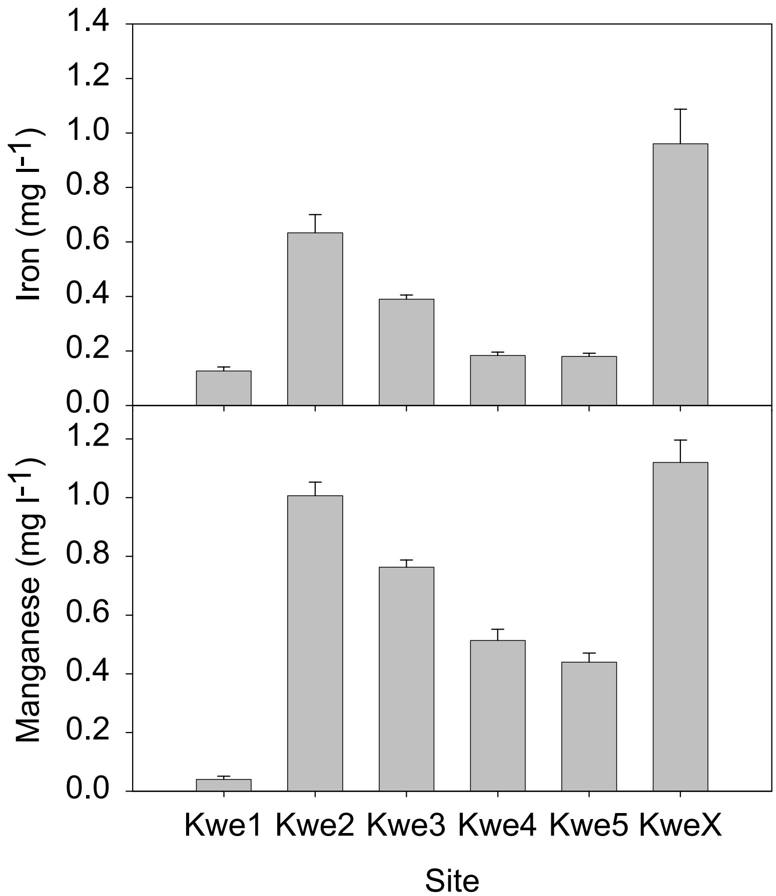

Figure 6. Mean ± (SE) concentrations of iron and manganese in Kwekwe Rive industrial effluent (KweX)

The calculated discharge rate at each of the five sites showed no pattern, with site Kwe 4 having the highest mean discharge rate (Figure 7). The highest mean velocity was recorded at the upstream site, Kwe 1, after which it decreases gradually downstream of the river. Chemical Oxygen demand (COD) changed markedly downstream of the discharge point ($p<0.05$). Dissolved Oxygen increased with increase from the discharge point (Figure 8). There was slight variation between sites in the mean temperature levels.

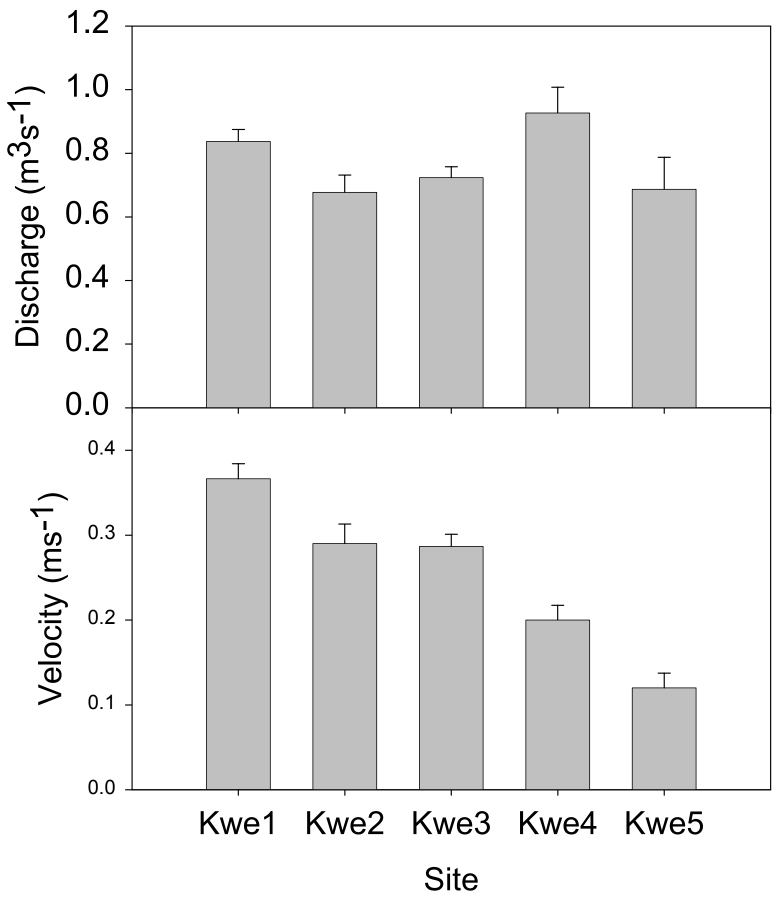

Figure 7. Mean ± (SE) velocity and discharge of 5 sites along Kwekwe River

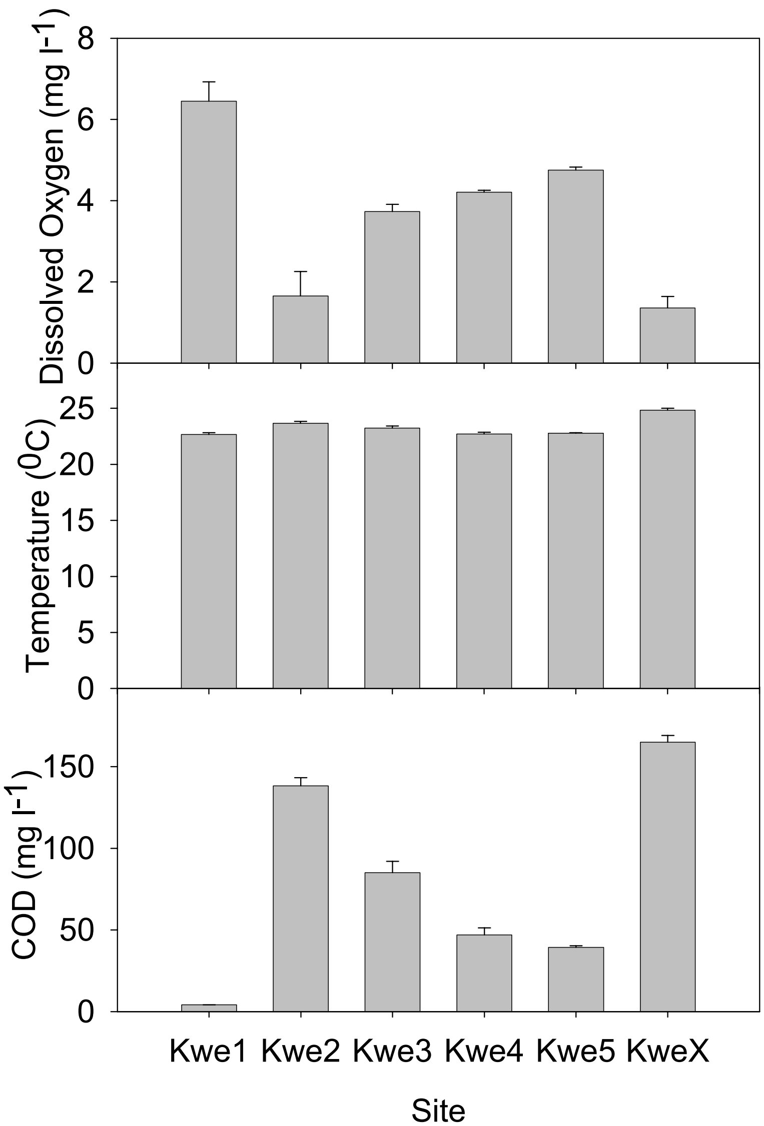

Figure 8. Mean ± (SE) chemical oxygen demand (COD), temperature and dissolved oxygen demand along Kwekwe River and for the discharged effluent (KweX)

Table 4 shows that the difference in the mean levels of water quality variables between the sites was significant ($p<0.05$), as indicated by the p values, with the exception of discharge ($p=0.1$).

Table 4. One-way analysis of variance for water quality variables in Kwekwe River

Variable	F	P
pH	17.38	0
temperature	8	0.004
conductivity*	97.51	0
DO	23.85	0
COD	141.33	0
NH-N	261.13	0
Cr	5.34	0.015
Ca	78.58	0
Fe*	7.61	0.004
Mn	125.21	0
SO4	133.43	0
NO3	61.88	0
tot.PO4	33.83	0
TDS	311.76	0
velocity	27.12	0
discharge	2.61	0.1

* $\log_{10}(x + 1)$ transformed, ** not significant.

Two clusters were obtained, A and B, as shown in the Dendrogram (Figure 9). The clusters were identified at the linkage level of approximately 63%. Group A consists of Kwe 2 (point of effluent discharge) and Kwe 3 (800m from Kwe 2) and group B consists of Kwe 1 (reference site), Kwe4 and Kwe 5 (12 and 15 km, respectively, from Kwe 2).

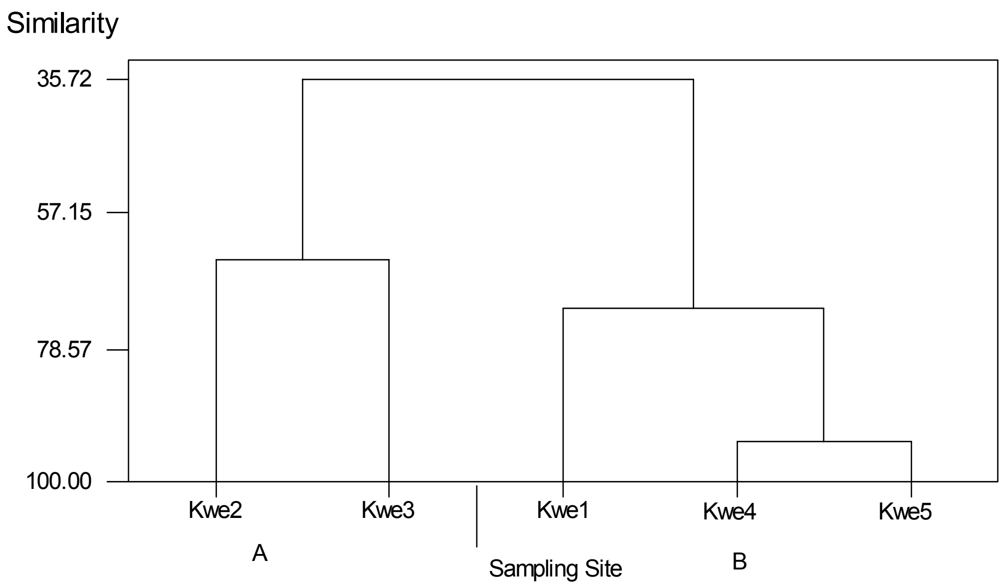

Figure 9. Dendrogram results of hierarchical average linkage cluster analysis of the water quality variables' mean values for each site

Mean levels of cations in sediments and bank soils decreased with increase in distance from the discharge point, as shown in Table 5 and 6. At site Kwe 1, levels of the cations were higher in the bank soils than in sediments, in contrast to sites downstream of the discharge point where higher levels were observed in sediments than in bank soils. The sites varied greatly ($p<0.05$) with respect to heavy metal levels in sediment and bank soils (Table 7).

Table 5. Mean ± (SE) of chromium, cadmium, calcium, iron, lead, and manganese Concentrations (mg l^{-1}) in river sediments

Site Variable	Kwe1	Kwe2	Kwe3	Kwe4	Kwe5
Fe	18.50 ± 5.0	36.50 ± 6.50	40.75±7.50	27.50 ± 5.00	18.00 ± 4.50
Cr	1.85 ± 1	8.35 ± 0.40	9.25 ± 0.75	7.80 ± 0	6.1 ± 1
Cd	0.05 ± 0.4	0.09 ± 0.5	0.08 ± 0.4	0.06 ± 0.1	0.04 ± 0.2
Ca	8 ± 0	59.25 ± 0.25	70.5 ± 2.5	45 ± 2	30 ± 1
Pb	0.2 ± 0	4.15 ± 0.35	1.23 ± 0.38	1.5 ± 1	1 ± 0
Mn	32 ± 3	63.5 ± 3.5	73.5 ± 2.5	83 ± 0	80.5 ± 0.5
Zn	0.13 ± 0.08	19.5 ± 2.5	2.25 ± 0.75	0.28 ± 0.3	0.3 ± 0

Table 6. Mean ± (SE) of chromium, cadmium, calcium, iron, lead, and manganese concentrations (mg l^{-1}) in bank soils

Site Variable	Kwe1	Kwe2	Kwe3	Kwe4	Kwe5
Fe	21.00 ± 2.00	48.00 ± 1.00	37.50±2.50	15.15 ± 1.50	8.75 ± 2.50
Cr	2.48 ± 0.75	8.83 ± 0.40	8.18 ± 0.75	6.60 ± 0.70	5.40 ± 0
Cd	0.04 ± 0.45	0.08 ± 0.40	0.079 ± 0.35	0.04 ± 0.30	0.04 ± 0.25
Ca	13 ± 0	69.75 ±1.75	62 ± 2.00	34 ± 3.00	20.25 ± 2.75
Pb	1 ± 0	8.25 ± 0.75	2.9 ± 0.30	3.85 ± 0.15	6.25 ± 0.75
Mn	35.5 ± 1.5	112 ± 3	96.5 ± 1.50	93.5 ± 3.00	93 ± 3.00
Zn	0.03 ± 0	6.75 ± 1.75	0.83 ± 0.13	0.08 ± 0.01	0.08 ± 0.00

Table 7. One-way analysis of variance for heavy metal concentrations in river sediments and bank soils collected from each site

Variable	F		P	
	Sediments	Bank soils	Sediments	Bank soils
Chromium	169.72	169.72	0.000	0.000
Cadmium	42.32	42.32	0.000	0.000
Calcium	267.10	267.10	0.000	0.000
Iron	120.65	120.65	0.000	0.000
Lead	8.88	8.88	0.017	0.017
Manganese	77.32	77.32	0.000	0.000
Zinc*	8.4	52.19	0.078	0.000

NH_3-N was the most accumulated variable downstream of the industrial effluent (Table 8). The amounts of self-purification (Table 9) were measured between two sampling sites, namely Kwe 2 (point of effluent discharge) and Kwe 5 (11.46 Km downstream of Kwe 2). The river had the highest amount of self-purification with respect to TDS and lowest for chromium. Iron was the most accumulated metal in the river sediments downstream of the effluent discharge point (Table 10).

Table 8. Accumulation factors (AF) of the selected variables in the water-column phase

Variables	Accumulation Factor
Ammonia-nitrogen	40.00
Chromium	1.86
Calcium	17.49
Iron	1.92
Manganese	14.25
Sulphate	21.19
Total phosphate	22.50
Nitrate-nitrogen	8.00
Total dissolved salts	2.35

Table 9. Self-purification amounts (mg $l^{-1}km^{-1}$) of the river with respect to selected water Variables

Variable	S_m (mg $l^{-1}km^{-1}$)
NH_3-N	0.04
Cr	0.01
Ca	1.23
Fe	0.03
Mn	0.04
tot. PO^{-3}_4	0.32
SO^{-2}_4	1.10
$NO^{-2}3$	0.01
TDS	16.60

Table 10. Accumulation factors (AF) of the selected heavy metals in the sediments of Kwekwe River

Variable	AF
Chromium (Cr)	4.16
Cadmium (Cd)	1.31
Calcium (Ca)	6.06
Iron (Fe)	7.77
Lead (Pb)	6.2
Manganese (Mn)	2.47
Zinc (Zn)	7.52

4.2 Benthic macroinvertebrates composition and distribution, upstream and Downstream of effluent discharge point

Macroinvertebrate identifications revealed the presence of 18 taxa from 4 sampling sites; no organisms were collected from the point of effluent discharge, Kwe 2 (Table 11). The downstream sites were dominated by the pollution tolerant taxa, Chironomidae (Table 12). Taxa of the order Ephemeroptera and Trichoptera were present at the upstream of discharge point but virtually disappeared at the point of discharge with only one of the five taxa, Baetidae resurfacing further downstream at site Kwe 4 and Kwe 5.There were no benthic macroinvertebrate fauna immediately after the effluent discharge point, with only pollution tolerant taxa appearing at site Kwe 3 and a gradual increase in the number of taxa was noted, with some organisms observed at the reference site, Kwe 1, resurfacing at site Kwe 4 and Kwe 5.

Table 11. Benthic macroinvertebrates composition and distribution at 5 sampling sites along Kwekwe River, presence (1)/ absence (0) data

Family	Kwe1	Kwe2	Kwe3	Kwe4	Kwe5
Baetidae	1	0	0	1	1
Belostomatide	0	0	0	0	1
Caenidae	1	0	0	0	0
Chironomidae	1	0	1	1	1
Corduliidae	1	0	0	0	0
Corixidae	0	0	1	1	1
Ecnomidae	1	0	0	0	0
Hirudinea	1	0	0	1	1
Hydropsychidae	1	0	0	0	0
Leptophlebiidae	1	0	0	0	0
Melaniidae	1	0	0	0	1
Notonectidae	1	0	0	1	1
Oligochaeta	1	0	0	1	1
Simuliidae	1	0	0	1	1
Potamonatiudae	1	0	1	1	1
Tabanidae	1	0	0	1	1
Tipulidae	1	0	0	0	0
Veliidae	1	0	0	0	0

Table 12. The relative percentage abundance of benthic fauna at 5 sampling sites along Kwekwe River

Order	Family	Sampling Sites				
		Kwe1	**Kwe2**	**Kwe3**	**Kwe4**	**Kwe5**
Annelida	Hirudinea	1.53	0	0	0.08	0.20
	Oligochaeta	1.22	0	0	0.93	0.27
Decapoda	Crab	3.98	0	0.16	0.42	0.37
Diptera	Chironomidae	17.68	0	99.77	94.55	94.16
	Simuliidae	7.34	0	0	2.28	2.60
	Tabanidae	1.53	0	0	0.25	0.13
	Tipulidae	0.92	0	0	0	0
Ephemeroptera	Baetidae	41.28	0	0	0.84	0.87
	Caenidae	14.37	0	0	0	0
	Leptophlebiidae	4.59	0	0	0	0
Hemiptera	Belostomatidae	0.61	0	0	0	0.10
	Corixidae	0.00	0	0.08	0.25	0.37
	Notonectidae	0.92	0	0	0.38	0.87
	Veliidae	1.22	0	0	0	0
Mollusca	Melaniidae	0.31	0	0	0	0.07
Odonata	Corduliidae	0.92	0	0	0	0
Trichoptera	Economidae	0.61	0	0	0	0
	Hydropsychidae	0.92	0	0	0	0

More families were collected from the upstream site than the downstream site and no organisms were collected from the discharge point, Kwe 2 (Figure 10). There was however, a gradual increase in the number of families downstream of Kwe 2, but mainly of pollution tolerant taxa.

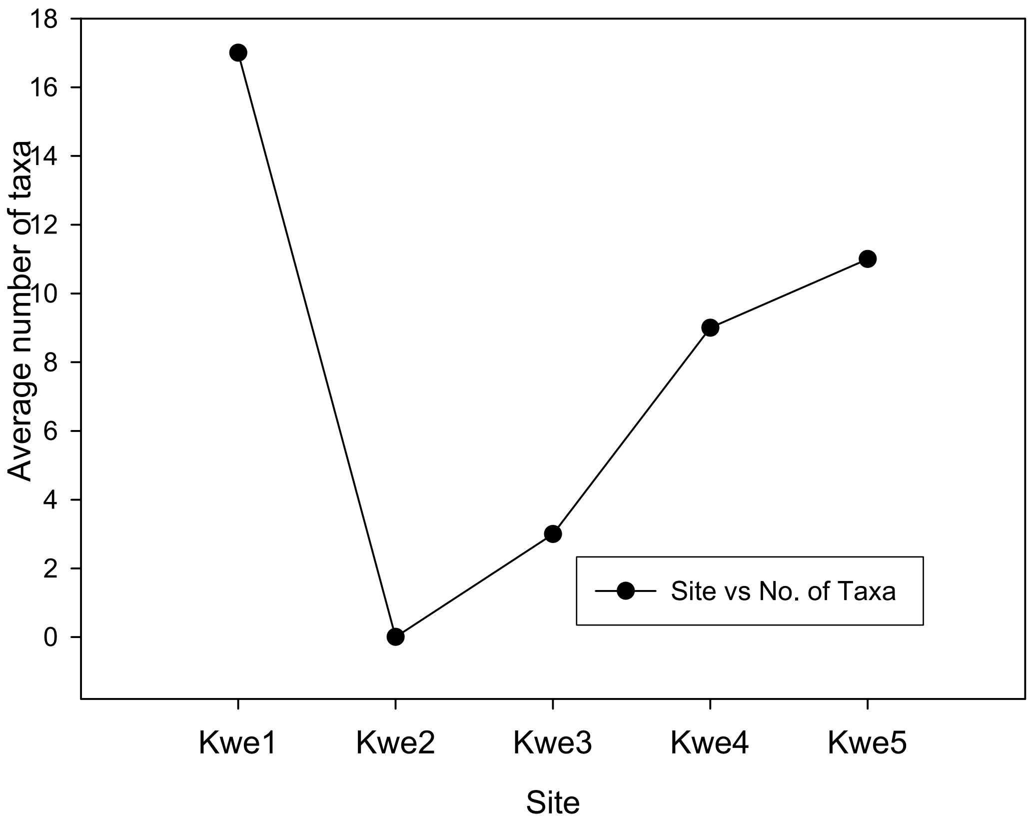

Figure 10. Taxa richness at 5 sampling sites along Kwekwe River

The highest number of benthic organisms was collected from downstream of the effluent discharge point (Figure 11). The organisms collected from downstream were largely dominated by pollution tolerant benthic fauna, whilst at the reference site, the few oraganisms collected were of mixed taxa.

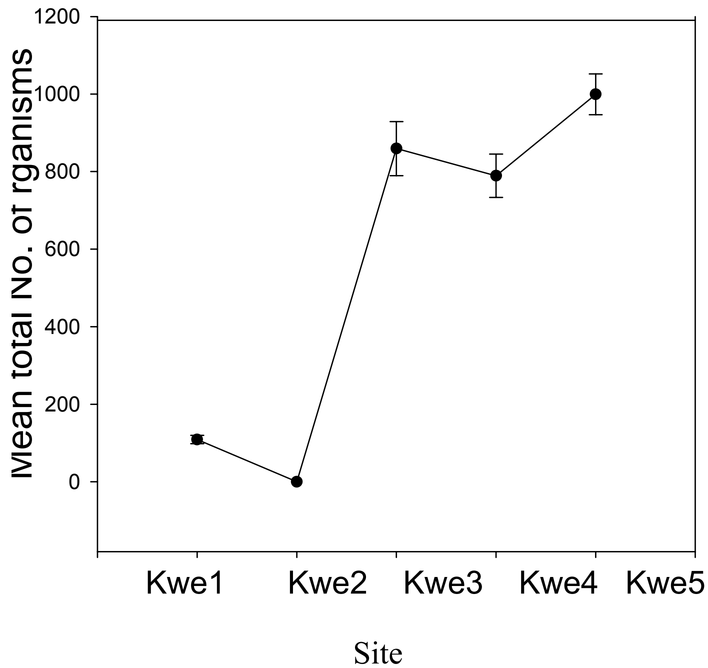

Figure 11. Mean ± (SE) number of organisms collected from sites along Kwekwe River

4.3 Water Quality in Kwekwe River Based on the SASS4

The habitat score assessment suggests that the site did not differ much with respect to the biotope substrates sampled (Table 13). The mean SASS4 and ASPT score generally suggests that the water in Kwekwe River is of poor quality. The mean SASS4 and ASPT scores declined to zero at the point of discharge (Figure 12).

Table 13. Classification of water in Kwekwe River based on South African Scoring System Version 4 (SASS4), the condition of the water and habitat is shown in in brackets

Site	Habitat score (habitat quality)	Mean SASS4 score (water quality)	Mean ASPT score (water quality)
Kwe1	75 (fair)	68.33 (fair)	4.99 (fair)
Kwe2	80 (good)	0 (very poor)	0 (very poor)
Kwe3	80 (good)	6.0 (very poor)	2.45 (very poor)
Kwe4	75 (fair)	27 (very poor)	3.24 (fair)
Kwe5	80 (good)	31.67 (poor)	3.17 (fair).

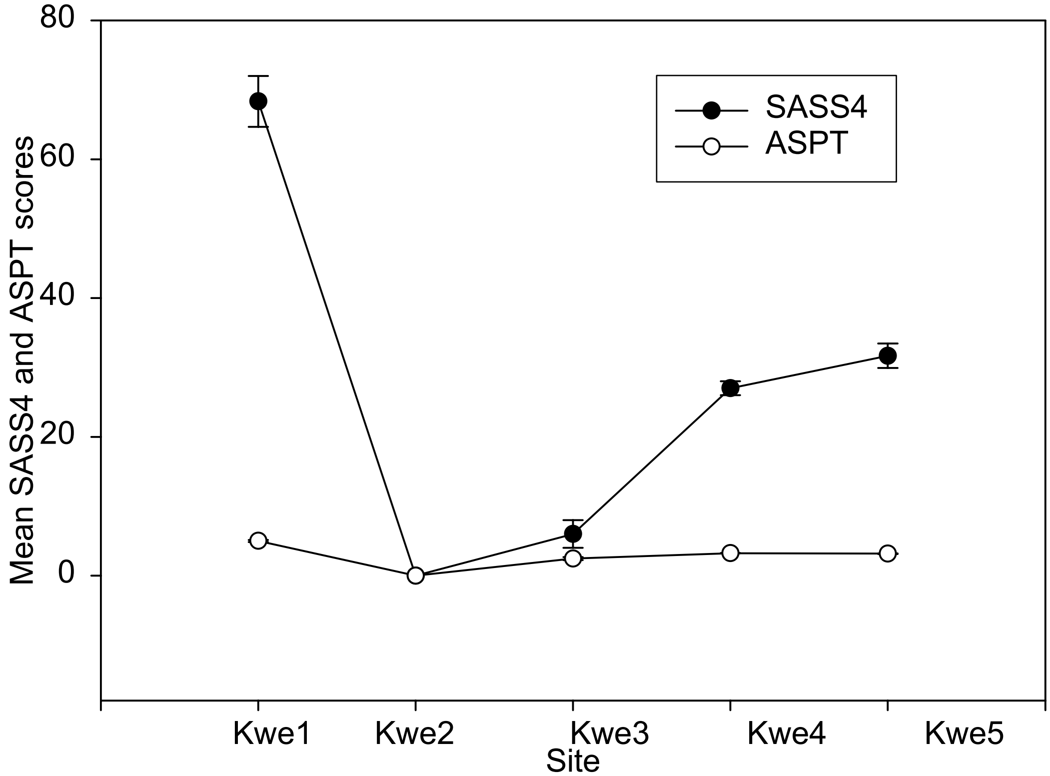

Figure 12. The mean ± (SE) SASS4 and ASPT scores of benthic macroinvertebrates collected from sites along Kwekwe River

4.3 Water Quality in Kwekwe River Based on Diversity Indices

The mean Shannon index varied between 0 and 1.79 (Figure 13). The mean Simpson's index varied between 0 and 0.75. There was significant variation in the mean levels of the metric indices (Table 14) between the sampling sites ($p < 0.05$).

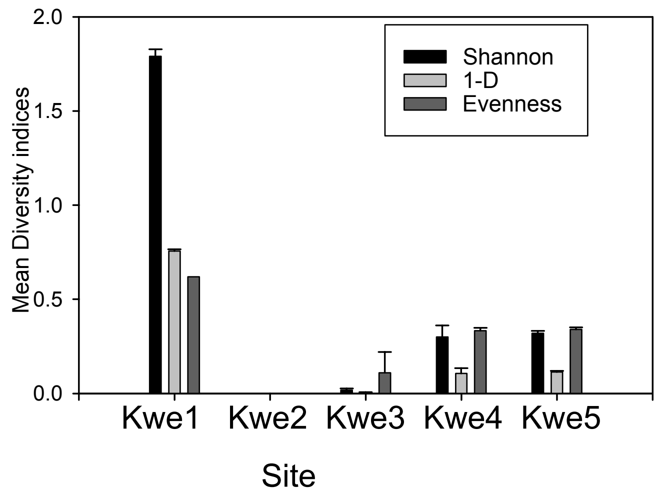

Figure 13. Mean ± (SE) of Shannon (H^1), Simpson's index of diversity (1-D) and Evenness (E) for benthic fauna at 5 sites along Kwekwe River

Table 14. One-way analysis of variance ($p<0.05$) for metric indices between sampling sites

Indices	P
% EPT**	0.000
% Tolerant **	0.914*
% Moderately tolerant**	0.943*
% Intolerant**	0.699*

* not significant ** arcsine transformed for the analysis.

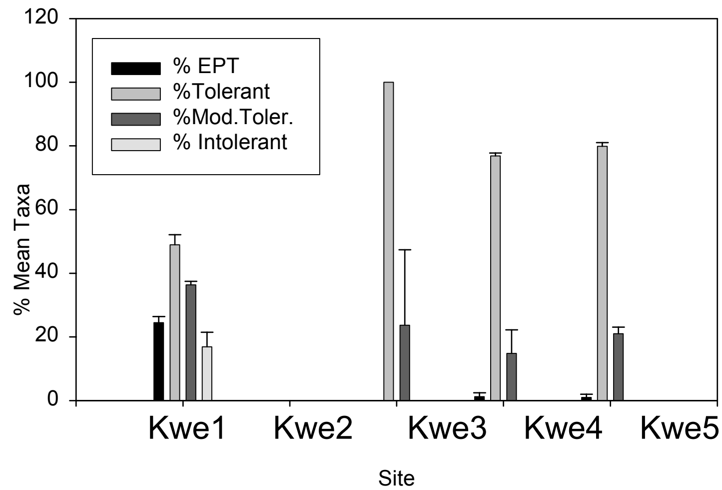

Figure 14. The % EPT, % intolerant, % moderately tolerant and the % tolerant taxa of benthic macroinvertebrate communities collected from sites along Kwekwe River

Table 15. Mean ± (SE) concentrations of cations in *Phragmites australis* leaves collected from each sampling site

Site Variable	Kwe1	Kwe2	Kwe3	Kwe4	Kwe5
Fe	352.5 ± 19.5	727.5 ± 26.5	729.5 ± 15.5	572.5 ± 19.5	52.0 ± 10.0
Cr	40.25 ± 1.25	108.25 ± 6.75	98.0 ± 1.0	87.25 ± 4.25	79.75 ± 0.75
Cd	7.5 ± 1.0	19.0 ± 0.0	20.25 ± 1.25	17.75 ± 2.75	18.0 ± 1.02
Ca	2.1 ± 0.6	11.25 ± 0.25	7.8 ± 0.5	6.8 ± 0.3	3.0 ± 1.0
Pb	14.25 ± 2.25	74.75 ± 4.75	69.0 ± 3.0	57.25 ± 5.75	43.0 ± 6.0
Mn	55.5 ± 2.50	88.5 ± 2.5	81.25 ± 5.25	65.0 ± 4.5	60.5 ± 2.5
Zn	12.0 ± 1.0	37.0 ± 6.0	39.75 ± 1.25	31.25 ± 6.25	17.0 ± 0.0

Table 16. Mean ± (SE) concentrations of cations in *Phragmites australis* rhizomes collected from each sampling site

Site Variable	Kwe1	Kwe2	Kwe3	Kwe4	Kwe5
Fe	352.5 ± 2.5	533.0 ± 46.0	496.5 ± 6.5	403.5 ± 8.0	394.0 ± 6.0
Cr	47.25 ± 4.25	123.5 ± 4.0	106.0 ± 7.0	91.75 ± 1.75	83.25 ± 1.75
Cd	11.25 ± 1.25	23.5 ± 0.5	23.75 ± 1.25	21.00 ± 1.50	21.00 ± 0.00
Ca	3.6 ± 1.1	13.25 ± 1.75	10.15 ± 1.1	8.25 ± 0.75	3.0 ± 1.00
Pb	12.25 ± 2.75	79.75 ± 1.75	81.75 ± 1.25	75.25 ± 3.75	50.0 ± 9.00
Mn	58.5 ±3.0	97.75 ± 4.25	92.25 ± 4.25	73.0 ± 3.0	67.25 ± 1.75
Zn	13.75 ± 2.25	44.0 ± 1.0	42.25 ± 0.25	36.25 ± 3.0	31.5 ± 4.5

Table 17. One-way analysis of variance for metal concentrations in *Phragmites australis* leaves and rhizomes collected from each sampling sites

Variable	F		P	
	Leaves	Rhizomes	Leaves	Rhizomes
Chromium	50.9	45.60	0.000	0.000
Cadmium	11.81	23.29	0.009	0.002
Calcium	39.34	13.27	0.001	0.007
Iron	68.99	12.64	0.000	0.008
Lead	27.67	40.51	0.001	0.001
Manganese	14.91	24.77	0.005	0.002
Zinc	9.24	20.84	0.014	0.003

5. DISCUSSION

5.1 Water quality in Kwekwe River based on water and sediment chemistry

It was evident from the study that water quality in the river was severely impaired by the effluent discharged at site Kwe2 by a Kwekwe-based iron and steel manufacturing company. The sharp decrease in dissolved oxygen, increases in total dissolved solids and a corresponding increase in conductivity between the reference site, Kwe1 and Kwe2, (Figure 4) and is all suggestive of degraded water. The low oxygen demand detected in the effluent corresponded to an increase in chemical oxygen demand. The sharp decrease in dissolved oxygen between Kwe1 and Kwe2, (Figure 8) suggests the introduction of organic loads into the river, which required high levels of oxygen for chemical oxidation. The formation of ferric hydroxide, for example, decreases oxygen availability and may result in a complete blanketing of a stream bottom (Magadza and Masendu, 1986; Hoehn and Sizemore, 1977).

The mean water temperature levels ranging between 22.6^{o}C and 23.7 ^{o}C (Figure 8) were consistent with permissible limits set for Zimbabwe's raw water (Government of Zimbabwe, 2000). The highest mean temperature of 24.8^{o}C was recorded for the effluent. This may be attributed to exothermic reactions taking place between the ionic species. The mean values of sulphates, nitrate-nitrogen and conductivity were below the maximum prescribed limits for Zimbabwe's raw water (Table 1). The levels of sulphates were lower than obtained by Moyo *et al.,*(1998). This may be attributed to the co-precipitation of sulphates with metal ions. The mean values of water quality variables at site Kwe1 were all below the maximum prescribed limits set for Zimbabwe's raw water, further suggesting that the river was slightly disturbed at this site.

The mean pH levels measured at sites downstream of the effluent discharge point varied between 7.6 and 7.8 (Figure 3) and were highest at the discharge point, Kwe2. The mean pH values are typical of tropical rivers (Moyo and Worster, 1997). Mean conductivity levels at site Kwe2 and Kwe3 were above the maximum prescribed limits for Zimbabwe's raw water (Table 2) and was highest for the effluent (Figure 3). The sharp increase in conductivity between site Kwe1 and Kwe2 corresponded to the observed increase in total dissolved solids (Figure 3). Conductivity is proportional to the ionic concentration, which is a result of the dissolved solids. The higher reading at Kwe2 was probably due to the effluent and the decrease downstream may be a sign that ions are precipitating out settling on the riverbed or being absorbed by aquatic plants.

The gradual decrease in total dissolved solids after site Kwe3 and the corresponding decrease in conductivity may be attributed to the salting-out of the dissolved salts from the water-column phase and the subsequent settling at the riverbed. The reference site, Kwe1 was shown to be significantly ($p<0.05$) different from sites downstream of the effluent discharge point (Appendix A). The presence of the cations and anions in water at Kwe1 may be attributed to natural phenomena such as weathering of rocks and soils, and not to anthropogenic activities. The degree of contamination as a result of effluent discharge was estimated by the accumulation factor (AF), which is the ratio of the average level of a given variable downstream after the point of effluent discharge to the corresponding average level upstream (Fakayode, 2005). Ammonia-nitrogen was the most accumulated variable downstream, in the water-column phase, with an accumulation factor of 40 (Table 8) and iron was the most accumulated variable in the sediments, with an accumulation factor of 7.77 (Table 10). The calculated accumulation factors provide further evidence that the effluent was impacting heavily on the water quality of the river.

The mean levels of manganese, chromium, ammonia-nitrogen, total phosphates, total dissolved solids and chemical oxygen demand were above the maximum prescribed limits for Zimbabwe's raw water (Table 1). Iron concentrations at the discharge point, Kwe2 and site Kwe3, about 0.46km from Kwe2, were above the maximum permissible limits for Zimbabwe's raw water. These levels, however, declined downstream at site Kwe4 and Kwe5 to 0.18mg l^{-1}. The sharp increase of iron, manganese, calcium, chromium, ammonia-nitrogen, sulphates and total phosphates between Kwe1 and Kwe2 implied significant discharge into the river of effluent containing these cations and ions.

The decrease of the cations and anions observed downstream of the effluent discharge point may be attributed to precipitation and co-precipitation of these ionic species. The results of the study are consistent with Schmitz (1996) observation that heavy metal solubility decreases at high pH. According to Kelly (1988 cited by Ravengai *et al.,* 2005), dissolved cations may co-precipitate when ferric hydroxide flocs form. The decrease in iron concentrations at site Kwe4 and Kwe5, therefore, may be attributed to its co-precipitation with reactive soluble phosphorus (Maine *et al.,* 2004). According to Jackson

(1958, cited by Machena, 1997), heavy metals and phosphate complex with each other to form insoluble precipitates. The high levels of cations and anions recorded for site Kwe2 were not consistent with the high pH levels measured at this site. This is so, for at high pH, iron is expected to precipitate (Maine *et al.,* 2004). The high levels of cations at Kwe2 were probably due to the fact that the elements were in suspension when the water samples were collected for analyses.

The levels of manganese decreased slightly downstream of the discharge point (Figure 6). This is consistent with the observations of Hoehn and Sizemore (1977) that manganese precipitates at pH above 10. Manganese, can, therefore, be carried for long distances downstream of a source. The reduction in ammonia-nitrogen concentrations (Figure 2) at Kwe4 and Kwe5 may be explained by the observed increase in dissolved oxygen. In the presence of oxygen, ammonia is oxidised to nitrate ions. This may also explain the observed increase in nitrate ions downstream of the effluent discharge point. The reduction of ammonia downstream of the effluent discharge point may also be attributed to the fact that at high pH, most ammonia will be in gaseous state, therefore, the gas volatilises as the river flows (Goering, 1972, cited by Machena, 1997).

Zinc, cadmium and lead were not detected in the water column phase, but were detected in the sediments (Table 5). This may be explained by the fact that these elements were present at very low levels below the detection limit of spectrophotometer. Zinc salts have low solubility (Allen and Minear, 1983). This further explains why Zn was absent in the water column phase but present in the sediments. The higher levels of chromium, cadmium, calcium, iron, lead, manganese and zinc in bank soils than in the river sediments at Kwe1, suggests that the elements were mobilised into solution. The concentrations of the cations were higher in the sediments than in bank soils at sites downstream of the discharge point. This suggests that the cations were not mobilised into water-column phase. Sediments have been described as ready sink or reservoir of pollutants (Awofolu *et al.2005*). High chromium and calcium levels were recorded for sites downstream of the effluent discharge point (Figure 5), in contrast with the low levels at Kwe1, suggesting possible water contamination downstream.

Hierarchical cluster analysis using average linkage method on mean values of water quality variables (Figure 9) indicated that the discharge point, Kwe2, was similar to site Kwe3. The analysis, however, failed to separate the reference site, Kwe1, from Kwe4 and Kwe5, suggesting that the three sites were similar. The calculated amounts of self-purification (Table 9), together with high levels of cations in the sediments, suggest that the river has high self-purification capacity.

The study did not include other potentially important variables observed at the sites such as total suspension solids, grease and oil. The variables analysed, however, reflect the status of river health degradation by the Kwekwe-based iron and steel manufacturing company.

5.2 Heavy metal concentrations in leaves and rhizomes of *Phragmites australis*

High mean levels of cations in plant tissues (Table 15 and 16) were recorded for plants collected from downstream of the discharge point, providing further evidence that the water downstream was polluted. The concentrations of cations in ***Phragmites australis*** tissues were shown to be significantly ($p<0.05$) different between the sampling sites. Riparian vegetation zone serves as a buffer to pollutants entering an aquatic ecosystem by accumulating the cations in their tissues.

5.3 Benthic macroinvertebrates composition and distribution, upstream and downstream of the effluent discharge point

Changes in water quality are reflected by changes in the biota (Sues, 1982). However, the structure and distribution of benthic fauna may be influenced by other factors other than water quality. The factors include: current stream velocity, vegetation (Sues, 1982), season (Gratwicke, 1999; Cowell *et al.,* 2004; Dallas, 2004b), habitat availability (Armitage and Pardo, 1995; Artmitage *et al.,* 1995 cited by Dallas 2004b). Dallas (2004b) cited some studies showing distinct seasonal effects and others showing fewer effects. The absence of some taxa in Kwekwe River may be attributed to the effect of season since the study was conducted for one season. The short duration of the study did not allow for any understanding of seasonal variability. It makes the results of the study comparable though, as both sites were examined at the same period.

The sites downstream of the effluent discharge point generally showed low family diversity (Figure 13), and were dominated by Chironomidae (Table 12). The dragonfly larvae of the family Corduliidae (Table 11) were limited to the reference site, Kwe1 and there was a complete disappearance of macroinvertebrate at the point of effluent discharge, Kwe2. Results further suggest possible disturbance or pollution of the river water downstream of the discharge point. According to O' Toole (1995), Corduliidae larvae require oxygen for their survival. This may explain the absence of the larvae downstream of the discharge point. The decrease in the number of taxa observed between Kwe1 and sites downstream of the discharge point is consistent with Resh and Grodhaus (1983) observation that total number of taxa generally decreases as a stream is polluted or disturbed. The observed increase in the number of individual organisms (Figure 11), and low number of families (Figure 10), downstream was consistent with Connell's (1978) explanation that most disturbed areas have high densities and low number of taxa due to low interspecific competition.

Winner *et al.,* (1980), found that Chironomidae larvae dominated macroinvertebrate communities of site heavily polluted by heavy metals. Pollution tolerant species such as *C. perenguei* have haemoglobin, which binds oxygen and allows them to thrive under anoxic environments and can tolerate as low as 20% dissolved oxygen. The decrease in dissolved oxygen observed downstream may explain the dominance of Chironomidae and the absence of other benthic organisms. Chutter (1994), also observed that domination of taxa by single taxon instead of a more even distribution indicate possible perturbation or pollution.

Death (2002) showed a positive correlation between primary productivity and the number of benthic fauna. However, no floating macrophytes were observed at any of the sites during the study period to suggest the presence of elevated nutrient levels downstream. The presence of large number of individual organisms downstream, therefore, could be attributed to disturbance (Connell, 1978) of the aquatic ecosystem. According to Rossillon (1989), catastrophic and unpredictable fluctuations of abiotic factors provoke perturbation in stream invertebrate communities. Different taxa, however, respond differently to disturbance resulting in some organisms being tolerant, moderately tolerant or sensitive to the perturbation.

Mean Evenness, Shannon and Simpson's indices of diversity were much higher for Kwe1 than sites at the downstream of the discharge point (Figure 13), suggesting that Kwe1 was relatively undisturbed. The diversity indices, therefore, suggests that the water in the river is polluted. The mean percentage metric indices, namely, percentage tolerant taxa, percentage tolerant Ephemeroptera, Plecoptera and Trichoptera (Figure 14), suggests that the water downstream of effluent discharge point was polluted. Ephemeroptera and Trichoptera taxa disappeared downstream of the effluent discharge point, with only organisms from the family, Baetidae, resurfacing, suggesting some signs of recovery. The decrease in SASS4 and ASPT scores between Kwe1 and Kwee3 (Figure 12) may be attributed to the observed decrease in dissolved oxygen (Figure 8). The decrease in dissolved oxygen may result in few organisms surviving in a given aquatic environment because very few taxa tolerate anoxic conditions, hence the observed lower SASS4 score at sites downstream of the discharge point.

Increase in mean SASS4 score after the effluent discharge point indicates some sign of recovery. The mean SASS4 and ASPT scores indicated Kwe1 as having fair water quality and Kwe2 and Kwe3 as having very poor water quality. The mean SASS4 and ASPT gave different results for site Kwe4 and Kwe5, whereas the mean SASS4 indicated the water at these two sites as of poor quality, the mean ASPT indicated the water as of fair quality. ASPT score gives the average pollution tolerance, of the macroinvertebrate present. The results are consistent with Lenat (1993) observation that different species of the same family may respond differently to disturbance, resulting in the variation between biotic indices.

The findings of the study are consistent with other research studies in which anthropogenic perturbation has influenced the composition and distribution of benthic fauna in aquatic ecosystems (Phiri, 1998; Magadza and Masendu, 1986; Moyo and Phiri 2002). According to Madikizela and Dye (2003), physico-chemical variables have been found to influence the distribution and composition of the benthic fauna.

6. CONCLUSION

Results of the present study, both water chemistry and biological suggest that water quality of Kwekwe River is polluted by the effluent discharged into the river by a Kwekwe-based iron and steel manufacturing company. The river exhibited poor water quality downstream of the effluent discharge point, the mean SASS4 scores and mean ASPT scores suggest that the water is unfit for the sustenance of aquatic ecosystem. The reference site, Kwe1, was not of high water quality as evidenced by low number of families and the contaminated sediments. River's self-purification capacity over the stretch of the studied area was fairly good. There is need for a continuous assessment of water quality in aquatic ecosystems and environmental laws should be implemented.

The results obtained in the study indicate the need to conduct a detailed study on the management of waste and wastewater at the Kwekwe-based iron and steel manufacturing company. Further research is needed to determine levels of heavy metals in benthic macroinvertebrates, as they are food to aquatic organisms such as fish, which is an important protein source for human beings.

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Appendices

Appendix A. One-way analysis of Variance for water quality variables in Kwekwe River water

Analysis of Variance for pH

```
Source     DF        SS        MS        F        P
Site        4    1.3440    0.3360    17.38    0.000
Error      10    0.1933    0.0193
Total      14    1.5373
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level    N     Mean  StDev  -+---------+---------+---------+-----
1        3  7.1667 0.1528   (----*----)
2        3  8.0667 0.2082                              (----*-----)
3        3  7.8333 0.0577                        (----*----)
4        3  7.6333 0.0577                  (----*----)
5        3  7.5667 0.1528                (----*----)
                            -+---------+---------+---------+-----
Pooled StDev = 0.1390     7.00      7.35      7.70      8.05
```

```
Analysis of Variance for temperature.
Source     DF        SS        MS        F        P
Site        4    2.2627    0.5657     8.00    0.004
Error      10    0.7067    0.0707
Total      14    2.9693
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level    N    Mean  StDev  ----+---------+---------+---------+--
1        3  22.667  0.289  (------*------)
2        3  23.667  0.289                     (------*------)
3        3  23.233  0.321             (------*------)
4        3  22.700  0.265   (------*------)
5        3  22.767  0.115    (------*------)
                             ----+---------+---------+---------+--
Pooled StDev = 0.266           22.50     23.00     23.50     24.00
```

```
Analysis of Variance for Dissolved oxygen
Source     DF        SS        MS        F        P
Site        4    36.189     9.047    23.85    0.000
Error      10     3.793     0.379
```

Total 14 39.982

Appendix A.(cont.)

```
                                 Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level   N    Mean  StDev  ------+---------+---------+---------+
1       3  6.4500 0.8261                        (---*---)
2       3  1.6533 1.0451  (---*---)
3       3  3.7300 0.3132             (---*---)
4       3  4.2100 0.0794               (---*---)
5       3  4.7500 0.1323                  (---*---)
                           ------+---------+---------+---------+
Pooled StDev =   0.6159       2.0       4.0       6.0       8.0
```

Analysis of Variance for Chemical Oxygen Demand

Source	DF	SS	MS	F	P
Site	4	31318.4	7829.6	141.33	0.000
Error	10	554.0	55.4		
Total	14	31872.4			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level   N      Mean  StDev  --+---------+---------+---------+----
1       3    4.17   0.06   (-*-)
2       3  138.33   8.50                              (-*-)
3       3   85.00  12.00                   (-*-)
4       3   46.90   7.64           (-*-)
5       3   39.33   1.53          (-*-)
                           --+---------+---------+---------+----
Pooled StDev = 7.44          0        50       100       150
```

Analysis of Variance for ammonia-nitrogen

Source	DF	SS	MS	F	P
Site	4	1.12111	0.28028	261.13	0.000
Error	10	0.01073	0.00107		
Total	14	1.13184			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean   StDev  --+---------+---------+---------+----
1      3 0.01000 0.00000   (*-)
2      3 0.78000 0.03464                               (*-)
3      3 0.61667 0.02887                        (-*)
4      3 0.35000 0.03000             (-*-)
5      3 0.23333 0.04933         (*-)
                          --+---------+---------+---------+----
Pooled StDev =  0.03276    0.00      0.25      0.50      0.75
```

Appendix A.(cont.)

```
Analysis of Variance for Chromium
Source     DF        SS        MS        F        P
Site        4   0.04757   0.01189     5.34    0.015

Error      10   0.02227   0.00223
Total      14   0.06984
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean   StDev  ---------+---------+---------+-------
1      3 0.07333 0.09238   (------*-------)
2      3 0.23000 0.01732                     (-------*------)
3      3 0.17333 0.02517              (-------*------)
4      3 0.10667 0.03512      (------*-------)
5      3 0.10667 0.02082      (------*-------)
                            ---------+---------+---------+-------
Pooled StDev = 0.04719          0.080     0.160     0.240
```

```
Analysis of Variance for Calcium
Source     DF        SS        MS        F        P
Site        4   1150.42    287.61    78.58    0.000
Error      10     36.60      3.66
Total      14   1187.02

                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N   Mean  StDev  --+---------+---------+---------+----
1      3  0.700  0.087  (--*-)
2      3  26.213  0.295                           (-*--)
3      3  18.167  4.120                   (-*--)
4      3  10.590  1.091           (--*-)
5      3  7.953  0.206         (--*-)
                         --+---------+---------+---------+----
Pooled StDev =    1.913      0        10        20        30
```

```
Analysis of Variance for Manganese
Source     DF        SS        MS        F        P
Site        4   1.58269   0.39567   125.21    0.000
Error      10   0.03160   0.00316
Total      14   1.61429
```

Appendix A.(cont.)

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level    N   Mean  StDev  -+---------+---------+---------+-----
1        3 0.0400 0.0200  (-*-)
2        3 1.0067 0.0802                              (-*-)
3        3 0.7633 0.0416                       (-*-)
4        3 0.5133 0.0666                (-*-)
5        3 0.4400 0.0529              (-*-)
                          -+---------+---------+---------+-----
Pooled StDev =  0.0562        0.00      0.35      0.70      1.05
```

```
Analysis of Variance for Sulphate
Source     DF        SS        MS        F        P
Site        4      906.69    226.67   133.43    0.000
Error    10    16.99    1.70

Total      14    923.68
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N   Mean  StDev  --+---------+---------+---------+----
1      3  0.467  0.029  (--*-)
2      3 23.667  2.843                             (--*-)
3      3 14.167  0.115                  (-*-)
4      3  8.333  0.577          (-*--)
5      3  7.267  0.252         (-*-)
                        --+---------+---------+---------+----
Pooled StDev = 1.303   0.0       8.0      16.0      24.0
```

```
Analysis of Variance for Nitrate-nitrogen
Source     DF        SS        MS        F        P
Site        4     0.67160   0.16790    61.88    0.000
Error      10   0.02713   0.00271
Total    14  0.69873

                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean   StDev  -+---------+---------+---------+-----
1      3 0.05667 0.08083  (---*--)
2      3 0.17667 0.02517        (---*--)
3      3 0.28333 0.04726              (--*---)
4      3 0.53333 0.05774                          (---*--)
5      3 0.61667 0.02887                              (---*--)
                          -+---------+---------+---------+-----
Pooled StDev =0.05209    0.00      0.20      0.40      0.60
```

Appendix A.(cont.)

```
Analysis of Variance for total Phosphorus
Source     DF        SS        MS        F        P
Site        4      99.597    24.899    33.83    0.000
Error    10    7.361    0.736

Total      14   106.958

                                 Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level   N   Mean  StDev  ----+---------+---------+---------+--
1       3 0.2000 0.0173  (----*---)
2       3 7.0667 0.1155                               (---*----)
3       3 6.5000 0.5000                             (---*---)
4       3 4.6667 1.1547                     (----*---)
5       3 2.3333 1.4434           (---*----)
                         ----+---------+---------+---------+--
Pooled StDev = 0.8579      0.0       2.5       5.0       7.5
```

```
Analysis of Variance for Total dissolved salts
Source     DF        SS        MS        F        P
Site        4         173506     43376        311.76     0.000

Error      10      1391       139
Total      14    174897
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level   N   Mean  StDev  ---+---------+---------+---------+---
1       3  90.67    9.87   (*-)
2       3  400.67   12.90                                (*-)
3       3  288.67    7.09                      (-*)
4       3  178.67   18.04            (-*)
5       3  172.67    7.51            (*-)
                         ---+---------+---------+---------+---
Pooled StDev = 11.80      100       200       300       400
```

```
Analysis of Variance for Velocity
Source     DF        SS        MS        F        P
Site        4        0.107760      0.026940        27.12        0.000

Error      10  0.009933  0.000993
Total      14  0.117693
```

Appendix A.(cont.)

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean   StDev  ---+---------+---------+---------+---
1      3 0.36667 0.03055                            (---*---)
2      3 0.29000 0.04000                    (---*---)
3      3 0.28667 0.02517                    (---*---)
4      3 0.20000 0.03000           (---*---)
5      3 0.12000 0.03000   (---*---)
                          ---+---------+---------+---------+---
Pooled StDev = 0.03152    0.10      0.20      0.30      0.40
```

Analysis of Variance for Discharge

Source	DF	SS	MS	F	P
Site	4	0.1405	0.0351	2.61	0.100
Error	10	0.1347	0.0135		
Total	14	0.2752			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+-
1      3  0.8367 0.0666             (---------*---------)
2      3  0.6767 0.0950  (---------*---------)
3      3  0.7233 0.0603     (---------*---------)
4      3  0.9267 0.1401                   (---------*---------)
5      3  0.6867 0.1750   (---------*---------)
                           -----+---------+---------+---------+-
Pooled StDev = 0.1161       0.60      0.75      0.90      1.05
```

Analysis of Variance for conductivity

Source	DF	SS	MS	F	P
Site	4	0.301627	0.075407	97.51	0.000
Error	10	0.007733	0.000773		
Total	14	0.309360			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N   Mean  StDev  ----+---------+---------+---------+--
Kwe1   3 2.0900 0.0300   (-*--)
Kwe2   3 2.4900 0.0173                              (-*-)
Kwe3   3 2.3967 0.0351                       (--*-)
Kwe4   3 2.2233 0.0321            (-*--)
Kwe5   3 2.2200 0.0200            (-*-)
                        ----+---------+---------+---------+--
Pooled StDev = 0.0278    2.10      2.25      2.40      2.55
```

Appendix A.(cont.)

Analysis of Variance for Iron

Source	DF	SS	MS	F	P
Site	4	0.055000	0.013750	52.88	0.000
Error	10	0.002600	0.000260		
Total	14	0.057600			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level  N    Mean   StDev  ------+---------+---------+---------+
Kwe1   3 0.05000 0.01000   (--*---)
Kwe2   3 0.21333 0.02887                             (---*--)
Kwe3   3 0.14333 0.01155                (---*--)
Kwe4   3 0.07333 0.01155       (--*---)
Kwe5   3 0.07000 0.01000      (---*--)
                          ------+---------+---------+---------+
Pooled StDev = 0.01612       0.060     0.120     0.180     0.240
```

Appendix B. One-way analysis of variance for sites with respect to heavy metal levels in river sediments

Analysis of Variance for Zinc

Source	DF	SS	MS	F	P
Site	4	569.39	142.35	52.19	0.000
Error	5	13.64	2.73		
Total	9	583.02			

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level N      Mean    StDev-----+---------+---------+---------+-
Kwe1  2     0.125    0.106  (---*---)
Kwe2  2    19.500    3.536                              (---*---)
Kwe3  2     2.250    1.061     (---*----)
Kwe4  2     0.275    0.035  (---*----)
Kwe5  2     0.300    0.000  (---*----)
                            -----+---------+---------+---------+-

Pooled StDev =1.652             0.0       7.0      14.0      21.0
```

Appendix B. (CONT.)

Analysis of Variance for Chromium

Source	DF	SS	MS	F	P
Site	4	6816.5	1704.1	169.72	0.000
Error	5	50.2	10.0		
Total	9	6866.7			

```
                                   Individual 95% CIs For Mean
                                    Based on Pooled StdDev
Level N      Mean     StdDev -----+---------+---------+---------+-
Kwe1  2    18.500     2.121  (-*--)
Kwe2  2    83.500     2.121                            (-*--)


Kwe3  2    92.050     5.586                                (-*-)
Kwe4  2    78.000     2.828                          (-*--)
Kwe5  2    61.000     1.414                   (-*--)
                             -----+---------+---------+---------+-
Pooled StdDev = 3.169             25        50        75       100
```

Analysis of Variance for Cadmium

Source	DF	SS	MS	F	P
Site	4	41.984	10.496	42.32	0.000
Error	5	1.240	0.248		
Total	9	43.224			

```
                                    Individual 95% CIs for Mean
                                    Based on Pooled StdDev
Level N      Mean     StdDev ------+---------+---------+---------+
Kwe1  2    4.6000    0.5657      (----*----)
Kwe2  2    9.0000    0.7071                            (----*----)
Kwe3  2    8.4000    0.5657                         (----*----)
Kwe4  2    5.9000    0.1414             (----*---)
Kwe5  2    3.8000    0.2828  (----*----)
                             ------+---------+---------+---------+
Pooled StdDev =  0.4980          4.0       6.0       8.0      10.0
```

Analysis of Variance for Calcium

Source	DF	SS	MS	F	P
Site	4	4834.60	1208.65	267.10	0.000
Error	5	22.63	4.53		
Total	9	4857.23			

Appendix B. (cont.)

```
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level N      Mean     StDev --------+---------+---------+--------
Kwe1  2     8.000     0.000 (-*-)
Kwe2  2    59.250     0.354                           (-*-)
Kwe3  2    70.500     3.536                                (-*-)
Kwe4  2    45.000     2.828                    (-*)
Kwe5  2    30.000     1.414            (-*-)
                            --------+---------+---------+--------
Pooled StDev =    2.127                   20        40        60
```

Analysis of Variance for iron

```
Source     DF         SS         MS         F        P
Site        4      1.943E+09 485726500  120.65    0.000
Error       5  20130000   4026000
Total       9 1.963E+09
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level N      Mean     StDev --+---------+---------+---------+----
Kwe1  2      1850        71  (-*--)
Kwe2  2     36500      3536                        (-*--)
Kwe3  2     40750      1061                           (-*--)
Kwe4  2     27500      2121                  (-*--)
Kwe5  2     18000      1414            (-*-)
                            --+---------+---------+---------+----
Pooled StDev = 2006          0     15000     30000     45000
```

Analysis of Variance for lead

```
Source     DF         SS         MS         F        P
Site        4      17.944     4.486     8.88    0.017
Error       5     2.526     0.505
Total       9    20.470
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level N      Mean     StDev ------+---------+---------+---------+
Kwe1  2    0.2000    0.0000  (-----*-----)
Kwe2  2    4.1500    0.4950                    (------*-----)
Kwe3  2    1.2250    0.5303      (-----*------)
Kwe4  2    1.5000    1.4142       (-----*------)
Kwe5  2    1.0000    0.0000    (-----*-----)
                            ------+---------+---------+---------+
Pooled StDev =  0.7108          0.0       2.0       4.0       6.0
```

Appendix B. (cont.)

Analysis of Variance for Manganese

```
Source     DF        SS        MS        F        P
Site        4    3433.0     858.3    77.32    0.000
Error       5      55.5      11.1
Total       9    3488.5
```

```
                                     Individual 95% CIs For Mean
                                      Based on Pooled StDev
Level  N      Mean      StDev  --------+---------+---------+--------
Kwe1   2    32.000      4.243  (--*--)
Kwe2   2    63.500      4.950                 (--*--)
Kwe3   2    73.500      3.536                      (--*--)
Kwe4   2    83.000      0.000                          (---*--)
Kwe5   2    80.500      0.707                         (--*--)
                               --------+---------+---------+--------
Pooled StDev =    3.332                     40        60        80
```

Appendix C. One-way analysis of variance for Kwekwe metric indices

One-way ANOVA: %EPT versus Site

```
Analysis of Variance for %EPT
Source     DF        SS        MS        F        P
Site        3    1946.2     648.7    32.71    0.000
Error       8     158.7      19.8
Total      11    2104.8
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  -----+---------+---------+---------+-
1           3    31.567     2.205                            (----*----)
2           3     0.000     0.000  (----*----)
3           3     3.697     6.403    (----*----)
4           3     3.340     5.785    (----*----)
                                   -----+---------+---------+---------+-
Pooled StDev =    4.453                 0        12        24        36
```

One-way ANOVA: %Tolerant versus Site

```
Analysis of Variance for %EPT
Source     DF        SS        MS        F        P
Site        3       590       197     0.17    0.914
Error      20     22949      1147
Total      23     23540
```

```
                                          Individual 95% CIs For Mean
                                          Based on Pooled StDev
Level        N      Mean     StDev   ---------+---------+---------+-------
1            6     37.83      7.37      (--------------*-------------)
2            6     45.00     49.30          (--------------*-------------)
3            6     32.48     31.79    (-------------*--------------)
4            6     33.35     33.09    (--------------*-------------)
                                     ---------+---------+---------+-------
Pooled StDev =     33.87                     20        40        60
```

One-way ANOVA: %Moderate tolerant versus Site

```
Analysis of Variance for %EPT
Source     DF        SS        MS        F        P
Site        3       325       108     0.13    0.943
Error      32     27126       848
Total      35     27451
                                     Individual 95% CIs For Mean
                                     Based on Pooled StDev
Level        N      Mean     StDev   ----+---------+---------+---------+--
1            9     37.64      5.85         (------------*------------)
2            9     30.00     45.00    (------------*------------)
3            9     31.23     25.21     (------------*------------)
4            9     31.11     26.38     (------------*------------)
                                     ----+---------+---------+---------+--
Pooled StDev =     29.12                 15        30        45        60
```

One-way ANOVA: %Intolerant versus Site

```
Analysis of Variance for %EPT
Source     DF        SS        MS        F        P
Site        3      1111       370     0.48    0.699
Error      44     34045       774
Total      47     35156
                                     Individual 95% CIs For Mean
                                     Based on Pooled StDev
Level        N      Mean     StDev   -----+---------+---------+---------+-
1           12     34.17      8.50             (------------*-------------)
2           12     22.50     40.70   (-------------*------------)
3           12     23.42     25.72    (-------------*------------)
4           12     23.34     26.54    (------------*-------------)
                                     -----+---------+---------+---------+-
Pooled StDev =     27.82                  12        24        36        48
```

Appendix D. Comparison of diversity indices between sites using Kruscal-Wallis test (excluding site Kwe2, where no benthic macroinvertebrate organisms were collected)

Indices	H	P
H^1	9.46	0.024
1- D	10.38	0.016
E	7.94	0.047