

# ESTUARINE ALGAL TISSUE AND SEDIMENT TRACE METAL CONTAMINATION ALONG THE WESTERN COAST OF MAURITIUS

**Final Report** 

June 2001

# **MAURITIUS RESEARCH COUNCIL**

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# UNIVERSITY OF MAURITIUS FACULTY OF SCIENCE

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# Estuarine Algal Tissue and Sediment Trace Metal Contamination along the Western Coast of Mauritius.

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**Final Report** 

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# List of abbreviations.

AAS- Atomic Absorption Spectrometry.

ha- hectares

D.O- Dissolved Oxygen.

AES- Atomic Emission Spectrometry.

EDTrA- Ethylenediaminetriacetic acid.

km<sup>2</sup>- square kilometres.

mm - millimetres.

ms<sup>-1</sup> - metres per second.

ng mL<sup>-1</sup> - nonagrams per millilitre.

nm- nonametres.

ppm- parts per million (mg  $L^{-1}$  or  $\mu g m L^{-1}$ ; mg kg<sup>-1</sup> or  $\mu g g^{-1}$ ).

 $\mu g L^{-1}$  - microgrammes per litre.

 $\mu$ mol L<sup>-1</sup> - micromoles per litre.

 $\mu g g^{-1}$ - micrograms per gram.

mg  $L^{-1}$  - milligrammes per litre.

mg kg<sup>-1</sup> milligrams per kilogram.

 $^{\circ}/\infty$  - parts per thousand.

°C - degrees Centigrade.

#### Abstract

Zn and Pb were significantly higher in sediments downstream St Louis compared to Tamarin estuary at the 5% significance level. Zn was also significantly lower at the 5% significance level in Tamarin compared to Petite Riviere Noire estuary. Cr was not significantly different in sediments collected from GRNW, Tamarin and Petite Riviere Noire estuaries. Both Cr and Zn in sediments exceeded the target values of 100 and 180 mg kg<sup>-1</sup> in contaminated sediments adopted from the draft standards (24% clay and 10% organic matter by weight) from Netherlands (Van Veen and Stortelder, 1998) respectively at some stations. However, Pb was within the 50 mg kg<sup>-1</sup> target value as quoted Van Veen and Stortelder, 1998). For comparison purposes, the values of Pb in the sediments in the 6 estuaries were also below those reported by Miller et al. (2000) who reported high Pb (33-996 mg kg<sup>-1</sup>) whereas Cr in the 6 estuaries had values similar to Cr (120-300 mg kg<sup>-1</sup>) concentrations in Holy Loch sediments in Scotland. Cr, Zn and Pb were also not significantly different in Ulva sp. and Padina sp. collected along GRNW, Flic en Flac, Tamarin and Le Morne. Both Zn and Pb were also significantly higher in sediments downstream St Louis compared to the estuarine sediments at 5 % significance level. The presence of Cr, Zn and Pb in St Louis can be attributed to the high industrial activity, roadrunoff and urban activity prevailing in the area. The concentration of Zn and Pb were greatest in the more urbanised upper and lower reaches of the St Louis estuary during the period of study. Pb was higher in the sediments in the estuary of St Louis River compared to Tamarin indicating accumulation of Pb in estuarine sediments which may be released continuously into the lagoon. The potential sources of Pb in sediments in the St Louis estuary may be from the adjacent motorway and road runoff causing significant quantities to be trapped within the St Louis River. This study has showed that a phasedown of Pb in petrol is necessary in the near future. The decontamination of contaminated sites of the estuary and lagoon will become necessary to prevent harm to the environment in the long term. Any engineering solution for this problem in order to be implemented has to take into account the distribution of the amounts of Cr, Zn and Pb in the Grand River estuary. With the introduction of unleaded petrol and vehicles equipped with catalytic converters, it will become necessary to initiate studies on Pd and Pt to provide baseline data. Research projects should be undertaken in the future to further the understanding of the biogeochemical processes in estuaries which could be used in environmental development schemes and effective integrated coastal zone management of small island states.

#### Chapter 1

#### Introduction and Objectives.

#### 1.0 Introduction.

Industrialised countries in Europe have undergone four major stages of freshwater pollution involving domestic, industrial wastes, nutrients and micro-organics and a similar chains of events are likely to occur in the non-industrialized countries on different time-scales. Though, industrial wastes have started to be controlled since the 1970s, issues connected with acidification, organic micro-pollutants, nitrates and groundwater contamination in the 1990s were on the ascendant in highly developed countries. In the industrialising developing countries, a similar sequence of events is occurring with the problems appearing later on and succeeding one another more rapidly than in the industrialised ones. Wastewater management therefore increasingly needs to understand the assimilative capacity of sediments which are a major sink and the threat of reworking of contaminated sediments through natural and anthropogenic processes poses a long-term hazard which requires evaluation in Mauritius.

Over the last twenty years there has been a steady growth in the manufacturing industry of Mauritius. All of this has led to a rapid industrialisation and an increase in human related activities over the last twenty years (Anon, 1998). These industries produced increasingly more of various forms of pollutants, which is estimated daily production of 200 tonnes (Anon, 1997). Since much of the water remains untreated this results in the pollution of the aquatic environment with the consequence that the surface water quality and surface bottom sediment have been contaminated (Heeramun, 1997). On the other hand, whole arrays of experiment have shown that organisms are able to bioaccumulate metals, organochlorides, and even bacteria into their tissues from their ambient environment (Calow, 1993). The disposal of untreated water has therefore given rise to contamination of sediments and algal tissues in and around estuaries, whose river carries industrial wastes. Wastewater is also the carrier for nitrates, phosphates, nitrites, heavy metals, and organochlorides (Mc Lusky, 1990). It is thus evident to suspect the accumulation of deleterious industrial wastes into marine organisms such as algae. Dissolved or weakly adsorbed metals become available to aquatic flora and fauna (Chiffoleau et al., 1994). The characterisation of the total concentrations of trace metals together with the relative proportion of the component of dissolved and particulate species is essential because of its fundamental importance to the bioavailability and toxicity of trace elements in aquatic systems. Sediment serves as a source and a removal mechanism for some contaminants to and from the stream, and as a vehicle for contaminant transport downstream. Analysing contaminants in sediment and aquatic biota provides an efficient way to test whether hydrophobic contaminants are present in the stream. Hydrophobic chemicals have little or no affinity for water; such chemicals have a low solubility in water, a high solubility in lipids (fats), and a strong tendency to sob to organic material in soil and sediment. Many hydrophobic chemicals also are resistant to degradation, so they persist for a long time in the environment.

#### **<u>1.1 Objectives of the study.</u>**

The objectives of this project was to monitor trace metals (Cr, Pb and Zn) in sediments and in algal tissues *-Padina sp., Ulva sp.* and *Enteromorpha sp*, in the estuaries of GRNW, St Louis River, Flic en Flac rivulet, Grande Riviere Noire estuary, Petite Riviere Noire estuary and Tamarin estuary during summer and winter months starting July 2000. Dissolved nutrients (phosphate and nitrate) and master variables (temperature, salinity, dissolved oxygen, pH) were also monitored in the different estuaries.

The specific objectives of the project were as follows:

- a) To assess and compare Cr, Zn and Pb in sediments and algal tissues of selected macroalgae during summer and winter months at each station.
- b) To compare the variation of trace metals in different estuaries by statistical comparison.
- c) Discuss the possible factors, which might influence the enrichment of trace metals in sediment and recommend measures to reduce environmental contamination in the estuaries.

#### Chapter 2

#### LITERATURE REVIEW

#### 2.0 Estuaries and their importance.

In the inter-tidal zone are various critical habitats among which are estuaries. These estuaries maintain exceptionally high levels of biological productivity and play important ecological roles in 1) 'exporting nutrients and organic materials to outside waters through tidal circulation, 2) providing habitat for a number of commercially or recreationally valuable fish species, 3) serving as breeding grounds for adults and sanctuary for juvenile fishes Estuarine ecosystems play major roles in the life cycles of economically important finfish and shellfish and nursery habitats (Clark, 1992).

In Mauritius industrial development and a rise in the tourism industry has led to major concerns in pollution problems, especially in regions where fishermen communities operate like 'Bain des Dames'. The existing Port Louis and Plaines Wilhems sewerage system designed as separate foul sewer systems suffer from frequent blockages and overflow due to the large number of unauthorised stormwater connections and deterioration of the pipework resulting in overflow in adjacent rivers. There is at present a pressing need to accelerate the promotion of clean technology. The major areas for environmental and public concern in Mauritius are pollution of the surface water, lagoons and underground waters by industrial and domestic effluents, untreated sewage, agricultural and storm-runoff. Effluents from the sugar manufacturing industry and the textile industry are significant at present and the industrial use of surface waters has also resulted in low residual flows in rivers, removing dilution for subsequent direct effluent discharge. Other inadequate wastewater provisions of immediate concern relate to electroplating, battery production, galvanising, steel mill and metal-fishing plants. The increasing problem of pollution control and the maintenance of water quality has not been matched by an increase in pollution control measures. Chromium salts used in the textile industry in Mauritius were considered potential contaminants where dye industries were not connected to the sewerage system and depended on absorption pits for disposal of their wastes (Unesco, 1990).

The major potential sources of pollution today in Mauritius are sewage effluents, industrial processes, agricultural activities, urban and storm water run-off (Ramessur *et al.*, 1998). Industrial activities causing atmospheric emission also include steel mills and cement bagging plants whereas waste burning and vehicle emissions contribute to overall pollution levels. The use of leaded fuel (200 million litres annually with an average Pb content of 0.4 g  $\Gamma^1$ ) by 200, 320 vehicles in 1996 is potentially dangerous both as an atmospheric pollutant and through its introduction into foodchains via rain induced run-off from roads and measures for the introduction of unleaded petrol have not been accepted as costs outweigh benefits at present on the island (Anon., 1998). Mungur and Choong Kwet Yive (1998) indicated that vehicular emission was a major source of Pb in soil samples pollution (> 700 mg kg<sup>-1</sup>) collected near the M1 motorway adjacent to the GRNW catchment area which has a daily traffic density of about 20 000 vehicles.

# 2.1 Trace metals in estuarine sediments.

In contrast to the strong temporal and spatial variability in the aqueous concentrations of contaminants, sediments integrate contaminant concentrations over time and that by focusing on sediments the number of samples needed in contamination assessment can be reduced (Breward et al., 1998). The accumulation of toxic and persistent substances in the coastal environment continuously increases owing to anthropogenic activities as the estuaries and their adjacent coasts are the focus for many economic activities. (Chiffoleau et al., 1994; Pereira et al., 1998). Rees et al. (1998) reported that large quantities of Pb and Zn arising from mining related waste trapped in sediments within fluvial systems in the Trent and Ouse draining the Pennine orefields remained high between source areas and the Humber estuary whereas heavy metals associated with manufacturing industry such as Cr, Ni and Cu had high levels near source cities, but decreased rapidly in amount down the river systems because of dilution by other sediments. Vaithiyanathan et al. (1993) reported that trace metal transport reflected the tendency of trace metals to form insoluble hydroxides in the alkaline pH range during the processes of weathering and that more than 80% Cr, Zn and Pb were carried in suspension in particulate form in the Cauvery river Basin, India. The

observed presence of anoxic water significantly influences the trapping of Cd, Zn, Pb and Cu in the sediment phase and seem to be controlled by scavenging with iron sulphide according to various authors (Skei, 1983) whereas Calmano *et al.* (1993) reported that pH and redox conditions controlled the mobilization of metals (Cu, Zn, Pb and Cd) from contaminated sediments in a study from Hamburg harbour. Fernandez *et al.* (1994) assessed heavy metal pollution in Jacarepagua basin, Rio de Janeiro and proposed a pattern of seasonal washout in addition to the dilution by uncontaminated materials and found that Pb in sediments outside areas of industrial releases and close to motorways were high and originated from the combustion of leaded petrol. Wei and Morrisson (1993) found that storm events led to a significant change in organic profile by resuspension/deposition of cleaner background sediments and removal of organic rich sediments which were being washed downstream in a small urban river in Goteborg and reported that interstitial water during periods of dry and light rain combined with storm resuspension played a jey role in metal diffusion and distribution in the river.

Vasconcelos *et al.* (1995) also found strong positive correlations between Pb and Zn for sediments in a tidal estuary in Britanny, France. High correlation values which were not season dependent were found for Zn/Cr in sediments in the Cavado river Basin, Portugal by Goncalves *et al.* (1994) who also reported that washing of the river bed could occur, leading to lower levels of contamination at high flow rates whereas reduced flow rates could cause suspended particles to settle down and become incorporated into the bottom sediment. According to Chiffoleau *et al.* (1994), suspended particulate matter in the high turbidity zone (defined by a SPM>30 mgl<sup>-1</sup>) (HTZ) are responsible for the removal of dissolved Pb in estuaries and coastal waters whereas Zn can be released from resuspended sediments in estuaries via organic matter degradation, desorption or dissolution from riverine particles and resuspended estuarine sediments.

#### 2.2 Sources and toxicity of lead.

Lead is one of the most pervasive and widely dispersed environmental contaminant. There are no known beneficial effects of lead in humans but many identifiable adverse effects. Excess lead in the blood cause a variety of health problems depending on the subject's age and amount of lead exposed. The different affected organ systems are nervous system, hematopoietic system, renal system, endocrine system and the skeletal system. In recent years, there has been a growing interest in the potential human health risk associated with the exposure to lead in food sources. Moreover children absorb more lead and are also more sensitive to them due to their still immature neurological system. The response of the adult is both quantitatively and qualitatively different from that of children. Lead is a naturally occurring bluish-gray metal found in small amounts in the earth's crust. Lead behaves like many of the alkaline earth metals (Ca, Sr, and Ba) with respect to uptake, internal distribution, and secretion. Lead is a bone-seeking element so chemically similar to calcium that the two are processed together. In fish, lead deposits in active calcification areas such as scales, fin rays, vertebrae, and opercula. Lead is a heavy metal, which is very toxic to aquatic organisms, especially fish. Like arsenic, lead exposure can lad to excess mucous formation, which can coat the gills and impact respiration. Lead poisoning is particularly dangerous in young children (who may ingest lead by eating leadcontaining chips of paint); it may result in anorexia and--in severe cases--permanent brain damage. The release of lead to air is now less than the release of lead to soil. Most of the lead in inner city soils comes from landfills and leaded paint. Landfills contain waste from lead ore mining, ammunition manufacturing, and from other industrial activities such as battery production. Very little lead goes directly into water.

Higher levels of lead from car exhausts can be measured near roadways. Very low levels of lead from car exhausts are found at distances of 25 meters (about 80 ft) from the road edge. However, once lead goes into the atmosphere, it may travel thousands of miles if the lead particles are small or if the lead compounds are volatile. Lead is removed from the air by rain as well as by particles falling to the ground or into surface water. Once lead deposits on soil, it usually sticks to soil particles. Small amounts of lead may enter rivers, lakes, and streams when soil particles are displaced by rainwater. Lead may remain stuck to soil particles in water for many years. Movement of lead from soil particles into underground water or drinking water is

unlikely unless the water is acidic or "soft". Lead also tends to bioaccumulate in benthic organisms, mussels and clams.

The principal route of human exposure is food, but it is usually environmental & presumably controllable sources that produce excess exposure. These sources include lead in air from combustion of lead-containing auto exhausts or industrial emissions, lead-based paint, hand-to-mouth activities of young children living in polluted environments, and, less commonly, lead dust brought home by industrial workers on their clothes and shoes, and lead-glazed earthen ware. (Doull *et al*, 1986). Lead is dissolved out of lead water supply pipes to enter the diet through the drinking water. The disposal of metallic lead and demolition debris in landfills therefore poses a potential hazard if the leachate is allowed to pass into ground water feeding a water supply system. (Van Nostrand Rheinhold, 1979).

Lead enters water from atmospheric fallout, runoff or wastewater. If released into water, metallic lead will simply sink into the sediment. Surface layers of insoluble salts may form and protect the surface from further corrosion. In the dissolved state, it will form ligands, the dominant one varying with pH. In freshwater systems, the most important ligands are  $HCO_3^-$ ,  $CO_3^-$ ,  $^-OH$  and whereas in seawater they are  $C1^-$ ,  $CO_3^-$ ,  $^-OH$ ,  $Cl_2^-$ , and  $Cl_3^-$ . A characteristic of lead is its tendency to form compounds of low solubility with the major anions of natural water. As a result natural concentrations of lead in lead-ore deposits do not move appreciably in ground or surface water but rather any dissolved lead will tend to combine with carbonate or sulfate ions to form insoluble lead carbonates or sulfates or be absorbed by ferric hydroxide (USEPA, 1977).

#### 2.3 Sources and toxicity of zinc.

Zinc is normally considered to be present in much lower toxicological risk to humans and animals than lead. Recent evidence suggests that zinc dispersion into the environment and accumulation in soils especially from sewage sludge, may have far reaching infertility because of its toxicity to microorganisms. In humans the effects of zinc toxicity are variable. Symptoms are fever, nausea, vomiting, stomach cramps and diarrhoea in three to twelve hours following ingestion. Other symptoms may be swelling of lips and face, sweating tightness of chest, itching, low blood pressure, heart stop and even unconsciousness. Both of the zinc salts zinc sulfide and zinc oxide are used to make white paints, ceramics, and several other products. Zinc oxide is also used introducing rubber. Zinc salts, such as zinc acetate, zinc chloride, and zinc sulfate, are used in preserving wood and manufacturing and dyeing fabrics. Zinc is an essential food element needed by the body in small amounts. Zinc in low to moderate amounts is of very low toxicity in its ordinary compounds and in low concentrations is an essential element in plant and animal life.

Absorption of dietary zinc in higher animals is regulated in part by metal thioneins, low molecular weight proteins containing high levels of cysteine. Freshwater fish can regulate zinc over a wide range of ambient concentrations. Increased zinc intake can afford some animals some protection against cadmium exposure .Too little zinc in the diet can lead to poor health, reproductive problems, and lowered ability to resist disease. Too much zinc can be harmful to health. There have been cases of too much zinc causing poisoning in humans as well as fish and wildlife. Elevated concentrations of zinc in water are particularly toxic to many species of algae, crustaceans, and salmonids. In the aquatic environment, zinc toxicity is more often associated with direct toxicity of elevated concentrations of zinc in the water (through disruption of internal ion balance) rather than dietary or food chain toxicity.

Zinc is a human skin irritant (Van Nostrand Reinhold, 1984). It was concluded that an abnormal amount of zinc may enter & leave the body for years without causing symptoms or evidence which can be detected clinically or by laboratory examinations of gastrointestinal, kidney, or other damage (Hamilton, 1974). Zinc enters the air, water, and soil as a result of both natural processes and human activities. Waste streams from zinc and other metal manufacturing and zinc chemical Industries, domestic wastewater, and run-off from soil can discharge zinc into waterways. Most of the zinc in bodies of water settles on the bottom. However, a small amount may remain either dissolved in water or as fine suspended particles. The level of dissolved zinc in water may increase as the acidity of water increases (that is, as pH decreases). Fish that live in water containing zinc collect it in their bodies. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the characteristics of the soil, some zinc may reach groundwater. Contamination of groundwater from hazardous waste sites has been noticed.

Fish, especially those living or foraging in sediments contaminated by zinc, may accumulate zinc directly from the sediments. Zinc is one of the most common contaminants associated with urban runoff. Other zinc sources include soil erosion, industrial discharges, pharmaceuticals, and pesticides. In some areas up to 50% of the zinc comes from highway runoff. Zinc is also present in the leachate of some municipal landfills and is a common contaminant in sludge's generated by sewage treatment plants.

#### 2.4 Sources and toxicity of chromium.

Chromium can exist in oxidation states ranging from -2 to +6, but is most frequently found in the environment in the trivalent (Cr+3) and hexavalent (Cr +6) oxidation states. The +3 and +6 forms are the most important because the +2, +4, and +5 forms are unstable and are rapidly converted to +3, which in turn is oxidized to +6. Most compounds prepared from chromite ore (that is, aggregate of minerals from which chromium compounds can be extracted) contain chromium in the more stable +3 state. The chromium in essentially all environmentally important compounds is in one of these two oxidation states. Trivalent chromium is the most common form in rocks of the earth's crust, but both trivalent and hexavalent chromium occur as dissolved chromium. The hexavalent state is the second most stable state. However, hexavalent chromium rarely occurs naturally, but is produced from anthropogenic sources. Most of the chromium (+6) found in nature is a result of domestic and industrial emissions. Interaction of +6 chromic oxide, dichromate, or chromate compounds with organic compounds can result in reduction to the comparatively less toxic trivalent form.

### Potential hazard of Chromium:

1) The overall toxicity, carcinogenicity, and general hazard of chromium are highly related to chemical speciation. The biological effects of chromium depend on chemical form, solubility and valence.

2) The toxic mechanism of action differs for hexavalent versus trivalent chromium. Hexavalent chromium causes cellular damage via its role as a strong oxidizing agent, whereas trivalent chromium can inhibit various enzyme systems or react with organic molecules. In mammalian species, chromium is considered one of the least toxic trace elements, as normal stomach pH converts hexavalent chromium to trivalent chromium .One hundred to two hundreds times the normal total body load of chromium can usually be tolerated in mammals without evidence of negative effects.

3) Both chromium III and VI (especially hexavalent) are significant from the standpoint of potential impacts to fish and wildlife. However, although chromium in general has some notoriety as a potentially harmful environmental contaminant, most of that notoriety is due to the toxic, carcinogenic, oxidizing agent, general, and reproductive risk hazards of hexavalent chromium Cr 6+, chromium +6, chromate) compounds.

4) Little is known about the relation between concentrations of total chromium in a given environment and biological effects on the organisms living there. Depending on the physical and chemical state of the Cr, the same elemental concentration has a wide variety of mobilities and reactivities and thus has different effects. Chromium toxicity to aquatic biota is significantly influenced by biotic variables such as hardness, temperature, pH, and salinity of water; and biological factors such as species, life stage, and potential differences in sensitivities of local populations. For many metals, alkalinity is sometimes a more important co-factor for toxicity than hardness.

Chromium toxicity to aquatic biota is significantly influenced by abiotic variables such as hardness, temperature, pH, and salinity of water. In both freshwater and marine environments, hydrolysis and precipitation are the most important processes that determine the fate and effects of chromium, whereas adsorption and bioaccumulation are relatively minor. Both Cr+3 and Cr+6 can exist in water with little organic matter; Cr+6 is usually the major species in seawater. Under oxygenated conditions, Cr+6 is the dominant dissolved stable Cr species in aquatic systems. A very small amount of the chromium in soil, however, will dissolve in water and can move deeper in the soil to underground water. Chromium in water may originate from surface runoff, deposition from air, or release of wastewaters. Chromium may be transported in waters as suspended materials and deposited in estuaries and bays but it is more frequently removed from water by sedimentation. There is little tendency for chromium (+3) to biomagnify in food chains in the inorganic form. Most of the chromium in surface waters may be present in particulate form as sediment; some of the particulate chromium would remain as suspended matter and ultimately be deposited in sediments. Due to its association with suspended particulate phases, a large proportion of the Cr+3 discharged to surface water is transferred to sediment. In aerobic sediments, manganese oxides and hydroxides present at the sediment-water interface can oxidize some Cr+3. It has been suggested that the resulting Cr+6 can be

released to the overlying waters, especially by bioturbation processes. Temperature and salinity have been found to affect the acute toxicity of chromium to estuarine invertebrates; high temperature and low salinity causing the greatest toxicity. The presence of > 100 ppm chromium may adversely affect the biodegradation of sewage sludge.

#### **CHAPTER 3**

#### MATERIALS AND METHOD.

Samples of algae and sediments were collected from areas potentially affected by pollutants and compared to samples from pristine areas.

### **3.1 STUDY AREAS.**

The 6 estuaries identified for the project were those that were lying in the western coast of Mauritius extending from Grand River Bay to Petite Riviere Noire, Figure 1. The study areas, Fig 2-4 chosen are given as follows:

- 1) St Louis and GRNW estuaries (stations 1 and 2).
- 2) Flic en Flac rivulet (station 3).
- 3) Riviere du Rempart estuary, near Tamarin public beach (station 4).
- 4) Grande Riviere Noire estuary (station 5).
- 5) Petite Riviere Noire estuary (station 6).
- 6) Le Morne Public Beach lagoon (station 7). The lagoon of the public beach at Le Morne had also been included because of its relative remoteness from anthropological activity

#### Stations 1 and 2: St Louis and GRNW.

The GRNW, which discharges south of Port Louis, has a catchment area of 116 km<sup>2</sup> and is fed by small southern tributaries from Upper Plaines Wilhems and Moka district. The GRNW estuary receives wastewater from the St.louis River, which flows through Pailles and Plaine Lauzun industrial area (See Fig 2). The annual average rainfall in the Port Louis area is 1160 mm. The daily maximum and minimum temperatures are 33 °C and 24°Cin summer and 25°C and 19°C in winter. Site 1 is nearest to the capital city and is surrounded by many industries and human populations. The presence of many small boats commonly known as "pirogues" gives an indication of the importance of number of fisherman in the region who fish to earn a livelihood. However during field works we found out that there are also many people who fish in the estuary for leisure. According to the wastewater authority that

region is deserved by a sewer system where industrial and domestic are wastes are all subject to a pre-treatment before being discharge in nature. However field visits revealed that in certain parts of the estuary wastes in a concentrated form are actually discharged in the estuary with traces of oil which is against the EPA's second schedule (Regulation 4) where the maximum permissible limit for oil and grease should be none visible.

#### **Station 3: Flic en Flac.**

The Flic en Flac rivulet is just annexed to the hotel Sugar Beach Resort, where the lawn is heavily irrigated every evening and nutrient additives are added to the grass which suggests that eutrophication might be possible unless the excessive irrigation might dilute the nutrients to prevent eutrophication (See Fig 3). The actual situation is that construction works are being carried just within meters of the rivulet and abnormal readings might be possible. There are many individuals who collect water from that rivulet for various purposes including irrigation and the filling of swimming pools that are under construction.



Figure 1. Map of Mauritius (Source: Environmental studies Atlas for Mauritius, 1989, Scale 1: 100 000).

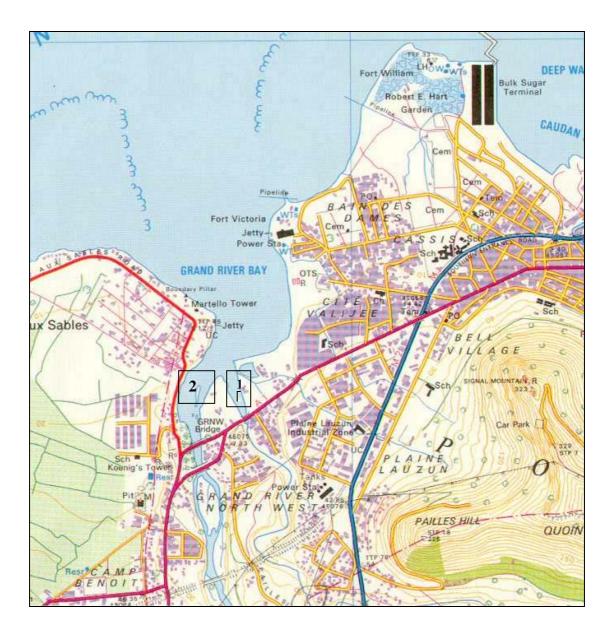


Fig 2. Study Site at St Louis and Grand River North West (stations 1 and 2, Source: Ministry of Environment and Land, 1990).

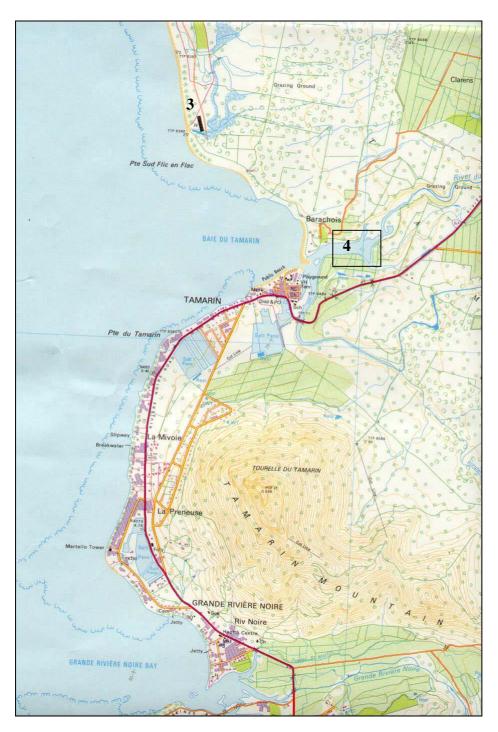


Fig 3. Study Site at Flic en Flac and Tamarin (stations 3 and 4, Source: Ministry of Environment and Land, 1990).

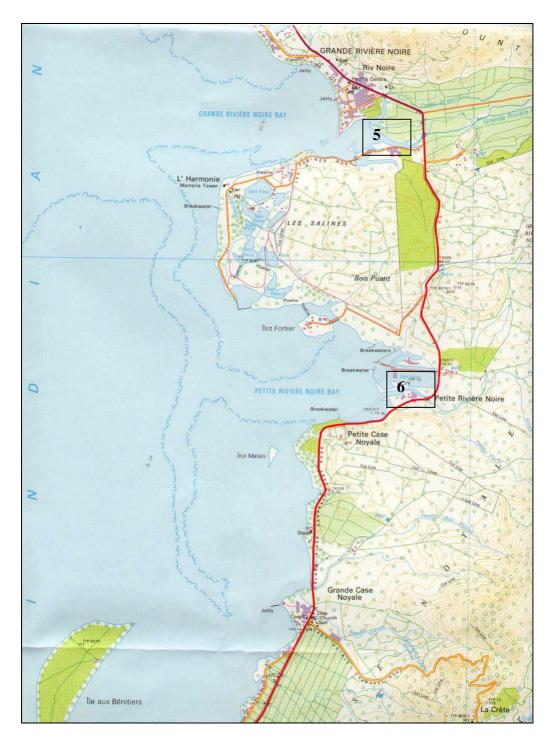


Fig 4. Study Site at Grande Riviere Noire and Petite Riviere Noire (stations 5 and 6, Source: Ministry of Environment and Land, 1990).

#### **Station 4: Tamarin.**

The Riviere du Rempart estuary is unique in its kind where the topology of the sandy beach might change overnight. Sand deposits often block the mouth of the river such that water is trapped in the estuary forming a sort of basin. People in charge for the maintenance of the beach thus usually have to remove the sand barrier to let the water flow into the sea. The estuary at the Tamarin public beach accommodates water from 2 rivers, which are Riviere Rempart and Riviere Tamarin. Anthropological activities that are near the estuary are mainly related to the tourism industry and also from human settlements more upstream (See Fig 3).

#### **Station 5: Grande Riviere Noire estuary.**

Grande Riviere Noire estuary is further south and no intense activity can be seen except that there are many fishing boats in the lagoon annexed to it. However field observations revealed that people use the river water upstream for domestic purposes which are washing clothes and bathing. Land reclamation is however being carried out in a marshy area neighbouring the estuary (See Fig 4).

## **Station 6: Petite Riviere Noire Estuary.**

Petite Rivière Noire is situated in the Black River district, south west of Mauritius. The river takes its source from the Black river gauges and it passes through agricultural lands (mainly sugarcane plantation) and Petite Rivière Noire village before joining the sea. It is situated in a rural non-industrial zone and therefore there are no discharges of industrial effluents. One of the major activities of the people in this village is fishing. The only industrial activity-taking place in the region is the Salts Pans, which is situated near the estuary. The Petite Riviere Noire estuary is perhaps where anthropological activity is the most visible. Human settlements have formed just by the side of the river and the estuary and domestic wastes can be seen getting discharged directly into the river and estuary. Furthermore the salinity of the river which reaches up to 40% which is very abnormal (See Fig 4).

#### **Station 7: Le Morne.**

Le Morne public beach has no estuary annexing it but however because of frequent water currents passing through the lagoon suggests a constant renewal system of pollutant free water and therefore sediments that are free from pollutants and also algae exposed to clean seawater. Thus in the absence of a good standard reference material Le Morne public beach can be used as a good site, free from anthropological activity, to find out the basal amounts of metals in algae and sediments.

#### **3.2 Sampling strategy and Field Measurements.**

Surface sediment were collected from 6 stations at fortnightly intervals from July 2000 – February 2001. A number of master variables (salinity, temperature, pH, D.O and SPM) were determined together with 3 trace metals (Cr, Zn, and Pb) in both surface sediments and algal tissues using atomic absorption spectrometry. Sampling was done at a sufficiently high sampling density to ensure data integrity and also to maintain a sufficiently broad spatial coverage to include relatively uncontaminated areas for reference purposes as recommended by Breward *et al.* (1998) The potential for a significant degree of localised distributional heterogeneity at each sampling incidence was considered and replicate sampling was done to obtain results within specified confidence limits. Sampling was carried out at the six stations during the sampling period as shown in Table 1 and the following master variables determined *insitu*:

- 1) pH.
- 2) Salinity.
- 3) Temperature.
- 4) Dissolved oxygen.

The above parameters were measured at weekly intervals using integrated Jenway pH meter model-3305, portable pH meter (Sension 156 portable) Jenway DO meter model-9071 and a Fisher Scientific salinometer, model-Digit-010ATC.

**Table 1.** Showing sampling period during winter and summer.

Winter	July 2000 to October 2000	
Summer	November 2000 to February 2001	

#### 3.3 Sample collection.

The water samples were collected in 250 ml polythene bottles (for dissolved nitrate and nitrite) and glass bottles (reactive dissolved phosphate). The bottles were previously acid washed (10% HCl) and then washed thoroughly with the water to be collected so as to ensure that all traces of the previous samples were removed. Then the samples were collected by dipping the bottle a few inches under the surface and then tilted so as to collect water from under the surface. Surface bottom sediment samples were hand-collected from a depth of 0.5m in polythene bottles while wearing plastic gloves, at the end of each month.

#### **3.4 Sample treatment**

The water and sediment samples were collected so as to be free from dirt and other organic material (such as dead plants). If solid waste was present, the water was immediately filtered. Filtration removed microorganisms, which are responsible for biological activity, and turbidity, which causes spectrophotometric interferences. The clear water samples were kept in isotherm boxes packed with ice to avoid decomposition and waste of the nutrients due to heat and action of sunlight. As far as possible, the samples were analysed on the same day. However, some samples were collected on the previous day (late afternoon) due to bad weather conditions. In such cases the samples were kept under refrigeration at about 3 <sup>o</sup>C and were analysed early on the following day.

# **3.5 Temperature and pH measurement.**

A single instrument (Jenway 3071 model), equipped with a glass electrode and a temperature sensor was used for the measurement of both parameters. The pH-meter was calibrated with three buffer solutions of pH 4.0, 7.0 and 9.0 before pH at the

stations could be measured. The electrode was rinsed in between measurements at different stations. The temperature and the pH were simultaneously measured.

#### 3.6 Dissolved oxygen.

The dissolved oxygen (DO) measurement, membrane electrode of the polarographic is used, as they are completely submersible. The DO of the water was measured using a  $\langle \text{Clark} \rangle$  type polarographic oxygen electrode (model: 9071 DO<sub>2</sub> meter). The amount of oxygen is measured in milligrams per litre (mg/L) and had a temperature measurement range of -30 <sup>o</sup>C to 150 <sup>o</sup>C. The apparatus was calibrated using sodium sulphite solution. The probe was immersed in the water sample and the DO reading was noted after stabilization.

#### 3.7 Salinity measurement.

The salinity was measured using a hand refractometer of model: Digit – 010 ATC and serial number 37278. Scale: double; precision: 0.2 %; salinity range: 0-100 %. After application of a drop of sample water on a light sensitive part of the instrument, salinity reading was directly viewed on an internal scale through the eyepiece. The glass was rinsed with deionised water and wiped dry with a piece of tissue in between measurements at different stations.

#### 3.8 Determination of nutrient ions.

Colorimetric is the usual technique to measure the concentration of nutrient ions in river and seawater. The Beer-Lambert law has been used for the determination of the level of nutrient ions in the collected sample. The apparatus used was the (ATI UNICAM, PPU 8700) UV/VIS spectrophotometer. The nutrient's ions on reacting with specific chemical give coloured solutions having an intensity depending on the concentration of the nutrient ion. The absorption of the spectrophotometer is obtained by the formula; A = ECL

Where A: absorbance.

E: Molar absorption coefficient,

- L: Length of cell,
- C: Concentration of sample.

First the spectrophotometer (PU 8700, ATI UNICAM) was zeroed for each blank solution and the reading of the standard and samples were taken. Calibration curves were used to convert relative absorption values to nutrient ion. Dilution was done to any sample whose concentration lay outside the range of the method.

#### 3.9 Nutrients analysis.

Several methods exist for the detection of the three nutrients ions mentioned above in water, but the ones selected here were considered most suitable for the kind of sample being tested and the equipment available in the laboratory. They were also rapid and obtained reliable results Determination of nitrite was carried out using the colorimetric method, that of nitrate involved the cadmium reduction method and the ascorbic acid method was employed for phosphate ion's analysis.

## 3.10 Determination of nitrite ions using colorimetric method.

## Principle:

Nitrite  $(N0_2^{-})$  is determined through the formation of a reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotised sulphanilamide with N-(1-naphthyl)-ethylenediamine dihydrochloride. The applicable range of the method for spectrophotometric measurements is 10 to 1000 mg nitrite ions per litre (Parsons *et al.*, 1984). The absorbance is measured at 543 nm against a distilled reagent blank. Nitrite is first converted to diazonium salt.

 $R_1NH_2 + HNO_2 + HC1 \rightarrow R_1N = NC1 + 2H_2$ 

The diazonium salt is then reacted with an amine to give a pink coloured azo dye.

 $R_1N = NCI + R_2NH_2 \rightarrow R_1N = NR_2NH + HC1$ 

The absorbance measured is proportional to the amount of azodye present.

# 3.11 Determination of nitrate ions using the cadmium reduction method.

# <u>Principle:</u>

Nitrate ions (N0<sub>3</sub><sup>-</sup>) is reduced almost quantitatively to nitrite ion in the presence of Cadmium. This method uses commercially available Cadmium-granules treated with copper sulphate and packed in a glass column. The nitrate ions produced is thus determined by diazotising with sulphanilamide and coupling with N-(l-naphthyl)-ethylenediamine dihydrochloride to a highly coloured azo dye that is measured colorimetrically. The applicable range of this method is 0.01mg to 1.0mg nitrate ions per litre (Parsons *et al.*, 1984). The absorption is measured at 543 nm against a distilled water reagent blank.

# 3.12 Determination of phosphate ions using the ascorbic acid method.

# Principle:

Analysis of phosphate is usually carried out by treatment of aliquot of the sample with an acidic molybdate reagent containing ascorbic acid and a small proportion of potassium antimonyl tartrate. Phosphate yields a blue purple complex. The reaction takes place with the immediate formation of phosphomolybdic acid, which is then reduced to a heteropoly and containing phosphorus, molybdenum and antimonyl in the ratio 1:2:1 by atoms (Parsons *et al.*, 1984). The absorbance is measured at 882 nm against acidified distilled as reference.

# 3.13 Algal samples identified for monthly sampling and analysis.

Algae and sediments were sampled as from July 2000 on a monthly basis and analysed for zinc, lead and chromium. The algal species chosen for the study were

- 1) Padina,
  - a) Padina boergesenii
  - b) Padina boryana
- 2) Ulva
  - a) Ulva pulchra
  - b) Ulva fasciata
  - c) Ulva pertusa
  - d) Ulva reticulata

# 3) Enteromorpha.

- a) Enteromorpha kylinii
- b) Enteromorpha ramulosa

The genus *Enteromorpha* is a thallus tubular, cylindrical or compressed, simple or branched, sometimes branched with much thinner proliferation, very supple composed of a single cell layer; mostly light green. It is well adapted to extreme ecological conditions, frequent in strongly isolated and heated eulittoral pools where their great abundance indicates eutrophication (Richmond, 1997).

*Ulva* or commonly known as the sea lettuce are foliose plants, composed of two cell layered blades composed of rounded lobes, linear straps or forming cabbage like structures which may or may not be perforated. *Ulva* are well adapted to extreme ecological conditions and therefore frequent in strongly isolated and heated eulittoral pools, but also present in exposed areas and even sublittoral. Great abundance of most species generally indicates eutrophication. They are heavily grazed by snails and siganid fish (Richmond, 1997).

*Padina* has a thallus that is erect and brown in colour. The thalli are funnel shaped fans with concentric rings of hair lines often with a whitish deposit of lime on the surface.the blade margin composed of the growing region is inrolled in itself (Richmond, 1997). However because a single site did not contain all the three types of algae, the table below shows the types of algae available and therefore sampled.

SITE	Enteromorpha	Ulva	Padina
GRNW (1)	Available	Available	Not available
Flic en Flac (2)	Not available	Available	Available
Tamarin (3)	Not available	Available	Available
GRN estuary (4)	Not available	Not available	Available
PRN estuary (5)	Not available	Not available	Not available
Le Morne (6)	Not available	Available	Available

Table 2. The specimens of algae available for sampling in the different sites.

#### 3.13.1 Algal tissue analysis.

The algal samples to be analysed were brought to the laboratory and rinsed several time (> 3 times) with de-ionised distilled water. The rinsed samples were then placed in clean watch glasses and left in the drying cabinet for 48 hours at a temperature of  $35-40^{\circ}$ C. After drying, the algal tissues were crushed to a fine powder using a glass mortar and pestle. The powdered sample (~0.75g) was then used for digestion in a microwave digester using concentrated nitric acid (5ml, 65%) and hydrogen peroxide (2ml) as catalyser. The digest produced at the end of the process was filtered through ordinary filter paper. The filtrate was made up to 25ml and used in the AAS for determination of the metals Zn, Pb and Cr. The range used for the standards while analysing the algal digest were for Zn (0.0-5.0 ppm), Cr (0.0-5.0 ppm) and Pb (0.0-5.0 ppm).

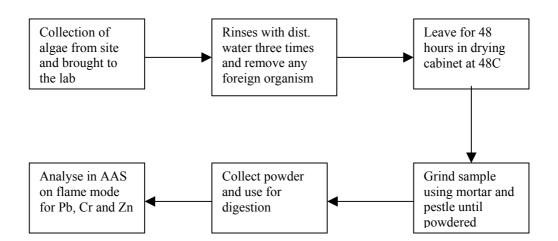


Figure 5 Summary of the procedures undertaken before coming to the analytical part.

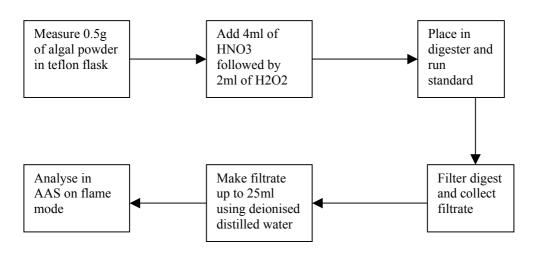


Figure 6 Summary of the major steps in microwave digestion of algal tissue.

## 3.14 Sediment analysis.

Sediments were collected from each of the estuaries (stations 1-6). These were analysed for the following metals; zinc, lead and chromium following standard methods of digestion. After drying, the sediment was crushed to a fine powder using a glass mortar and pestle. The powder is sieved through a sieve of mesh size of 250µm. The powdered sample (~0.5g) is then used for digestion in a microwave digester using concentrated hydrogen fluoride (5ml, 40%) and hydrogen peroxide (2ml) as catalyser. The digest produced at the end of the process was filtered through ordinary filter paper. The filtrate was made up to 25ml and used in an atomic absorption spectrophotometer (AAS, Model, UNICAM 929) for determination of the metals Zn, Pb and Cr. Standards solutions for the metals Chromium, Zinc and Lead were prepared their respective stock solutions (1000ppm) in the following ranges as shown in table 3. Additional care was taken to use plastic wares instead of glass ones since HF erodes glass. Accuracy of the analysis was checked using Standard Reference Material SRM 1646a Trace Elements in Estuarine Sediments from National Institute for Science and Technology (Colorado, U.S.A).

Metals	Range analysed/	Maximum detection for linear
metuis	mg/L	range/mg/L
Lead	0 to 10	20
Chromium	0 to 10	10
Zinc	0 to 2.5	2.6

Table 3. Standards used for determination of Cr, Zn and Pb in sediments.

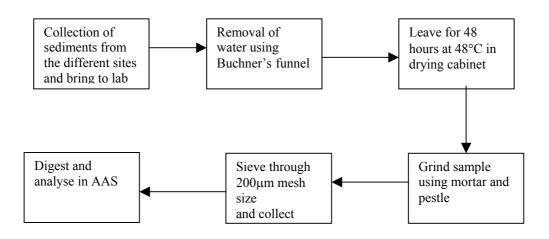
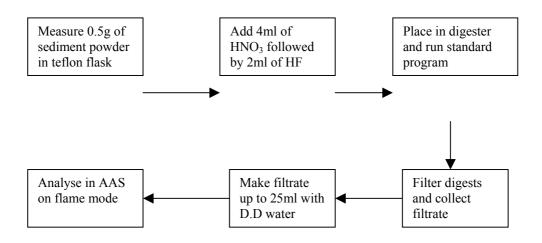
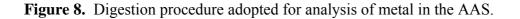


Figure 7. Procedure adopted after collection of sediments and prior to digestion.





#### **CHAPTER 4**

### **RESULTS AND DISCUSSION.**

The linearity for the calibration line for dissolved nitrate and phosphate was good showing a correlation coefficient of 1.0 (The calibration curves for dissolved nitrate and phosphate were as follows: nitrate: y = 0.003 x + 0.0005; phosphate: y = 0.021 x+ 0.001). The linearity for the calibration lines for Cr, Zn and Pb showed correlation coefficient ranging from 0.95-0.99. The calibration curves for Cr, Zn and Pb were as follows: Cr: y = 0.21 x -0.08; Zn: y = 0.12 x + 0.03; Pb: y = 0.02 x. Values for contaminated sediments adopted from the draft standards (24% clay and 10% organic matter by weight) from Netherlands (Van Veen and Stortelder, 1998) in the Cauvery Basin, India and the Humber estuary (Vaithiyanathan, 1993; Rees et al., 1998) are shown in Table 4 as no international standards for sediment quality yet exist. Below the target and standard values, the metal contaminants do not have any environmental impact or known ecological effects whereas remedial action is necessary if the concentrations exceed the limit. Mean values for master variables (temperature, salinity, pH and D.O) along the 6 estuaries are shown in Tables 5 and 6. Tables 7 below show the winter and summer mean values for dissolved nitrate and dissolved phosphate. The reported results of Cr, Zn and Pb in surface sediments and algal tissues for summer and winter are the mean values of duplicate determinations as shown in Tables 8-11. Pairwise comparisons of trace metal concentration in sediments and algal tissues at GRNW, St Louis, Tamarin and Petite Riviere Noire using t-test at 5% significance level is shown in Tables 12-14. Monthly variations of Cr, Zn and Pb in estuarine sediments and algal tissues in winter and summer months are shown in Fig 9-14.

	Target <sup>1</sup> mg kg <sup>-1</sup>	Standard <sup>1</sup> mg kg <sup>-1</sup>	Limit <sup>1</sup> mg kg <sup>-1</sup>	River mg kg <sup>-1</sup>	Estuary mg kg <sup>-1</sup>	Macroalgae mg kg <sup>-1</sup>
CHROMIUM	100	125	600	22-295 <sup>2</sup>	5.6-15 <sup>4</sup>	4 <sup>5</sup>
				$20-250^3$		
ZINC	180	750	2500	75-1264 <sup>2</sup>	62-470 <sup>4</sup>	400 <sup>5</sup>
				$15-230^3$		40-63.0 <sup>6</sup>
LEAD	50	125	700	22-484 <sup>2</sup>	12-64 <sup>4</sup>	5 <sup>5</sup>
				$5-60^3$		

Table 4. Draft standards for contaminated sediments and trace metal concentration in sediments in rivers and estuaries.

Source

1 Van Veen and Stortelder (1998).

Rees *et al.* (1998), rivers discharging in the Humber estuary.
 Vaithiyanathan *et al.* (1993), Cauvery Basin, India.

4 Fernandez et al. (1994), lagoon sediments.

5 Woodward (1984). Fucus vesiculosus, Humber Estuary, U.K.

6. Wright and Mason (1999). Enteromorpha sp, Eastern England.

Table 5 Calinity	- and	tommomotumo	:	winton on	1 aumman	in actuanias
Table 5. Salinity	anu	temperature	ш	winter and	i summer	m estuaries.

Stations	Salinity °/∞		Temperature °C		
	winter	summer	winter	summer	
St Louis	$28 \pm 5.8$	$27 \pm 4.9$	$24.2\pm1.0$	$28.5 \pm 1.5$	
GRNW	$10.2\pm4.0$	13.4± 3.1	24.8 ±0.6	$27.2 \pm 1.4$	
Flic en Flac	$1.0 \pm 1.1$	$1.8 \pm 3.2$	$23.2\pm2.3$	$30.0 \pm 1.4$	
Tamarin	$13.0 \pm 5.6$	$26.5\pm8.7$	$23.1 \pm 1.1$	$24.4 \pm 2.4$	
Grande Riviere Noire	34 ± 2.4	$34 \pm 2.8$	$24.2 \pm 1.3$	29.7 ± 1.9	
Petite Riviere Noire	36.6 ± 1.1	34.3 ± 1.5	25.5 ± 1.3	31.6 ± 1.0	

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Table 6. pH and	dissolved ox	vgen in winter	and summer	in estuaries.
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Stations	pН		<b>D.O mg </b> $l^{-1}$				
	winter	summer	winter	summer			
St Louis	$8 \pm 0.4$	$7.9 \pm 0.4$	$6.1 \pm 0.37$	5.7±0.7			
GRNW	$8.5 \pm 0.2$	$7.9 \pm 0.1$	$11.2 \pm 1.4$	$7.0 \pm 1.0$			
Flic en Flac	$8.2 \pm 0.4$	$8.1 \pm 0.4$	$6.4 \pm 2.9$	$3.9 \pm 0.7$			
Tamarin	$8.3 \pm 0.4$	$8.3 \pm 0.2$	$6.1 \pm 2.0$	$4.9 \pm 0.4$			
Grande Riviere Noire	8.1 ± 0.4	8.1 ± 0.3	5.8 ± 1.2	$4.6 \pm 0.7$			
Petite Riviere Noire	8.1 ± 0.2	$8.2 \pm 0.1$	$6.0 \pm 1.3$	$4.7 \pm 0.3$			

Stations	Dissolved nitrate µmol l <sup>-1</sup>		Dissolve phosphate µmol l <sup>-1</sup>		
	winter	summer	winter	summer	
St Louis	65.7 ± 13.3	$38.97 \pm 24.4$	$1.7.7 \pm 0.8$	$2.67 \pm 1.2$	
GRNW	80.3 ± 41.3	82.2 7 ± 21.4	$1.3\ 7\pm 0.3$	$1.7.7 \pm 0.3$	
Flic en Flac	$15.2 \pm 32.9$	4.97 ± 5.9	$1.53\ 7\pm 2.0$	$1.2.7 \pm 0.8$	
Tamarin	$9.8 \pm 11.9$	$11.87 \pm 8.8$	$0.98~7\pm~0.7$	$1.25\ 7\pm\ 0.9$	
Grande Riviere Noire	$2.45 \pm 1.4$	$2.987 \pm 2.3$	$1.2.7 \pm 0.8$	$1.37 \pm 0.7$	
Petite Riviere Noire	$13.1 \pm 16.2$	3.07±1.9	$1.87 \pm 0.6$	$1.87 \pm 0.6$	

 Table 7. Dissolved nitrate and phosphate in winter and summer in estuaries.

# Table 8. Mean trace metal concentrations in estuarine sediments in winter in mg/kg.

Station	Mean	Std dev	Mean Zn	Std dev	Mean Pb	
	Cr					St Dev
Upstream St						
Louis	192.1	85.8	268	46.1	45	6.6
Downstream St						
Louis	229.2	75.1	261	33.8	55	6.1
St Louis estuary	177.64	86.1	159.46	61.7	31	8.8
GRNW	278.18	108.0	174.05	58.75	36.26	17.27
Flic en Flac	138.07	52.3	25.91	11.22	26.6	17.61
Tamarin	215.15	88.2	57.58	55.30	22.7	17.71
Grande Riviere						
Noire	259.07	116.4	87.21	2.33	19.2	13.15
Petite Riviere						
Noire	283.90	84.6	137.35	12.44	25.9	16.06

•

Station	Mean	Std dev	Mean Zn	St dev	Mean Pb	St dev
	Cr					
Upstream St						
Louis	266.0	116.7	223	42.7	40	17.7
Downstream						
St Louis	233.7	62.0	262	23.9	78	17.0
St Louis						
estuary	206.3	8.4	131	9.9	40	12.0
GRNW	290.68	180.0	130.7	12.1	31.8	27.1
Flic en Flac	83.26	45.6	36.40	49.1	34.6	27.6
Tamarin	109.97	91.0	46.0	26.7	32.7	26.0
Grande						
Riviere						
Noire	197.23	82.8	80.9	15.5	29.19	23.9
Petite Riviere						
Noire	251.91	100.3	150.9	33.2	33.90	25.6

Table 9. Mean trace metal concentrations in estuarine sediments in summer in mg/kg.
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Station	Species name	Mean	Std	MeanZn	Std Dev	Mean Pb	Std Dev
		Cr	Dev				
GRNW	Enteromorpha sp.	18.9	14.0	79.2	85.6	13.2	6.5
	Ulva sp.	20.6	13.7	42.1	46.1	7.8	3.9
Flic en	Padina sp.	12.8	7.8	53.0	52.4		
Flac	_					3.6	0.1
Tamarin	Padina sp.	17.0	10.1	59.8	46.2	5.1	1.7
	Ulva sp.	33.4	20.6	74.6	85.9	9.8	7.4
Riviere	Padina sp.	29.8	14.6	65.6	85.0	8.1	4.0
noire							
Le Morne	Padina sp.	31.4	15.3	24.4	20.3	7.3	3.4
	Ulva sp.	25.5	9.7	65.1	70.3	8.5	3.2

Table 10. Mean trace metal concentrations in algal tissues in winter in mg/kg.

Table 11. Mean trace metal concentrations in algal tissues in summer in mg/kg.

Station	Species name	Mean	Std	MeanZn	Std Dev	Mean Pb	Std Dev
		Cr	Dev				
GRNW	Enteromorpha sp.	73.6	42.4	39.5	19.9	38.4	8.4
	Ulva sp.	38.8	5.8	14.0	1.8	19.1	6.0
Flic en	Padina sp.	50.3	12.6	28.8	14.7	34.4	14.5
Flac							
Tamarin	Padina sp.	42.7	5.8	14.6	3.7	30.3	14.9
	Ulva sp.	55.9	16.8	35.1	24.3	41.3	18.0
Riviere	Padina sp.	55.7	17.5	22.9	9.1	46.7	26.6
noire							
Le Morne	Padina sp.	46.9	5.0	24.2	0.4	34.9	3.7
	Ulva sp.	29.2	4.3	17.9	20.9	36.7	5.1

Table 12. Pairwise comparisons of estuarine sediments at GRNW, St Louis, Tamarin and Petite Riviere Noire and during 2001 using t-test at 5% significance level. (ns- not significantly different).

	Comparisons at 5% significance level using t-test (2tail)					
	GRNW and St Louis	St Louis and Tamarin	Tamarin and Petite Riviere Noire			
CHROMIUM	ns	ns	ns			
ZINC	ns	significant t =10.633 t (crit.) = 2.179 n=7	significant t =-4.992 t (crit.) = 2.179 n=7			
LEAD	ns	significantsignificant $t = 4.481$ $t = 3.833$ $t (crit.) = 2.179$ $t (crit) = 2.306$ $n=7$ $n=7$				

Table 13. Pairwise comparisons of estuarine sediments upstream, downstream and in estuary along St Louis and during 2001 using t-test at 5% significance level. (ns- not significantly different).

	Comparisons at 5% significance level using t-test (2tail)						
	Upstream and downstream St Louis	Downstream and estuary St Louis	Upstream and estuary				
CHROMIUM	ns	n.s	ns				
ZINC	ns	significant t =5.616 t (crit.) = 2.179 n=7	significant t =4.4064 t (crit.) = 2.179 n=7				
LEAD	ns	significant t =3.907 t (crit.) = 2.179 n=7	ns				

Table 14. Pairwise comparisons of algal tissues *Padina sp* and *Ulva sp* at GRNW, Flic en Flac, Tamarin and Le Morne and during 2001 using t-test at 5% significance level. (ns-not significantly different).

	Comparisons at 5% significance level using t-test (2tail)						
	GRNW and Tamarin <i>Ulva sp</i>	GRNW and Le Morne <i>Ulva sp</i>	Flic en Flac and Tamarin <i>Padina sp</i>				
	ns	ns	ns				
CHROMIUM							
ZINC	ns	ns	n.s				
	ns	ns	n.s				
LEAD							

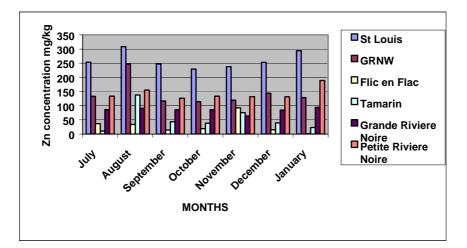


Figure 9. Zinc concentration in estuarine sediments.

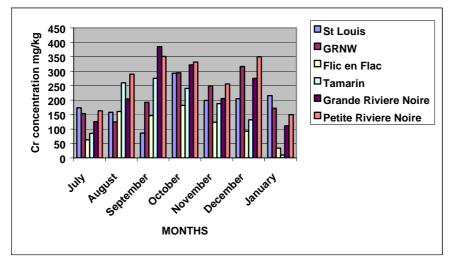


Figure 10. Chromium concentration in estuarine sediments.

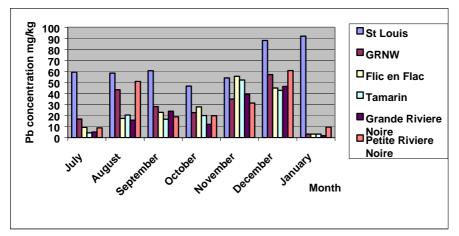


Figure 11. Lead concentration in estuarine sediments.

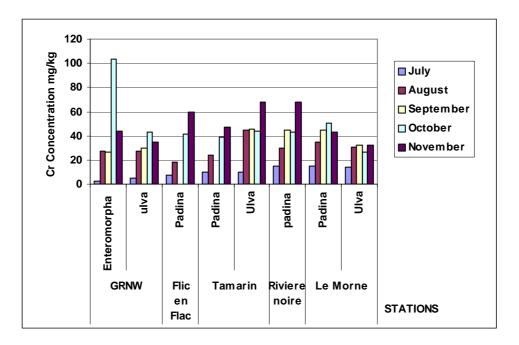


Figure 12. Cr concentration in algal tissues at different stations.

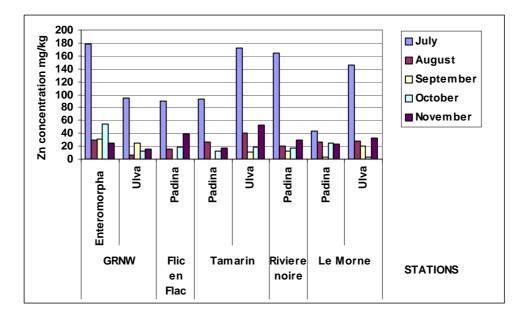


Figure 13. Zn concentration in algal tissues at different stations.

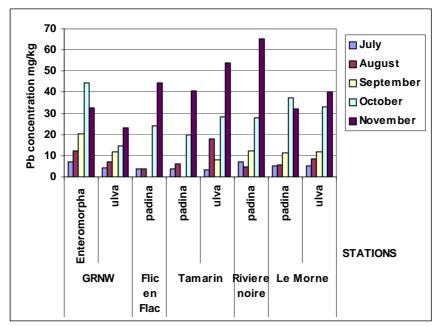


Figure 14. Pb concentration in algal tissues at different stations.

### Discussion.

The general water quality of the 6 estuaries were reasonably good with somewhat elevated concentrations of dissolved phosphate and nitrate in the St Louis estuary. Dissolved oxygen were generally higher in the estuaries south Grand River Bay and fell within a range which is considered to be acceptable for the adequate protection of fish and estuarine life in all 6 estuaries. Zn and Pb were significantly higher downstream St Louis compared to Tamarin estuary at 5 % significance level. Zn was also significantly lower in Tamarin compared to Petite Riviere Noire estuary. Cr was not significantly different in sediments collected from GRNW, Tamarin and Petite Riviere Noire estuaries. Both Cr and Zn in sediments exceeded the target values of 100 and 180 mg kg<sup>-1</sup> in contaminated sediments adopted from the draft standards (24% clay and 10% organic matter by weight) from Netherlands (Van Veen and Stortelder, 1998) respectively at some stations. However, Pb was within the 50 mg kg<sup>-</sup> <sup>1</sup> target value (Van Veen and Stortelder, 1998) and much less than values exceeding 700 mg kg<sup>-1</sup> as indicated by Mungur and Choong Kwet Yive (1998) for soil samples pollution collected near the M1 motorway adjacent to the GRNW catchment area which has a daily traffic density of about 20 000 vehicles. For comparison purposes, the values of Pb in the sediments in the 6 estuaries were also below those reported by Miller et al. (2000) who reported high Pb (33-996 mg kg<sup>-1</sup>) whereas Cr in the 6 estuaries had values similar to Cr (120-300 mg kg<sup>-1</sup>) concentrations in Holy Loch sediments in Scotland. Cr, Zn and Pb were also not significantly different in Ulva sp. and Padina sp. collected along GRNW, Flic en Flac, Tamarin and Le Morne. Both Zn and Pb were also significantly higher in sediments downstream St Louis compared to the estuarine sediments at 5 % significance level. The presence of zinc, chromium and lead in St Louis can be attributed to the high industrial activity, roadrunoff and urban activity prevailing in the area. The concentration of Zn and Pb were greatest in the more urbanised upper and lower reaches of the St Louis estuary during the period of study. It also seemed that environmental factors such discharges to the estuary, rainfall and runoff may have an overall influence in the different estuaries. River transportation patterns may be dependent on climatic conditions, especially on rainfall events. Cr, Zn and Pb were not significantly different in the estuarine sediments in the wet and dry season during the period of study and a pattern of seasonal wash-out in

addition to the dilution by uncontaminated materials may occur during periods of heavy rains and cyclonic conditions.

The temporal patterns in metal concentrations in estuarine sediments and algal tissues Enteromorpha, Ulva and Padina sp did not show seasonal variations. The level of Pb and Zn in the algal tissues Ulva, Padina and Enteromorpha sp in the estuaries were in the range similar to those found in algal tissues of Fucus vesiculosus in the not seriously polluted Humber estuary, U.K as reported by Woodward (1984). The patterns found in the estuaries may be the result of local anthropogenic sources and mixing of contaminated sediments with relatively clean marine sediments. The distribution suggests that local elevations in metal concentrations are the result of direct anthropogenic inputs rather than the fluxes between sediment mixing. It did not appear that microbial activity within the sediments increased metal levels by accumulation or decreased them by mobilisation. The decontamination of contaminated sites of the estuary and lagoon will become necessary to prevent harm to the environment in the long term. Any engineering solution for this problem in order to be implemented has to take into account the distribution of the amounts of Cr, Zn and Pb in the Grand River estuary. Furthermore, the evaluation of sediment remedial alternatives should consider their feasibility, contaminant losses, overall environmental impacts and total project costs. Capping is a recent applied technology to remediate contaminated bottom sediments that avoids the removal of the contaminants. The cap can be constructed of clean sediments, sand or gravel or may involve a more complex design using geotextiles and multiple layers as reported by Pereira et al. (1998) for mercury contaminated sediments in Aveiro's lagoon, Portugal. The more common solution to contaminated areas remain dredging.

## CHAPTER 5

## **Conclusions and Recommendations**

## Main Conclusions.

- The general water quality of the 6 estuaries along the western coast were reasonably good with somewhat elevated concentrations of dissolved phosphate and nitrate in the St Louis estuary. Dissolved oxygen were generally higher in the estuaries south Grand River Bay and fell within a range which is considered to be acceptable for the adequate protection of fish and estuarine life.
- The mean concentration of Cr, Zn and Pb in the estuarine sediments in both summer and winter were well below the limits of 600, 2500 and 700 mg kg<sup>-1</sup> quoted for contaminated sediments adopted from the draft standards (24% clay and 10% organic matter by weight) from Netherlands (Van Veen and Stortelder, 1998).
- The levels of Pb and Zn in the algal tissues *Ulva, Padina* and *Enteromorpha sp* in the estuaries along the western coast of Mauritius were in the range similar to those found in algal tissues *Fucus vesiculosus* in the not seriously polluted Humber estuary, U.K as reported by Woodward (1984).
- The concentrations of Cr, Zn and Pb in the estuaries along the western coast of Mauritius generally fall within a range which is considered to be acceptable for the adequate protection of fish and other estuarine life.
- The significant levels of Zn, however, in sediments in the St Louis compared to Tamarin estuary suggest that the potential sources may be from the adjacent motorway and road runoff causing significant quantities to be trapped within the St Louis River.
- Pb was higher in the sediments in the estuary of St Louis River compared to Tamarin indicating accumulation of Pb in estuarine sediments which may be

released continuously into the lagoon. The potential sources of Pb in sediments in the St Louis estuary may be from the adjacent motorway and road runoff causing significant quantities to be trapped within the St Louis River.

#### **Recommendations for Future Work.**

There is at present a need for long-term perspectives in water resource management to involve integrated strategies in which water-sediment interactions need to be considered and international standards for sediment quality developed. Wastewater management increasingly needs to understand the assimilative capacity of sediments and biota which are major sinks and the threat of reworking of contaminated sediments through natural and anthropogenic processes poses a long-term hazard which requires evaluation in Mauritius. The sediment environment should provide a long term record of the effects of anthropogenic discharges, such as industrial effluents as it is an area where impacts often occur before effects are manifest in the water column. In contrast to the strong temporal and spatial variability in the aqueous concentrations of contaminants, where a large number of samples is required, sediments integrate contaminant concentrations over time and by focusing on sediments, the number of samples needed in contamination assessment can be reduced.

A number of research projects which could be undertaken in the future have been identified.

1. Trace metal content in various fractions of sediments (organic matter, exchangeable, bound to carbonates, bound to Fe-Mn oxides) and suspended particulate matter could be assessed as well as trace metal bioavailability and toxicity to local flora and fauna.

2. Other trace metals such as Al, Ni, Cd and Mn in sediment and biota samples collected along an axial transect of St Louis River covering a wide salinity range from upstream to estuarine environment could also be investigated to assist further geochemical interpretation.

3. The dynamics of particulate trace metals could also be examined to differentiate permanently suspended particulate material (PSPM) from temporarily suspended

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material (TSTM) and desorption of labile trace metals investigated on encountering the salinity.

4. The study could also be focused on cyclone events to assess changes in organic profiles and the importance of diffusion of metals from interstitial waters to the water column as compared to storm resuspension.

6. An estuarine model for trace metal and nutrient export and fluxes from the estuary to the lagoon could then be developed following measurement of currents, tides and river flow as estimated in Aveiro 's lagoon, Portugal for Hg and in some tropical coastal environments.

7. A computer assisted budget analysis could then help in the understanding of biogeochemical fluxes in estuaries as established by the Land-Ocean Interactions in the Coastal Zone (LOICZ) programme under the International Geosphere Biosphere Programme.

This study has showed that a phasedown of Pb in petrol is necessary in the near future. With the introduction of unleaded petrol and vehicles equipped with catalytic converters, it will become necessary to initiate studies on Pd and Pt to provide baseline data. These research projects undertaken in the future would then further the understanding of the biogeochemical processes of estuaries which could be used in environmental development schemes and effective integrated coastal zone management of small island states.

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# **APPENDIX.**

Site Name	July	August	September	October	November	December	January
St louis	173.663	157.838	85.700	293.375	198.763	204.838	215.346
St louis	72.413	203.888	157.600	265.375	222.113	223.700	75.038
Grnw	154.513	223.225	348.125	386.875	393.875	396.375	81.800
Grnw	153.475	123.975	192.563	294.875	249.538	316.625	171.588
Flic en Flac	62.750	160.938	146.575	182.013	123.488	92.588	33.713
Tamarin	84.563	260.000	275.375	240.675	188.025	131.900	9.975
Grande	125.675	203.725	385.000	321.875	205.463	275.625	110.588
Riviere							
Noire							
Petite	162.988	289.625	351.250	331.750	256.000	350.125	149.613
Riviere							
Noire							

Figure A1. Chromium levels in sediment samples (mg/kg)

 Table A2 Lead levels in different sediment samples (mg/kg)

Site name	July	August	September	October	November	December	January
St Louis	59.363	58.488	60.725	46.775	54.225	88.113	92.021
St louis	17.000	64.813	98.088	67.550	55.838	78.025	82.250
Grnw	8.138	53.200	38.875	34.575	46.500	52.025	49.838
Grnw	16.775	43.400	28.163	22.588	35.000	57.113	3.200
Flic en Flac	9.250	17.375	22.950	27.850	55.563	44.975	3.200
Tamarin	4.325	20.450	16.713	20.038	52.175	42.838	3.200
Grande Riviere Noire	5.150	15.763	23.938	11.975	39.388	46.400	1.775
Petite Riviere Noire	8.800	50.888	18.925	19.863	31.313	60.788	9.588

 Table A3. Zinc levels in the different sediment samples (mg/kg)

Site name	July	August	September	October	November	December	January
St louis	253.500	308.125	247.075	229.150	237.463	253.163	294.234
St louis	124.525	296.500	244.275	202.463	190.925	221.900	274.750
Grnw	138.050	259.750	164.675	133.725	187.938	167.463	254.250
Grnw	133.400	246.463	116.575	114.588	119.775	143.775	128.563
Flic en Flac	36.725	34.113	13.850	18.963	92.588	15.263	1.350
Tamarin	10.950	137.725	43.363	38.263	75.475	39.325	23.263
Grande	86.350	90.688	85.950	85.850	63.850	84.675	94.075
riviere noire							
Petite	134.050	155.288	126.513	133.550	131.825	131.675	189.288
rivierenoire							

Table A4. Chromium levels in the different algar samples (hg/kg)							
	TIME	July	August	September	October	November	
STATION	ALGAL						
	SPECIES						
GRNW	Enteromorpha	2.763	27.4375	26.64	103.5625	43.6	
	ulva	4.8375	27.22	29.65	42.9125	34.65	
Flic en Flac	Padina	7.285	18.25	Not	41.4375	59.2375	
				available			
Tamarin	Padina	9.9	24.15	Not	38.5625	46.7625	
				available			
	Ulva	9.6375	44.928	45.725	44.0125	67.7375	
Riviere	padina	15.1125	29.85	44.35	43.3875	68.1	
noire							
Le Morne	Padina	14.775	34.6875	44.96	50.4	43.35	
	Ulva	14.25	30.25	31.9125	26.1875	32.2	

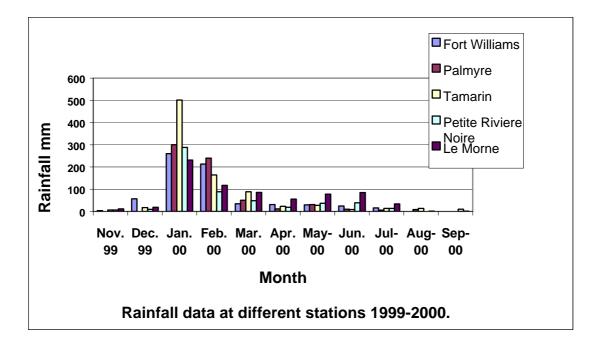
**Table A4.** Chromium levels in the different algal samples (mg/kg)

Table A5. Zinc levels in the different algal samples (mg/kg)

	TIME	July	August	September	October	November
<b>STATION</b>	ALGAL SPECIES					
GRNW	Enteromo rpha	178.125	28.95	30.6625	53.575	25.405
	Ulva	94.35	6.8875	25.1	12.612 5	15.175
Flic en Flac	Padina	90.025		Not available	18.4	39.1375
Tamarin	Padina	92.44	27.0875	Not available	11.937 5	17.1625
	Ulva	172.313	40.875	10.66	17.9	52.3
Riviere noire	Padina	163.6	20.075	13	16.45	29.2875
Le Morne	Padina	43.9125	25.8375	3.425	24.487	23.85
	Ulva	146.2125	28.55	20.625	3.1625	32.6625

## **Table A6.** Lead levels in the different algal samples (mg/kg)

	TIME	July	August	September	October	November
STATION	ALGAL SI	PECIES				
GRNW	Enteromo rpha	7.2825	12.275	20.15	44.35	32.4125
	Ulva	4.225	7.325	11.8875	14.7875	23.3125
Flic en Flac	Padina	3.586	3.6875	Not available	24.125	44.6625
Tamarin	Padina	3.9125	6.2875	Not available	19.7	40.825
	Ulva	3.4875	17.875	8.0625	28.6125	54.0375
Riviere noire	Padina	7.2625	4.5	12.3875	27.8875	65.4875
Le Morne	Padina	5.125	5.6875	11.2125	37.5	32.2375
	Ulva	5.1875	8.525	11.675	33.125	40.3375





# Photo 1 GRNW Estuary.



Photo 2 GRNW Estuary.



Photo 3 Rivulet at Flic en Flac.

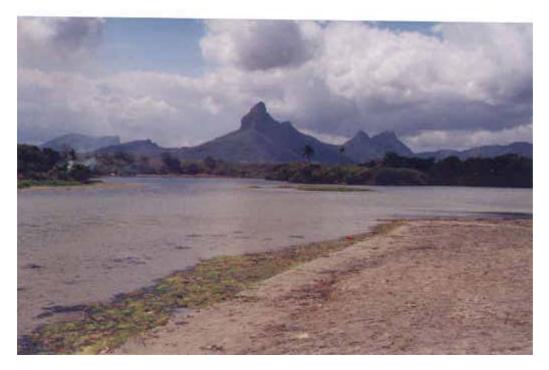


Photo 4 Tamarin estuary.



Photo 5 Tamarin estuary.



Photo 6 Grande Riviere Noire.

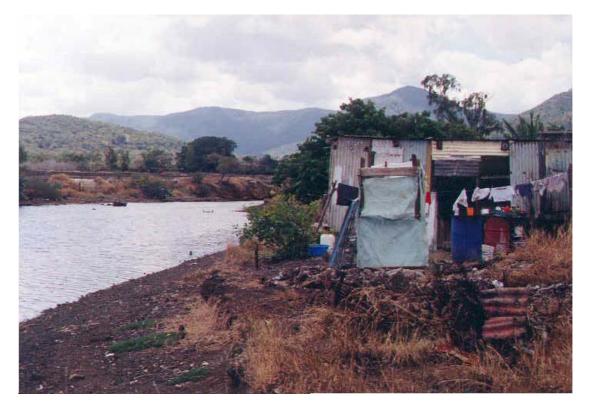


Photo 7 Petite Riviere Noire.



Photo 8 Domestic effluents at Petite Riviere Noire.