AN ASSESSMENT OF THE EXTENT OF MERCURY POLLUTION OF THE MNGCEWENI STREAM, THE UMGENI RIVER AND THE INANDA DAM IN KWA ZULU NATAL

by

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I, Graham James Barratt, do declare that the dissertation is representative of my own work.

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ABSTRACT

The debate surrounding mercury pollution of the river system below Thor Chemicals in Kwa Zulu Natal, South Africa has been of concern to the people of the region for several years. No scientific assessment of Mercury pollution has been carried out to date, other then a study conducted by Johnston *et al.* (1991) in 1990 in an area restricted to within 5 kilometres of the plant.

Due to elevated levels being detected directly below the plant, Johnston *et al.* (1991) have expressed concern that this could result in the mobilisation of Mercury into the ecosystem and possibly threaten the Ecology of the Inanda Dam which is located approximately 20 kilometres south of Thor Chemicals which is a major reservoir for Durban. Added to this, the community residing in the area has expressed a great deal of concern and the matter was taken up in parliament in 1998. These factors provide impetus for a follow up study to determine the extent of mercury transformation into the higher trophic levels in the area surrounding Thor Chemicals. In order to quantify the extent to which mercury has become mobilised in the ecosystem and to identify possible pathways of exposure to the community, samples of sediment, algae, cattle hair and fish were taken at ten sample sites. These sample sites were selected at intervals along the Mngceweni and Umgeni River. The first sampling site was situated below Thor and the final sample site was located at the head of the Inanda Dam. Sediment, algae, cattle hair and fish were specifically chosen as they are considered to be reliable indicators of mercury pollution and mobilization. Fish,form an important part of the diet of the community residing in the study area. Mercury concentrations for the above parameters, were compared to mercury concentrations found in the control area, upstream from Thor, as well as to international and local standards.

Composite sediment samples taken at the first sample site, within 500 metres of Thor Chemicals, revealed a mercury level of 54μg/gram. Mercury concentrations detected in the remainder of the composite sediment samples were significantly lower and revealed similar levels of magnitude throughout the rest of the study area. The higher concentration of mercury in the sediment at the site directly below Thor Chemicals may be attributed to a high

pH which could be preventing the mercury from leaching from the sediment bed. When comparing the concentration of mercury in only one composite sediment sample to those analysed 10 years previously by Johnston *et al.* (1991), the mercury levels in the sediment at the confluence of the Mngceweni and Umgeni River (approximately 8 kilometres down stream of Thor Chemicals) appear to have increased by 98%. This may indicate bio-transformation, although other factors could attribute to the significant increase in mercury concentration since 1990. Mercury concentrations in algae, cattle hair and fish, obtained from the Umgeni River were all below detectable limits, which suggests that the mercury has not bio-accumulated or transferred to these higher trophic levels within the study area.

Although the concentrations of mercury analysed in the fish obtained from Inanda Dam were lower than the FDA action level (US. EPA, 1997) and the South African Foods, Cosmetics and Disinfectants Act (FDC Reg, 1994), the scenario that emerges is considerably different when comparing the above action levels to consumption levels as given by the US EPA[3]. In terms of the guidelines provided by the US EPA, 60 % of the fish sampled in Inanda Dam have sufficiently elevated mercury levels that would indicate that consumption should be restricted to three to four fish meals from this area in a month[3]. These preliminary findings strongly suggest a need to quantify the risk of mercury poisoning to the fish eating population residing in the study area.

TABLE OF CONTENTS

CHAPTER 2

CHAPTER 4

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

ANNEXURES

LIST OF ABBREVIATIONS

CNS	-	Central Nervous System
CVAA	-	Cold Vapour Atomic Absorption
DOC	-	Dissolved Organic Carbon
ELEL	-	Estimated Lowest Effect Level
Hg	-	Mercury
IPCS	-	International Programme on Chemical Safety
IRIS	-	Integrated Risk Information System
NOAEL	-	No Observed Effect Level
RfD	-	Reference Dose.
SABS	-	South African Bureau Of Standards.
SA FCD Act	-	South African Food, Cosmetics and Disinfectants Act
US EPA	-	United States Environmental Protection Agency
US FDA	-	United States Food and Drugs Administration
TDI	-	Tolerable Daily Intake
WHO	-	World Health Organisation

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CHAPTER 1

INTRODUCTION

1. BACKGROUND.

Elemental mercury is a heavy, silvery-white liquid at typical ambient temperature and atmospheric pressure. Mercury can exist in 3 oxidation states: Hg^0 (metallic), Hg_2^{2+} (mercurous) and Hg^{2+} (mercuric). The properties and behaviour of mercury depend upon it's oxidation state. Most of the mercury in water, soil, sediments or biota (i.e., all environmental media except the atmosphere) is in the form of inorganic mercury salts and organic forms of mercury, particularly methylmercury (US EPA, 1997).

The major natural sources of mercury are degassing of the earth's crust, emissions from volcanoes, and evaporation from natural bodies of water. Natural emissions are of the order of 2700-6000 tonnes per year. Human activities account for an estimated release of 3000 tonnes per year. Other important sources are fossil fuel combustion, metal sulfide ore smelting, gold refining, cement production, refuse incineration, and industrial applications of metals. Mercury vapour is converted to soluble forms and deposited by rain onto soil and water. The atmospheric residence time for mercury vapour is as long as 3 years, whereas soluble forms have a residence time of only a few weeks (Clarkson, 1992).

Mercury, usually in trace amounts, is found throughout the ecosystem: in soils, water, air and in living species. Because mercury can undergo a variety of physical and chemical transformations, and because it can be ingested in foods, it is readily transported in, and transferred between, these media. Mercury is extremely mobile in the environment. Natural cycles transform and transport mercury in a wide variety of ways throughout air, water and soil. Mercury in bottom sediments of waterways is converted by bacteria into methylmercury, being the more lethal toxic form of mercury (Sittig, 1976). Once in aquatic systems, mercury can exist in dissolved or particulate forms and can undergo a number of chemical transformations. Contaminated sediments at the bottom of surface waters can serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer. Mercury has a long retention time in soils. As a result,

mercury that has accumulated in soils may continue to be released to surface waters and other media for long periods of time, possibly hundreds of years (US EPA, 1997).

According to Clarkson (1992) the change in speciation of mercury from inorganic to methylated forms is the first step in the aquatic bio-accumulation process. This can occur non-enzymatically or through microbial action. In broad terms it can therefore be stated that methylmercury enters the food chain of predatory species where biomagnification occurs. Kannan *et al.* (1998) have described that the path way of mercury biomagnification begins where rivers and estuaries receive sewage and industrial effluent which constitutes the principal source of aquatic pollution. Sediments play a critical and beneficial role in reducing the availability of mercury to water or the biota, by acting as a sink where the metal is bound to the sediment. Later, however, when the primary sources of the metal pollution are eliminated, the sediments may act as secondary sources, posing a potential long term threat to the aquatic ecosystem.

Clarkson (1992) further discovered that among sediment bound metals, mercury in particular is of major eco-genotoxological concern because it not only undergoes transformation to highly toxic methylmercury, but is also biomagnified through the food chain. A world wide survey of mercury discharges into the environment, indicates that most of the increase in environmental mercury occurs in the less developed regions of the world due to poor environmental protection regulations or economic constraints preventing industries from introducing effective control measures. Several hot spots of mercury sediment have been reported around the world and the highest concentrations of mercury occur near industrial sites such as chlor-alkali plants.

Control of aquatic mercury pollution would be possible through effective management approaches, which require comprehensive data base of the distribution, and the availability of the metal in the sediment. Analysis of sediment has been widely applied to monitor the mercury pollution of aquatic environments. However, Kannan *et al.* (1998) concluded that the disadvantage of using sediment for monitoring purposes is that it does not provide a direct estimate of the metal to the biota. Organisms based bio-monitoring is therefore preferred.

Aquatic organisms derive most of their energy from algae at the base of the food chain. From this initial point of entry the element is concentrated up the food chain (Milta, 1986). A study by Bailey and Stokes (1985) in soft water lakes in Canada, also indicated the capacity of algae to bio-concentrate mercury to levels 1000 to 10 000 higher than in water. Clarkson (1992) found that from the early stages of transfer into the aquatic food chain, small organisms, such as plankton will absorb mercury and eventually transfer this metal into much higher concentrations in large predatory fish. Methylmercury is not readily eliminated from fish so that it accumulates throughout the lifetime of the fish. The highest concentrations of methylmercury are found in the oldest, top predatory fish. The bio-accumulation factor from water to edible fish tissue, exceeds 10 million for certain species of fresh and ocean water fish. Several other factors affect methylmercury levels in fish. Lower pH values in rivers, or impounded water, favour methylation over demethylation reactions in sediments, thereby increasing the probability that methylmercury will concentrate in the higher trophic levels of fish. The impounding of rivers and lakes also raises methylmercury levels in fish. In conclusion Clarkson (1992) proposed that the flooding of vegetation could also result in enhanced substrate supply to microorganisms, including those species that methylate mercury.

Humans are most likely to be exposed to methylmercury through fish consumption. Exposure may occur through other routes as well, including the ingestion of methylmercury contaminated drinking water and food sources, other than fish, and dermal uptake (from soil and water). However, the fish consumption pathway dominates these other pathways among people who eat fish regularly (USEPA 1997). The most widely documented and severe case of methylmercury pollution to date, occurred at Minamata in Japan during the 1950s. Clarkson (1992) relates how an acetaldehyde manufacturing plant near Minamata Bay was using inorganic mercury salts as catalysts in production processes. Some of the mercury was chemically converted to methylmercury compounds and accidentally released in waste waters which was discharged into the large ocean bay. This had devastating consequences for fisherman, their families and fish consumers in the area. The pollution episode illustrated the unique property of methylmercury to accumulate in such high concentrations in fish tissue and caused widespread fatalities among fish consumers.

1.2 MOTIVATION FOR THE STUDY.

Thor Chemicals (Plate 1) is located near Cato Ridge between Durban and Pietermaritzburg in Kwa Zulu Natal, South Africa and was until recently the worlds largest mercury incinerator plant (Clarke, 1994). According to an American news paper report (Lambrecht, 1989) this factory processed mercury waste from as early as 1986. Their supplies came from a variety of local sources, namely AECI, and from overseas companies, such as Lederle Laboratories, a division of the American Cyanamid Company. These companies shipped spent mercury chemicals, mercury contaminated water and mercury sludge as well as contaminated pipes and rings in drums to Thor Chemicals for processing. The American newspaper (Lambrecht, 1989) concluded that toxic organic mercury waste was incinerated at Thor Chemicals in order to reclaim mercury.

The occupational exposure of workers to mercury and the subsequent manifestations of classic signs and symptoms made headlines worldwide in the early 1990's. The senior management of the plant were subsequently prosecuted for their negligence and failure to enforce proper occupational hygiene control measures (Nichols, 1995).

Plate 1.1 The Northern Boundary of Thor Chemicals, Kwa Zulu Natal and of a Holding Pond situated at the Boundary Fence of the Factory from Where Discharges May Have Taken Place.

A lengthy article in the Sunday Tribune (Clarke, 1990) declared that as early as 1989 that effluent comprising of mercury had overflowed into the Mngceweni River from holding ponds situated at Thor Chemicals. The source of Mngceweni River is situated near the eastern boundary of the chemicals plant. The article also stated that in early April 1990, drums containing spent mercury were emptied into this river. At the time, a Green Peace spokesman expressed concern about the probability of these contaminants rapidly being converted into methylmercury in the environment. Within that same month Green Peace had conducted an "under wraps" investigation of mercury leakage. Their findings showed that the mercury levels a few hundred metres from the boundary of Thor Chemicals plant were 8600 times higher in soil and sediment than the United States limit for toxic waste. The environmental group reported that families living downstream from the Thor Chemicals Plant, were using the contaminated water for both domestic and agricultural use. However, Green Peace was of the opinion that mercury pollution probably did not pose a threat at the lower reaches of the river system. Nevertheless there were fears that the mercury could undergo biological change to methylmercury and threaten the drinking water supplies of the greater Durban area. Of particular concern was the Inanda Dam, which is a major reservoir in the Durban water supply system. Further, it was reported that the mercury was being carried along with sediments into the major river basin and as such could compromise the integrity of the ecosystem. It also was reported that gross environmental contamination had taken place over a number of years. However as the Sunday Tribune article (Clarke, 1990) concluded that this claim has never been adequately investigated and the potential impact of such pollution on local communities is yet unknown.

Since then, Thor Chemicals has attracted considerable media attention, culminating in certain matters being discussed in the South African Parliament. However, most of the attention centred around the occupational exposure of workers. The environmental aspects were never satisfactorily dealt with (Clarke, 1994). In recent years Chief Malaba and the community of the Valley of Thousand Hills began to express their concern about the possible effects that mercury pollution may have had on people living there.

Although several years have passed since the last recorded discharge of waste from Thor Chemicals, several questions remain unanswered. Of particular concern is the extent of

mercury contamination of the ecosystem and the possible negative implications for the community. Seeking answers for these critical questions contributed to the motivation for this study.

The objectives therefore are:

i) To determine the extent of environmental mercury contamination of the river system downstream from Thor Chemicals, up to and including the Inanda Dam.

ii) To quantify the extent to which mercury has become mobilised in the ecosystem and to identify pathways of exposure to people living in the area.

iii) To recommend appropriate interventions, if deemed necessary.

1.3 RATIONALE FOR THE STUDY :

I) Studies of industries similar to Thor Chemicals, in Northern Canada and the Amazon have indicated significant risk to exposed communities in these areas (Jackson, 1991; Rasmussen, 1994; Barbosa *et al.*, 1995; Guimares *et al.*, 1998). It is, therefore, imperative that the risk to people residing in the vicinity of Thor Chemicals be scientifically quantified.

ii) Fish forms an important part of the diet of the community living near Thor Chemicals, in particular children and pregnant females, thus placing these individuals at a potentially elevated risk (Soria *et al.*, 1992).

CHAPTER 2

2. MERCURY IN THE ENVIRONMENT AND ITS EFFECT ON HUMANS.

Mercury cycles in the environment as a result of natural and anthropogenic activities. The amount of mercury mobilized and released into the biosphere has increased since the beginning of the industrial age. Most of the mercury in the atmosphere occurs in the form of elemental mercury vapour, which circulates in the atmosphere for up to a year, and hence can be widely dispersed and transported thousands of miles from likely sources of emission. Most of the mercury in water, soils, sediments, or plants and animals is in the inorganic form. Inorganic mercury, when either bound to airborne particles, or in a gaseous form, is readily removed from the atmosphere by precipitation and dry deposition. Wet deposition is the primary mechanism for transporting mercury from the atmosphere to surface waters and land. Even after it is deposited, mercury is commonly emitted back to the atmosphere either as a gas or in association with other particles, to be re-deposited elsewhere. As it cycles between the atmosphere, land and water, mercury undergoes a series of complex chemical and physical transformations, many of which are not completely understood (WHO, 1991).

2.1 CHEMICAL TRANSFORMATION OF MERCURY IN THE ENVIRONMENT

The WHO (1991) describes that inorganic forms of mercury undergo transformations in the environment, mainly by oxidation-reduction reactions. Mercury vapour is oxidised to ionic, divalent mercury (Hg^{++}) when in water and in the presence of oxygen. The oxidation of metallic mercury to inorganic divalent mercury is greatly favoured when organic substances are present in the aquatic environment.

Hg^{++}once present in water, is capable of forming a wide variety of complexes and chelates with organic materials. Of considerable importance is the reaction with the sulfide (S^{-}) ion to form highly insoluble mercury sulfide. This reaction is likely to occur in anaerobic aquatic environments owing to the presence of hydrogen sulfide gas. This sulfide complex of mercury is highly stable and will not normally become involved in transformation under anaerobic

conditions. However, in the presence of oxygen, the insoluble mercury sulfide can become oxidised to the soluble mercury sulfite salts which allow the metal to ionise and to enter subsequent chemical reactions. In addition to the oxidation of metallic vapour, Hg^{++} can be formed by the breakdown of a variety of organic mercury compounds. The alkoxyalkylmercury compounds are very unstable in acid conditions within humid soil. Methoxyethylmercury has a half life of only three days.

Hg^{++} can undergo two important reactions in the environment. The first is the reduction to metallic mercury vapour, a reaction that will occur in nature under appropriate reduction conditions. An example is with certain bacteria, particularly the genus Pseudomonas, which can convert divalent mercury, into metallic mercury. This formation of Hg^{++} in nature and it's reduction to metallic mercury vapour are probably key processes in the global mercury cycle. The reduction to metallic mercury vapour is a key step in degassing of mercury from the earth's surface. The oxidation of metallic mercury vapour to divalent, ionic mercury is a critical step in the uptake of mercury vapour in rainwater and the oceans. Hg^{++} in nature is converted to methylmercury and dimethylmercury compounds. Methylmercury is the predominant form of mercury in fish, regardless of the nature of the mercury pollutant. Two biochemical pathways of methylation of mercury have been identified, one anaerobic and the other aerobic. Methylation significantly increases the ability of mercury to cross biological membranes. The WHO (1991) concluded that this was the reason why aquatic organisms contain mainly methylmercury.

Mercury compounds from agricultural and industrial sources are converted by bacteria into methylmercury which is soluble, mobile, and rapidly incorporated into aquatic food chains. Mercury concentrates as it moves up the food chain, accumulating in carnivorous fish to levels of up to 10 000 - 100 000 times the concentrations in surrounding water. Between 70% and 90% of the mercury detected in fish muscle is in the bio-available form of methylmercury and hence is readily absorbed (WHO, 1993).

Smith *et al.* (1996) found that mercury present in bottom sediment of rivers and lakes is subject to methylation by microorganisms. Methylmercury enters aquatic food chains, starting with uptake by small organisms, such as plankton, and eventually attaining its highest

concentration in large predatory fish. Methylmercury is poorly eliminated from fish and as a result it accumulates throughout the lifetime of the fish. Thus, the highest concentrations are found in the longest lived, top predatory fish. Several other factors affect methylmercury levels in fish. These include the acidification of bodies of freshwater by acid rain where a lower pH favours methylating over demethylation reactions in water and sediments. The impounding of rivers and lakes also raises methylmercury levels in fish. It has been suggested that the flooding of vegetation results in enhanced substrate supply to microorganisms, including those species that methylate mercury. The raising and lowering of water levels causes further erosion of the banks as well as the deposition of vegetation into the water.

2.2 MERCURY IN SEDIMENT AND SOIL

Once mercury enters a water system, the mercury can remain in the water, be lost from the lake through drainage water, re-volatised into the atmosphere or settle into sediment and be taken up by aquatic biota (US.EPA 1997). The movement of mercury through any water system is dependent on many variables. Of particular importance and concern is the fact that once in aquatic systems, mercury can exist in dissolved or particulate forms and can undergo a number of chemical transformations. Contaminated sediments at the bottom of surface waters serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer. Mercury has a long retention time in sediments and, as a result, mercury that has accumulated in sediments may continue to be released to surface waters and other media for long periods of time, possibly hundreds of years. In river systems, total mercury concentrations have been found to decline sharply and progressively with distance downstream from point source of pollution. This is presumably due to dilution and settling out of mercury bearing suspended particles. In contrast, methylmercury concentrations decreased more gradually or showed no consistent change, or even increased with distance in several studies carried out by Jackson (1993).These studies extended over several hundred kilometres, a considerable distance compared to the distance of 20 kilometres of the study area. The lengthy period of mercury retention in sediment and release over extended distances, emphasises the need to evaluate the extent

of pollution resulting from mercury discharges from Thor Chemicals. Contaminated sediments have been shown to have direct toxic effects on aquatic life[1]. The bio-accumulation of toxic contaminants in the food chain can therefore pose a risk to humans, wildlife and aquatic organisms.

The transfer of mercury into aquatic systems is dependent on the methylation of the mercury. The W H O (1986), has referred to several studies which demonstrate that the methylation of inorganic mercury in the sediment of lakes and rivers is the key step in the transport of mercury in the aquatic food chain. Some of the studies reviewed showed that the degree of methylation correlated well with the overall microbial activity in the sediment. The WHO (1986) consider the following key factors in the methylation of mercury:

i) The rate of methylation is greater under oxidising conditions than under anaerobic conditions.

ii) The output of methylmercury doubles for a ten-fold increase in inorganic mercury.

iii) Temperature affects methylation as a result of its effects on overall microbial activity and higher microbial growth rates increase methylation.

These findings are confirmed by Aula *et al.* (1995) in a study of gold mining activities and the resulting mercury pollution of a water system in the Serra Pelada, South America. The mercury content in sediment was found to be dependent on the concentration of organic matter. Furthermore, the cause for the mobilisation of mercury pollution within a water system was related to the enhancement of microbial activity. The US. EPA (1997), reports that methylation is a key step in the entry of mercury into the food chain. The biotransformation of inorganic mercury species to methylated organic species in water bodies can occur in the sediment and the water column. These findings have been confirmed by many other researchers (Sittig, 1976; Jackson, 1987; Grosheva, 1992; Jackson, 1993; Bidone *et al.*, 1997; Kannan *et al.*, 1998; Fabbri *et al.*, 1998). Furthermore, Park and Curtis (1997) showed that the exchange of sediment-bound mercury returning back to the water column is generally

low because of the strength of mercury binding to humic matter within sediment. From there, mercury is likely to be transferred to other tropic levels. Water samples are, therefore, not considered a good sampling medium to quantify mercury pollution.

Several studies have clearly indicated the importance of the fraction of sediment to which mercury will bind. Aula *et al.* (1995) have shown that a decrease in mercury concentrations was due to the size of the particles analysed, since coarse particles adsorb less mercury. Further Aula found a positive correlation between the content of mercury and the percentage of organic material in sediment. This study emphasised the need to consider, in addition to the percentage of humic matter, the particle size of sediment samples collected for laboratory analysis.

Barghigiani *et al.* (1996) indicated that the highest concentration of mercury in sediment was found in the <20μm grain-size fraction. With the transportation of mercury from land to sea the mercury concentration in the >20μm fraction was negligible. A study by Johnston *et al.* (1991) conducted within the river system below Thor Chemicals, restricted sediment samples to those fractions less than 63 μm. Park and Cutis (1997) and Roulette *et al.* (1998) also confirmed that mercury has a strong affinity for finer particlulates and organic material in river sediments.

A particularly significant study was conducted by Guimaraes (1998) who found that mercury was generally within 4cm below the surface and that methylmercury was detected in only the upper layers (0-2cm) of the sediment with concentrations of methylmercury reaching 0.47% to 0.75% of total mercury. These findings are supported by other studies (US EPA 1997, Kannan *et al*, 1998) and that sediment samples were also obtained where it appeared that the sediment had a high humic (organic) content and a low fraction values. Sand or grit type sediments were discarded. Rasmussen (1994) confined sampling to the top 10 cm of the sediment surface and also restricted sediment sampling to the finer fraction and higher humic sediments.

This sampling methodology of river sediments is consistent with the sampling procedure prescribed by the USA National Water Quality Programme for sediment sampling of trace elements and organic contaminants (Shelton and Capel, 1994).

2.3 THE ROLE OF pH AND TEMPERATURE IN MERCURY MOBILIZATION

Several studies reviewed by the WHO indicated that temperature and pH have a significant influence on microbial activity and the resultant methylation of mercury (US EPA, 1997). Panda *et al.* (1990) in particular indicate that pH has a significant effect on the leaching of mercury from sediment. The pH of sediment at a chlor-alkali plant in India varied between 6.4 and 7.4, with an average value of 7. The leaching of mercury from the sediment samples increased with decreasing pH, irrespective of the site. Experiments carried out by selective leaching from sediment samples within a pH range from 2 to 6 also indicated that mercury removal from sediment increased with decreasing pH. The authors concluded that these findings provided an explanation for the elevated concentrations of mercury in fish from low pH lakes.

Table 2.1 The role of pH in the leaching of mercury from sediment as found at a chlor-alkali plant in India. (Panda *et al.*, 1990)

site	pH	Concentration of total mercury in sediment (μg/gram)
control	6.6	0.38
1	6.7	1.60
2	6.4	4.72
3	7.3	54.53
4	7.0	42.46
5	7.3	192.00
6	7.4	107.89
7	7.3	73.66
8	7.2	44.20

Table 2.1 illustrates the importance of pH in the transfer of mercury from sediment to other trophic levels within an aquatic system, particularly where the pH falls below 6.4. Therefore,

although sediments may provide a reservoir for mercury over a lengthy period, due to the mercury binding to humic matter, a low pH could accelerate the mobilization of mercury from the sediment (Panda *et al.*, 1990). Andersson *et al.* (1995) detected that a mean pH between 5.4 and 5.8 resulted in the greatest uptake of mercury in pike and perch fish. However, after these acidic lakes were limed there was an appreciable decrease in mercury uptake by the fish due to an increase of the pH in the water. Bonzongo *et al.* (1996) reported that methylmercury production tended to decrease with increasing pH in mercury contaminated waters.

Park and Curtis (1997), identified temperature as an important factor in the seasonality of mercury methylation and availability. Methylation increases from spring to late summer and decreases in the fall in the Oregon reservoirs of the USA. Similar findings were reported by Jackson *et al.* (1982), Jackson (1988) and Hintelmann and Winkleman (1995), where seasonal effects showed larger amounts of methylmercury compounds under warmer summer conditions than in cold winter and spring weather. The study area (Valley of 1000 Hills) is located in a sub tropical region with hot summers, where daytime temperatures reach into the mid to high 30's (degrees centigrade) and remain fairly high throughout the year (SAWB, 1990), thereby creating conditions favouring the methylation of mercury from the sediment bed

2.4. BIO-ACCUMULATION OF MERCURY.

Numerous factors influence the bio-accumulation of mercury in aquatic biota. These include the acidity of the water, length of the aquatic food chain, temperature and concentration of dissolved organic material. Physical and chemical characteristics of a watershed, such as soil type and rate of erosion, both affect the amount of mercury that is transported from soils to water systems (US. EPA 1997).

Once in surface water, mercury enters a complex cycle in which one form can be converted to another. Mercury can be brought to sediments by particle settling and then later be released by diffusion or re-suspension. In addition to this, mercury can enter the food chain,

or be released back to the atmosphere by volatisation. The concentration of dissolved organic carbon (DOC) and pH have a strong effect on the ultimate fate of mercury in an ecosystem. Higher acidity and DOC levels, enhance the mobility of mercury in the environment, thus making it more likely to enter the food chain, (Smith *et al.*, 1996). The exact mechanism(s) by which mercury enters the food chain remain largely unknown, and probably vary among ecosystems. It is generally accepted that certain bacteria play an important role. Studies have shown that bacteria that process sulfate (SO_4^+) in the environment, take up mercury in its inorganic form, and through metabolic processes convert it to methylmercury.

The conversion of inorganic mercury to methylmercury is important for two reasons:

i) Methylmercury is much more toxic than inorganic mercury.

ii) Organisms require considerably longer periods of time to eliminate methylmercury. The methylmercury containing bacteria may be consumed by the next higher level in the food chain. Alternatively the bacteria may release the methylmercury into the water where it can quickly be absorbed by plankton, which in turn are consumed by the next level in the food chain (Smith *et al.*, 1996).

2.5 ALGAE AS INDICATORS OF MERCURY POLLUTION

Bailey and Stokes (1985), have illustrated the capacity of algae to bio-concentrate metals through a comparison of metals in water, to metals in algae. This revealed a 1000 to 10 000 fold increase in concentration. In addition the WHO (1989) reported that cultures of algae *(Croomanas saline)* grown for 48 hours in the presence of mercuric chloride, retained approximately half the methylmercury. However, when the algae were fed to copepods for 5 days, neither the copepods, nor their eggs or faeces, retained mercury in detectable amounts. This suggested that algae may not be an effective route to biomagnify mercury into higher trophic levels within the ecosystem. A more recent study by Guimaraes *et al.* (1998) measuring mercury methylation in the Pantanal flood plains of Brazil, suggested otherwise.

Algal mats in this area were clearly demonstrated to be more important mercury methylation sites than sediment. This held true in different phases of the hydrological cycle and in river basins with different geochemical features. Aquatic vegetation was found to be a potentially important site for the production of highly bio-available methylmercury. This is because the aquatic vegetation is in close contact with the water, has a high relative area and is densely populated by a varied fauna of invertebrates including fish. It therefore represents a major pathway of methylmercury uptake into aquatic food webs. Studies by Lenka (1992) using a wide range of aquatic plants have shown that most plants bio-accumulate mercury to different degrees. As such, sampling both sediment and algae is a more effective sampling method. Ramussen (1994) confirmed these findings. Ramusen's study also stated that due to the hetrogenous nature of sediment and because some plants are better indicators of mercury pollution, it is preferable to sample a selection of sediments and aquatic plants. This technique would, therefore, provide valuable information about mercury bio-availability. The US EPA (1997) have reported that mercury and methylmercury complexes in soil are available theoretically for plant uptake and translocation, potentially resulting in the transfer of mercury through the terrestrial food chain.

Gonzales (1997) demonstrated the capacity of aquatic plants to accumulate mercury and showed that they act as a good indicator of the bio-accumulation of mercury. Furthermore, Shrivastava and Rad (1989) determined that certain aquatic weeds absorb and incorporate mercury into their tissue rapidly and effectively and can be used for the removal of mercury from contaminated environments. The US Geological Survey's National Water-Quality Assessment Program indicated the appropriateness of algae as an indicator of mercury pollution (Porter *et al.*, 1993). These findings were confirmed by Baily and Stokes (1985), who demonstrated the capacity of algae to bio-concentrate mercury in soft water lakes in Canada.

Due to the vastness of The Valley of Thousand Hills, the area in which this study was conducted, a provisional survey was carried out. The area is extensive, being approximately 20 kilometres in length with an elevation that ranges from150 metres to 721 metres above sea level, see Appendix A. During this provisional survey algae were found to be the most common aquatic plant in the entire region. In consideration of these findings it was therefore

decided to use algae samples as an indicator of mercury pollution and bio-accumulation.

2.6 BIO-ACCUMULATION OF MERCURY IN FISH

The US EPA (1997) found that throughout the USA fish had elevated mercury concentrations. This report to congress stated that fish mercury concentrations are now considered to be the single greatest public health concern associated with mercury pollution. Even fish far removed from the source of the pollution were found to contain mercury levels high enough to be of concern. Their report also quoted several references with respect to mercury accumulation in the aquatic food web. In general, the document pointed out that the trophic position of the species, as well as the size or age of the fish sampled, could noticeably increase or decrease the reported mean mercury concentration. Older and larger fish, which occupy higher trophic positions in the aquatic food chain, were expected to have higher mercury concentrations. The types of the fish also influence fish mercury concentrations. For example, predatory organisms at the top of the food web generally had higher mercury concentrations.

The US EPA (1997) report showed that nearly all of the mercury that accumulates in fish tissue was in the form of methylmercury. Inorganic mercury, which is less efficiently absorbed and more readily eliminated from the body than methylmercury, does not tend to bio-accumulate. Methylmercury is very "bio-available" and accumulates in fish through the aquatic food chain. Nearly 100% of the mercury found in fish muscle tissue is methylated. Methylmercury appears to be primarily passed to planktivores and piscivorous fish via their diet. Larger longer lived fish species at the upper end of the food chain typically have the highest concentrations of methylmercury in a given water body. A relationship exists between methylmercury content in fish and lake pH, with higher methylmercury content in fish tissue found in more acidic lakes.

The ability of methylmercury to extend readily into fresh water ecosystems could result in elevated methylmercury levels in water bodies that are remote from emission sources and which appear to be seemingly pristine, as well as in water bodies that are less isolated.

Methylmercury is efficiently passed through the aquatic food web to the highest trophic level consumed within the community, for example piscivorous fish. At this point it can be transferred to fish-consuming wild life and humans through ingestion. Methylmercury appears to pass from the gastrointestinal tract into the blood stream more efficiently than the divalent mercury species.

Elimination of methylmercury from fish is so slow that long-term reductions of mercury concentrations in fish are often due mainly to growth of the fish. By comparison other mercury compounds are eliminated relatively quickly, resulting in reduced levels of accumulation. Methylmercury production and accumulation in freshwater ecosystems is an efficient process for accumulating mercury which can then be ingested by fish-eating birds, animals and people (US EPA 1997). A recent mercury update report published by the US EPA in 1999 asserts that humans are most likely to be exposed to methylmercury through fish consumption. This particularly applies to recreational and subsistence fishermen who routinely consume large amounts of locally caught fish. Sensitive population groups such as pregnant women, nursing mothers and their children must be considered as particularly vulnerable. Skinning and trimming the fish does not significantly reduce the level of mercury concentration in the fillet, nor is it removed by cooking processes. Because moisture is lost during cooking, the concentration of mercury is actually higher then it is in the fresh uncooked fish[1]. The US EPA (1997) report to congress stated that exposure may occur through other routes as well. For example the report considered such pass ways as being the consumption of food, other then fish, dermal uptake through soil and water and the ingestion of methylmercury contaminated drinking water. However, the fish consumption pathway dominates all others (US EPA 1997). The US EPA findings are confirmed by a number of other author (Buzina *et al.*, 1995, Holsbeek *et al.*, 1996, Ikingura and Akagi, 1996).

According to the WHO (1993) methylmercury, which is soluble, mobile, and can be rapidly incorporated into the aquatic food chains concentrates as it moves up the food chain accumulating in carnivorous fish. Between 70% and 90% of the mercury detected in fish muscle is in the bio-available form of methylmercury and hence is readily absorbed. Andesson *et al.* (1995) have reported that the methylation of mercury appears to be clearly accelerated by low pH. The highest levels of mercury in fish were measured in a lake with an

annual mean pH just above 0.5. Following the liming of these waters mercury concentrations were markedly reduced after 2 years and an 80% decrease in methylmercury levels was observed over 10 years. Povari (1998) has shown that by lowering the pH of water, the mercury accumulation in fish increases and that a decrease in the organic content of water causes a decrease in methylmercury levels measured in fish. Smith *et al* (1996) validated these findings by showing that a lowered pH and a higher dissolved organic content resulted in a higher body burdens of mercury in fish for the same species of fish taken from the same study area.

Kannan *et al.* (1998) have observed that where the methylmercury content in sediment was only 0.77% of total mercury, the content of methylmercury in fish muscle from the same area accounted for 83% of the total mercury measured in the muscle of these fish. The highest concentrations were found in two different species of catfish. However, Kannan *et al.* (1998) have indicated that the mercury accumulation in fish is dependent on several variables namely; the combined effect of the abundance of available inorganic mercury in sediment, the water column, trophic interactions and the rate at which micro flora transform mercury to methylmercury. Despite these variables Kannan *et al.* (1998) concluded that irrespective of its state, mercury was shown to accumulate in higher trophic levels of fish. The study examined the relationship between mercury concentrations in fish and sediment collected from corresponding locations and showed that the concentration of total mercury in sediment were positively correlated with those in fish ($r=0.52$; $p < 0.05$). Similarly, total mercury in sediment was related to fish methylmercury concentrations ($r=0.42$; $p<0.05$) and sediment methylmercury concentration was correlated with methylmercury in fish ($r=0.33$; $p< 0.05$).

Bidone *et al.* (1997) has revealed that methylmercury concentrations in fish are ultimately determined by the water chemistry which controls the methylation of mercury and its uptake from the base of the food chain by other organisms. Bidone *et al.* (1997) have indicated that the highest proportion of methylmercury in fish is likely to be found in carnivorous as opposed to omnivores fish. Ikingura and Akagai (1996) clearly demonstrated that mercury levels in fish occur largely in the form of methylmercury, as reflected in Table 2.2 below where percentages of methylmercury in all the fish analysed ranged from 73% to 95%.

Table 2.2 Percentage of mean methylmercury values in fish obtained from Nungwe Bay, Lake Victoria. (Ikingura and Akagai, 1996)

n	mean weight grams	mean length cm	mean width cm	type of fish	mercury µg/g	MeHg %
1	600	54	8	Catfish	2.2	72.7
6	390	24.7	9.8	Tilapia	2.4	91.0
3	350	28.5	8.3	Nile Perch	9.7	94.9
3	83.3	18	5	Soga	13.7	87.8
3	48,3	12.8	3.8	Furu	6.7	80.0

Ikingura and Akagi (1996) confirmed that mercury accumulation could be partly attributed to different feeding habits in individual fish species. High trophic level fish, such as carnivorous fish, tend to have a higher mercury concentration than the lower trophic level herbivorous fish because of bio-accumulation. However Ikingura and Akagi's study found that some smaller fish species such as Soga and Furu, which are lower down the food chain, exhibited relatively higher mercury concentrations than larger fish such as the Nile Perch which is known to be a top predator in Lake Victoria, see Table 2.2. Ikingura and Akagi felt that the these particular findings may have been attributed to the limited sample size, although on the other hand there was a correlation between the feeding habits and the sub-environment, that the smaller fish inhabited.The smaller fish, in this case, probably spent more time in shallow water which is an organic-rich sub-environment that is favourable to mercury methylation and bioaccumulation. Therefore the environment as well as size and age of the fish have to be taken into account when assessing the pathway of mercury. Jackson (1991) draws attention to several factors which could attribute to differences in mercury uptake by fish species, even at the same trophic level.These differences could be attributed to the state of the mercury and that mercury can vary considerably within a region in terms of time and where it is situated. In addition such factors may also be ascribed to differences in habitat preference, metabolic rate, age, growth rate, size, biomass, diet and excretory pathways. The Jackson (1991) study emphasises again the complexities involved in the movement of mercury throughout aquatic systems.

Holsbreek *et al.* (1997) has clearly indicated that there is a clear difference in mercury levels among grazers and omnivorous fish on the one hand and predatory fish on the other. Even in the absence of data on the exact age and relative growth rate, this clear cut differences points towards biomagnification in the food chain. This is clearly demonstrated in Table 2.3. The piscivorus that feed on other fish and molluscs have the highest percentage of methylmercury, as opposed to the grazers that reveal the lowest percentage of methylmercury.

Table 2.3 Methylmercury content of grazers and omnivorous fish (Holsbreek *et al.*, 1997).

Type of fish	n	Diet	length (cm)	% MeHg
Grazers	48	vascular plants, algae,	80 to 90	69 to 75
Omnivores	225	insects, detritus,	30 to 60	51 to 79
Piscivores	122	fish, insects, molluscs,	60 to 186	83 to 92

Boischio and Henshel (1991) analysed mercury in fish flesh and the results of their study positively indicates that biomagnification is taking place in the food chain. Table 2.4 shows that piscivorus had the highest mercury levels. These levels were five times higher than the other species analysed. Boischio and Henshel (1991) presented evidence that suggested that the wide variation of fish mercury concentrations among and within trophic groups can be related to the species and the habitat from which the samples were collected. This study provides additional evidence that mercury bio-accumulates up the trophic food chain.

Table 2.4 Fish mercury concentrations by trophic levels and in terms of body weight in grams as obtained from the Madeira Basin , Amazon. (Boischio and Henshel (1991)

Trophic Level	Number	Mean Hg μg/g	Mean body weight(grams)
Detritivore	53	0.12	390
Planktophagus	8	0.14	280
Herbivore	26	0.16	2700
Omnivore	64	0.14	840
Piscivore	94	0.53	7950
Total	245	0.36	2250

In terms of this study, the choice of fish species for sampling are catfish and carp. The main motivation for this selection being that visual observations and interviews with the community indicated that these were the most popular species caught and consumed by locals. According to Skelton (1993) the species of carp, (*Cyprinus carpio Linnaeus*) found in the study area are the most abundant and most common species of Carp in Kwa Zulu Natal. They are omnivorous fish and consume a wide range of plant and animal matter, mainly by grubbing in sediment. Skelton (1993) also stated that the sharp tooth catfish (*Clarias gariepinus*) is also a very common resident fish of Kwa Zulu Natal and is the most abundant of the catfish in South Africa. The fish preys, scavenges or grubs on virtually any available organic food source, including fish, birds, frogs, small mammals, reptiles, snails, crabs, shrimps, insects other invertebrates and plant matter and is even capable of straining fine plankton if necessary.

Inanda Dam is the end point of the study area. It is situated approximately 20 kilometres from Thor Chemicals and was completed at the end of 1998, and is thus, a fairly recent impoundment [2]. The study by Povari *et al.* (1998), therefore, has relevance in that it states that the formation of new lakes or dams considerably increases the production of methylmercury soon after flooding takes place. Anaerobic conditions after the flooding result in large amounts of organic material. The subsequent increase in microbial activity are thought to cause the increased availability of mercury through methylation. However, other

environmental variables, such as temperature and pH, may also effect the uptake of mercury, particularly methylmercury, by fish. Povari's study extended over a period of 16 years and included fish from eighteen reservoirs. The study involved pH, concentration of organic matter in water, the water level and recording the reservoir age. The study indicated that mercury levels in fish will normally exceed 1mg/kg for the first twelve years after flooding. The author reported that the addition of organic material in the reservoir increases methylation of mercury which may lead to bio-accumulation of methylmercury in fish. These findings are confirmed by Jackson (1988) who reported that creating reservoirs by impounding river water and flooding of adjacent land commonly causes an appreciable increase in the mercury content of fish inhabiting the water. Inanda dam is a relatively recent impoundment and could be compared to the scenario as presented by Jackson (1988). Inanda Dam has a high organic load due to poor sanitation and access by livestock and it could be acquiring mercury as a result of discharges from Thor Chemicals. If this should be the case then one would expect it to have elevated methylmercury levels in terms of Jackson (1988) findings.

Park and Curtis (1997) have confirmed that point source pollution, (gold mining activities), contributed vast quantities of mercury, greatly in excess of mobilization from natural deposits and atmospheric deposition. The Park and Curtis study is similar in design to this study. Fish from two reservoirs, one above and one below a point source, were collected for analysis. Nagle Dam which is the control is relatively close to the study area being within an approximate 15 kilometres radius of Thor Chemicals and Inanda Dam. Further both the study and control areas share the same geographic location and the Umgeni River is common to both studies..

Kim *et al.* (1995) have indicated that there were distinct variations in methylmercury concentrations which were attributable to the length and age of trout. The older and larger fish had the highest levels. Holsbrook *et al.* (1996) also agreed with these findings in a study involving 433 fish specimens. There was a direct correlation between fish length or age and methylmercury levels. This accumulation pattern lead to a relative increase of the organic mercury fraction with age, eventually reaching 90-100% of organic mercury in full grown specimens. Furthermore it was found that total body length and body weight were significantly correlated for all species. Length was chosen as the basic measure to reflect age

since it is unlikely to be subject to major short term fluctuations. In the same conjecture, Bidone *et al.* (1997) found that mercury concentrations within specific species were positively related with fish size or weight, Spearman Correlation Coefficient ($p<0.05$). These findings were confirmed by Park and Curtis (1997). Because of the high cost of methylmercury analysis the US EPA in 1999 recommended that the total mercury rather then methylmercury concentrations be determined in fish. The EPA also recommends that the conservative assumption be made that all mercury is present as methylmercury in order to be most protective to health[3]. Over a twenty year period Lodenius *et al.* (1991) determined that fish mercury concentrations tended to accumulate in the muscle, liver, kidney and gonads and again the mercury levels in these tissues correlated with both fish weight and length. Although there was no significant difference between male and female specimens. Wagemann *et al* (1997) findings corresponded with the above where it was established that the methylmercury component of total mercury in the muscle of marine animals is as high as 100%.

2.6.1 Relationship between Methylmercury in Fish and Consumption by Humans.

Several studies have been conducted in areas where people consume large quantities of fish and there is reported to be a strong association between mercury levels in hair and fish consumption is well demonstrated in the literature. The levels of mercury in the human hair are dependent on the fish species and quantity consumed as well as the environmental levels of mercury pollution (Buzina *et al.*, 1995, Batista *et al.*,. 1996, Holsbeek *et al.*, 1996). Furthermore, Holsbeek *et al.* (1996) demonstrated a positive correlation between mean hair total mercury concentration and calculated daily methylmercury intake.

2.7 THOR CHEMICALS: CATO RIDGE, KWA-ZULU NATAL, SOUTH AFRICA

Thor Chemicals have been processing waste mercury for approximately 12 years.
The plant started to receive considerable media attention in 1989, which even extended to1995, concerning the apparent discharges of spent mercury waste into the Mngceweni

River, situated directly below the plant (Clarke, 1990; Clarke, 1994; Nichols, 1995). In 1990 unsubstantiated reports by a senior staff member of Umgeni Water, indicated that total mercury levels of 40, 1900, and 1500 ppb were being recorded as much 25 kilometres down stream from Thor chemicals, in the region of the Inanda dam, soon after the discharges took place. A report by the "St Louis Dispatch", an American newspaper (Lambrecht, 1989) claimed that they had obtained samples and had measured levels of 1.5 million ppb mercury in river water taken from a marsh area below the factory in November 1989. These results, in addition to the extensive media coverage of the Thor Chemicals "spill", emphasized the need to carry out a scientific study of the extent of contamination of the river system downstream from Thor Chemicals and to quantify the potential risk to the community. Subsequent and regular river water samples taken and analysed by Umgeni Water along the length of the river system have indicated that total mercury levels in free flowing water consistently fall within the Department of Water Affairs maximum permissible concentration of 0.02 mg/l (Dept Water Affairs, 1996; Umgeni Water, 1998).

An unpublished study by a graduate Bachelor of Technology student from the Department of Environmental Health; Natal Technikon further supported the hypothesis that the spilled mercury had transferred from the water phase into other trophic levels (Chester *et al.*, 1996). The results of the analysis of water, soil and vegetation samples, (Table 2.5) taken at three points along the river system, were all low, with the exception of a sample taken at site B, which appears to be an outlier. Sediment samples were found to be elevated with levels as high as 1150 ppm. Whereas vegetation, collected from the river within 50 metres of the flood plane, indicated low levels of mercury levels. Unfortunately, this study was not carried out within the parameters of strict scientific sampling methodology and therefore cannot be relied on in terms of accuracy. Nevertheless, the order of magnitude of some of the levels of mercury in the sediment and soil could indicate mercury contamination in the vicinity of Thor Chemicals.

Table 2.5 Mercury levels in the vicinity of Thor Chemicals and Surrounding Area (Chester *et al.*, 1996)

Sample No	Type of sample.	** mercury (ppm as μg/cm3)
A1-0m	sediment	174.0
A1-5m	soil	33.6
A2-0m	sediment	326.0
A2-0m	sediment	1150.0
A2-5m	soil	140.0
B1-0m	sediment	1.9
B1-50m	soil	155.0
B2-50m	soil	14.0
B2-50cm	soil	173.0
C-0m	soil	45.7
A1-0m	veg	4.88
A1-5m	veg	0.22
A2-0m	veg	0.56
A2-5m	veg	0.03
B1-50 m	veg	0.002
B2-50 m	veg	0.02
C-50 m	veg	1

* A = Marsh area directly below Thor Chemicals, B = River below Thor, C = Inanda Dam, upper confluence, m = distance from river bank

** Vegetation and soil sample results are reported as ug/cm^3 of extract and not μg/g of sample owing to the nature of the samples.

A further study was carried out by Johnston *et al.* (1991). Samples were obtained from the vicinity of the Thor plant, situated at the head of the Mngcweni River and a marshland area at the confluence of this river and at the permanent settlement of Fredville, which is situated within the Mngceweni River valley, (figure 2.1). A total of 15 samples were taken and included soil as well as sediment and river water to determine total mercury from each of the sample points. The results as determined by Johnston *et al.* (1991) are tabulated below, in Table 2.6.

Table 2.6 Mercury concentrations for environmental samples taken in the vicinity of the Thor Chemicals recovery plant in 1990 (Johnston *et al.*, 1991).

SITE	SAMPLE	TYPE	mercury (ppm dry mass)
1	1	Soil	21.4
2	2	Soil	12.5
3	3	Sediment (dry river bed)	49.6
4	4	Soil (dry riverbank)	11.4
5	5a	Sediment (dry riverbank)	6.40
5	5b	Soil (dry riverbank)	0.85
5	5c	Sediment (Mngeweni source)	1764.0
6	6	Sediment (river)	0.91
7	7	Sediment (un-named tributary)	0.03
8	8	Sediment (upstream, Fredville)	0.33
9	9	Sediment (Umgeni/Mngeweni)	0.03
10	10	Sediment (Umgeni/Mngeweni)	0.004
5	12	River water	nd
8	13	River water	nd

The results indicated that mercury contamination had taken place at the landfill site which was situated directly below Thor Chemicals and above the source of the Mngceweni River. Samples 1 to 5a and 5c indicate the excessive levels of mercury detected in this area. Johnston *et al.* (1991) pointed out that the level of 50 ppm (Sample 3) found in the river bed at the source of the Mngceweni River can be quantified as chemical waste. The Thor Chemicals plant was identified as the point source of the contamination due to the result of a sample taken from a river bank opposite the plant (Sample 5b). The mercury level at this site was considerably lower then those samples taken directly below the plant as indicated above. In addition there was a progressive reduction in mercury levels with increasing distance from Thor Chemicals as indicated by samples 7 to 10. An earth dam situated close to the plant had particularly high mercury levels (Sample 5c). According to Johnston *et al.* (1991) the earth dam, at this point, allowed the mercury to accumulate from upstream areas. Samples taken near the Mngceweni and Umgeni confluence show much lower mercury levels which could be regarded as normal for many soils. In this lower part of the Mngcweni river

(Sample 9) levels are similar to those in the sediment of the un-named tributary (Sample 7) which does not drain directly from the area where Thor Chemicals is situated. The location of where these levels were detected in relation to Thor Chemicals are indicated in figure 2.1 below

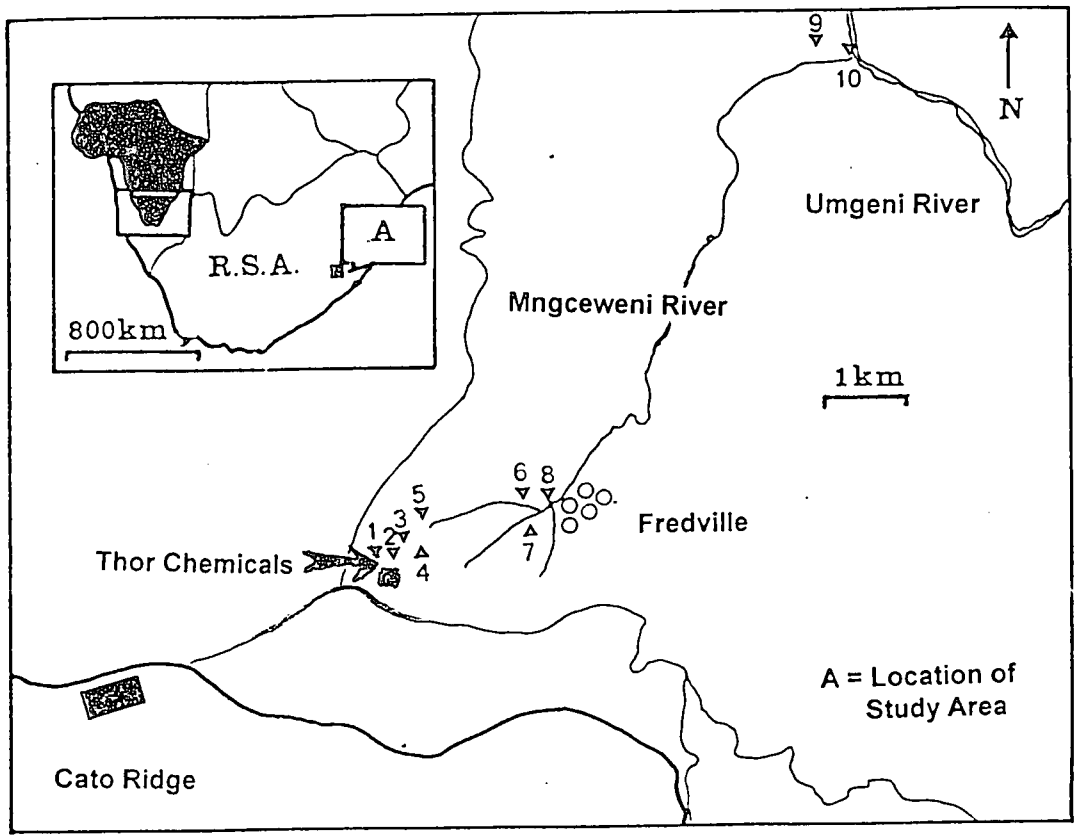

Figure 2.1 Map of Sampling Sites (1 to 10)selected and analysed by Johnston *et al.* (1991) to determine mercury concentrations in sediment and soil in the vicinity of Thor Chemicals and downstream of the Mngceweni River to the confluence of the Umgeni River (reproduced from Johnston *et al.* 1991)

Johnston *et al.* (1991) suggested that increased rainfall also helped to mobilize mercury from the contaminated soils and the river-bed areas found in the vicinity of the plant. Further that mercury contamination is likely to be associated with the fine fraction of sediments which tend to be transported to the Umgeni river during these vigorous wet-seasonal flows. Under dry conditions, the major mobilization pathway from soils would most likely be by volatilization. The authors (Johnston *et al.*, 1991) also advised that sediment transport from the Mngcweni

River may have important implications related to the disposal of material removed from the new Inanda Dam complex on the Umgeni as a result of siltation. This finding is confirmed by Povari (1998) and Johnston *et al.* (1998) concerning elevated mercury levels in recently completed reservoirs, which is discussed in greater detail under Section 2.6. As a result, any fishing activity taking place in the impounded waters should be monitored carefully to ensure adequate protection of public health. The authors also proposed that a hydro-geological survey be carried out to assess the effect the mercury may have on ground water and this pollution incident be fully evaluated to determine the repercussions it may have for the local and wider communities. It was also suggested the such extensive contamination will persist for many years, as mercury contamination does not respond well to retrospective action.

The Johnston (1991) study has provided motivation for a follow up study on the transformation of mercury into higher trophic levels. A limitation of the Johnston study was that it was restricted to the sampling of soil and sediment within 10 kilometres of Thor Chemicals. In addition, other sampling media such as aquatic plants, fish, and cattle hair was excluded. It is considered essential that all parameters be analysed in order to quantify properly the extent of pollution and the mobilization of mercury in the eco-system as well as to quantify the human health risk. It was therefore decided to sample river sediment and aquatic plants along the entire length of the two river systems all the way to the Inanda Dam. This study also included the sampling of cattle hair and fish.

2.8 ANIMAL SAMPLES AS AN INDICATOR OF MERCURY POLLUTION

Animals have been used as good environmental indicators in several studies where mercury levels in hair, flesh and internal organs of animals were taken (Shaw *et al.*, 1986, Burger *et al.*, 1994, Halbrook *et al.*, 1994). Burger *et al.* (1994) has clearly indicated the bio-accumulation of heavy metals (including mercury) in the tissue of animals. Once consumed by an animal, the heavy metal can be stored in tissue or the metal may be eliminated by excretion or by deposition in feathers or hair. Both mammalian hair and avian feathers can be used as indicators of heavy metal levels in other tissue and are thus reflective of exposure. Hair can be used as an indicator of heavy metal levels in other tissues, particularly

for mercury where there is little opportunity for external contamination. Mercury levels in hair correspond with internal tissue levels and can thus be used as bio-indicators. The hair mercury ratio is in the order of 200:1 (Burger *et al.*, 1994). The Palherta and Taylor (1995) study emphasised the appropriateness of animal hair as an indicator of long term exposure as opposed to the use of blood and organ analysis for recent exposures.

In order to determine the appropriateness of the animal group to be used in a study, Burger *et al.* (1994) suggests that the following criteria be considered.

i) The species should be relatively common and available.

ii) The animal should be sufficiently large to provide adequate sample for analysis.

iii) Age and gender should be determinable.

iv) Life span should be appropriate (use short lived or newborn animals to measure recent exposure and long lived animals to integrate cumulative exposure).

v) The animal should accumulate the chemical (or have a biological response) to an appropriate trophic level. The levels it accumulates should be sufficient to measure (not close to detection levels), yet not so high that additional exposure will have little effect, nor should it approach toxic levels.

vi) Home range must be appropriate (sessile animals to monitor point source; mobile animals to integrate exposure over space).

vii) Small or abundant animals will be particularly useful as bio-indicators because they are relatively sedentary and will thus reflect local contamination.

Cattle kept by the local community in the study area are of great social and cultural importance. Cattle are not only a source of meat or milk but they are an indicator of wealth

and status. In this relatively poor community, cattle are only slaughtered for traditional feasts and usually old (less productive) animals are used for this purpose. Cows however, are milked regularly. Cattle therefore tend to reside in the study area for long periods of time and interviews conducted with cattle owners suggested that, on average, the animals sampled in this study had been in the area for more than five years. The only source of water for these animals are the rivers contaminated by the spill. Cattle in the area were observed wading into shallow pools or along river banks where they stirred up the finer sediment when drinking. It is therefore assumed that they could be drinking mercury contaminated sediment during watering and cattle are potentially a prime source for the transformation of mercury from the sediment beds to higher trophic levels, within the ecosystem.

Consideration was given to the use of domestic chickens as a sample medium since chickens are consumed more regularly by the local community than cattle. However, according to Burger *et al.* (1994) there are physiological differences between hair and feathers in terms of their growth on the animal. Hair grows continuously and maintains a blood supply connection with the body. So growing from the base, each segment of hair contains a record of elements circulating in the blood at the time that segment of hair was formed. From base to tip a hair represents a continuous archive of blood levels of the elements that have an affinity for keratin. A feather, on the other hand, grows rapidly over a period of a few weeks after which the blood supply shrivels up and the feather remains on the bird for months as a dead structure. It represents an archive of metal exposure to which the bird was exposed during the weeks prior to feather formation. These findings were also confirmed by WHO (1989) and Becker (1994). Because the last known recorded discharge of mercury into the Valley of Thousand Hills had not occurred since early 1990, the use of chicken feathers was considered inappropriate and local cattle hair was deemed to be an appropriate sampling medium. Although several studies used flesh and internal organs of animals to determine mercury levels (Shaw *et al.*,1986; Halbrook *et al.*, 1994), sacrificing cattle in this study area would not have been an appropriate sampling technique.

2.9 REMEDIATION OF MERCURY CONTAMINATED SITES.

Reuther (1996) referred to the potential for plants to remove mercury from sediments. Plants are considered to be e efficient absorbers of highly toxic mercury ions from substrates. The pollutant would thereafter be reduced by the plants to the less toxic and relatively inert metallic form of mercury. Once the metal was converted to its metallic state, the mercury could then be transferred into the atmosphere as a vapour. Reuther (1996) stated that, as with most chemicals, the plants that grow in the contaminated medium accumulate large amounts of the toxic substances in their biomass, which must then be disposed of. However because the biomass represents around one thousand times less toxic material to be disposed of than in the soil, it was considered to be an efficient and effective alternative. Further the mercury does not necessarily accumulate in the plant due to its volatility. Thus the mercury vapour emitted by the plants would probably diffuse into the atmosphere, quickly reaching nontoxic levels. Generally the release of mercury vapour by such means would be insignificant on a global scale. However, Reuther (1996) indicated that there was concern by some, that regulatory agencies may not accept the transfer of metallic mercury into the air as a safe remediation strategy. The possibility that the mercury vapour in the air could precipitate into ground water where it can enter the aquatic food chain could not be discounted.

Reuther (1996) has reported on a particular significant study conducted at the University of Georgia. The study revealed that the most efficient plant for removing mercury was genetically manufactured by inserting a synthetic gene into the genome of the Mustard Plant (*Arabidopsis*). Despite the apparent effectiveness of this method of mercury remediation, the use of genetically modified plants is still in its infancy and that further research needs to be conducted. Nevertheless, this study was considered to be ground breaking and also demonstrated that the removal of mercury pollution was particularly suited to phytoremediation.

Lee *et al.* (1998) described a study using twenty-one different plants to determine the potential of metal absorption from aquatic systems. The results indicated that some of the plants used were effective and had promising potential for metal removal. Lee *et al.* (1998)

referred to literature in his study that suggested that aquatic plants provided a viable alternative for metal remediation in aquatic systems. Aquatic plants were considered to be more effective when compared to the more conventional methods such as ion exchange membrane technologies, evaporation processes and filtration. Scholes *at al.* (1998) also found that constructed wet lands exhibited considerable potential in the removal of metals from waste waters. The Scholes *et al.,* study included the investigation of six trace elements, and although mercury was not one of the metals used in the study, the results indicated the following. Although plants, and in particular reads, were found to be effective in removing the trace elements, uptake depended on several variables. These were seasonal variations in terms of run off, individual properties of the trace metals and plants, and that some metals formed insoluble compounds in the sediment. Scholes *et al.* (1998) concluded that these factors should be considered where constructed wetlands may be used for the removal of metals from contaminated waters.

2.10 HEALTH EFFECTS ASSOCIATED WITH MERCURY EXPOSURE

In order to quantify the potential health risks associated with community exposure to mercury it is necessary to review literature on human and animal health effects, as well as epidemiological studies.

2.10.1 Overview of Health Effects of Mercury on Humans.

Mercury is a known human toxin. The most common biological samples analysed for mercury are blood, urine and scalp hair. The methods most frequently used to determine the mercury levels in these sample types include atomic absorption. . Clinically, observable neurotoxicity has been observed following exposure to high amounts of mercury, for example, Mad Hatters Disease (US EPA 1997). Human symptoms of mercury exposure include impairment of peripheral vision and disturbances in sensations (pins and needles, numbness) usually in the hands and feet and sometimes around the mouth. Co-ordination of movement, particularly

in writing, impaired speech, hearing and walking are other classic symptoms of mercury poisoning (US EPA, 1997).

The absorption, distribution, metabolism and excretion of mercury is highly dependent on the form of mercury to which a receptor has been exposed. The absorption of elemental mercury vapour occurs rapidly through the lungs, but it is poorly absorbed from the gastrointestinal tract. Once absorbed elemental mercury is readily distributed throughout the body, it crosses both placental and blood-brain barriers. The distribution of absorbed elemental mercury is limited primarily by the oxidation of elemental mercury to mercuric-ion which has a limited ability to cross the placental and blood-brain barriers. Once elemental mercury crosses these barriers and is oxidized to the mercuric-ion, return to the general circulation is impeded, and mercury can be retained in brain tissue. Elemental mercury is eliminated from the body via urine, faeces, exhaled air, sweat and saliva. The pattern of excretion changes depending upon the extent the elemental mercury has been oxidized to methylmercury (US EPA, 1997). Studies in both animals and humans have demonstrated that more than 90% of ingested methylmercury is absorbed. Methylmercury is distributed to all regions of the body, within 30 hours 7% is found in the blood. Distribution to the brain takes approximately 3 days. On the other hand elimination from the body is a slow process and thus tissue concentrations stay relatively constant and do not fluctuate with excretion. In primates and humans the brain to blood ratio is in the range of 5 to 1. Blood levels are therefore predictive of levels in the target organ, this makes blood a valuable indicator media. Scalp hair is, however, the indicator medium of choice as it can reveal both past and present blood concentrations (Clarkson, 1992).

2.10.2 Acute Effects of Mercury Exposure.

Acute mercury poisoning primarily involves the kidneys and intestinal tract. Symptoms include a metallic taste, nausea, abdominal pain, vomiting, diarrhoea, headache, salivation and anuria. The stomach, gums and salivary glands may become inflamed. Acute exposure to elemental mercury can cause pulmonary irritation and neural damage. Chronic symptoms such as muscular tremor may persist in some cases. Extreme cases may lead to haemolysis,

insomnia, delirium and ultimately death from exhaustion. Most cases of acute exposure are related to occupational exposure from inhalation of inorganic mercury (Sittig, 1976).

2.10.3 Subacute / Chronic Effects of Mercury Exposure.

Clarkson (1992) states that overt signs and symptoms usually take weeks to months to manifest. Clarkson referred to the Iraq outbreak between 1971and1972 where victims found tp have ingested lethal doses of mercury without experiencing any untoward symptoms during the intake period. However, exposure primarily effects the nervous system resulting in anxiety, insomnia, muscular tremor which initially involves the hands, and other physiological disturbances (Sittig, 1976).

In 1968 reports from Japan indicated that people from the Shiranui Sea had consumed fish containing low doses of methylmercury over several decades. The effects of long term consumption of methylmercury on these people revealed a significantly higher frequency of neurological signs characteristic of methylmercury poisoning, namely hypothesia, poor muscular co-ordination, impairment of hearing, visual changes and speech disturbance. These results suggest that people on the coast of the Shiranui Sea were affected by long-term dietary exposure to methylmercury (Ninomiya *et al.,* 1995).

2.10.4 Human Toxicity of Mercury.

Outbreaks of severe accidental poisoning in Japan, Iraq and elsewhere have revealed important characteristics of methylmercury action in humans. Overt signs and symptoms usually take weeks or months to manifest themselves. However the length of the "latent" period has been shown to decrease with increased concentrations of mercury in the blood. Except at very high doses, all signs and symptoms are due to selective damage to the nervous system. In humans, the brain is the primary target and even within this organ, damage is selective or focal. Certain anatomical areas of the brain are therefore specially susceptible to damage. These include the visual cortex and the cerebellum. Severe damage

manifests itself as a loss of neuronal cells in these areas. In adults, the most conspicuous visual impairment associated with methylmercury exposure is a constriction in visual fields as well as deficits in spatial and temporal visual function. Developmental exposure at high levels may result in oculo-motor manifestations and blindness, whereas less severe poisoning may result in changes in acuity and constriction of visual fields. The primary visual cortex is a major site of damage (Rice, 1995). Since the earliest effect of methylmercury poisoning is the non-specific symptom of paraesthesia, the diagnosis of incipient methylmercury poisoning is very difficult (Clarkson 1992).

2.10.5 Pregnant Women and Children.

Pregnant women are at a particularly high risk in terms of methylmercury exposure, due to the fact that the fetus is the life form most susceptible to Mg and it's compounds (Soria *et al.*, 1992). In a study by Holsbeek *et al.* (1996) of 251 subjects, the correlation between maternal hair mercury and mercury in the hair of infants (less than 2 years of age) still breast feeding, was found to be statistically significant ($p=0.001$). Analysis was done on a sub-sample of 30 mothers. The results of this analysis showed a mean decrease of 20% in body burden during pregnancy, thus indicating the extent of placental transference of mercury to fetuses. The threshold of maternal mercury concentration indicative of adverse effects in the fetus is in the order of 10-20 μg /g mercury in hair. A positive correlation between mean total mercury concentration and calculated daily methylmercury intake was reported.

Prenatal toxicity was first reported during the Minamata outbreak in Japan. Prenatal exposure is the most hazardous form of methylmercury exposure. Pregnant women exposed to methylmercury have given birth to infants suffering from severe brain damage. The mothers only experienced asymptomatic or mild effects such as transient paraesthesia during pregnancy. In later follow up studies, a milder form of prenatal damage characterized by psychomotor retardation was also noted. The nature of prenatal damage appears to differ fundamentally from that of adult damage to the central nervous system. Unlike focal damage in adults, damage to the developing brain is diffuse and widespread. The fetus may be 5-10

times more sensitive than the adult brain to damage by methylmercury. Thus, prenatal dose-response relationships are the ones most relevant to human risk assessment (Clarkson, 1992).

The human brain forms over an unusually long time period, compared to other organs. While most of the basic structure is laid down before birth, neuron proliferation and migration continue in the postnatal period. The blood-brain barrier is not fully developed until the middle of the first year of life. The number of synaptic connections between neurons reaches a peak around age two and is then trimmed back by about half. Similarly, there is great postnatal activity in the development of receptors and transmitter systems as well as in the production of myelin. Many of the toxic agents known to damage the developing brain interfere with one or more of these developmental processes. Those agents with antimitotic action, such as X-rays and methylmercury, have distinctly different effects on structure depending on which neurons are forming at the time of exposure. Guidelines designed to protect human populations from developmental neurotoxicity need to take into account the changing sensitivity of the brain as it passes through different developmental stages (Rodier, 1995).

Following exposure to mercury mother-infant pairs suggest that infants are borne with higher blood mercury levels than their mothers had at the babies birth. Neonatal and *in utero* exposure to methylmercury often results in more severe signs of intoxication in the offspring than in the mother, these include cerebral palsy, mental retardation and delayed walking and speech, as well as deficits in motor, language, psychological, scholastic and behavioural tests. In postnatal exposure, damage is more diffuse with neuronal loss in all areas of the visual cortex, as well as in many other brain areas (Rice 1995).

2.10.6 Treatment of Methylmercury Poisoning.

In its severe form, methylmercury poisoning is essentially irreversible, due to the destruction of neuronal cells. Treatment is therefore directed toward early removal of methylmercury from the body before irreversible damage occurs. Only complexing or chelating agents that

contain SH- ligands are effective. D-penicillamine and N-acetyl-D-penicillamine are effective in reducing blood methylmercury levels. A method involving haemodialysis together with a diffusible thiol compound such as amino acid cysteine introduced into the arterial blood has also been used with success (Clarkson, 1992). It is of utmost importance that the health risk to people in the study area be properly quantified in order to establish if they should be treated to prevent further long-term neurological damaged.

2.10.7 A Synopsis of Minamata Disease and Other Notable Mercury Poisoning Incidents.

Minamata. is one of the first and most serious documented cases of disease resulting from environmental contamination and was named after the industrial town called Minamata where symptoms were first observed. The disease was caused by the discharge of waste water containing methylmercury from an industrial plant and subsequent ingestion by marine species. Early investigations revealed the following main findings:

i) The disease affected adults as well as children.

ii) The first case was reported in 1953. However, there were patients admitted prior to this date.

Minamata city was the only industrialized city in the area, where the Chisso Company operated a chemical plant. Given that it was never doubted that the cause of the disease was water contamination, it was obvious that the source could only have been the Chisso chemical plant. The plant accepted no responsibility and took no measures whatsoever to prevent further contamination, claiming that the cause of the disease was unknown. Chisso also refused to co-operate with investigations on the grounds that doing so would reveal confidential corporate information (WHO, 1991). During the 1950's people began to witness strange phenomena in and around Minamata Bay. For no apparent reason, fish rotated continuously and floated belly up to the surface, shellfish opened and decomposed and birds fell while in flight. The most shocking, however, was the frenzied death of cats. Cats suffered from excessive salivation and general convulsions or violent rotational movements, were unable to walk straight and often collapsed, dead. Many cats jumped into the sea to drown, and eventually cats were no longer seen in the area. Cats in fact played an important role in

helping to establish the etiology of the disease. In February 1957, cats were brought to Minamata from Kumamoto City, located 100 km away. All immigrant cats developed similar symptoms within 32 to 65 days after arrival. Mercury was detected in high concentrations in the brains of cats, livers, kidneys and hair. Tests showed that the degree of contamination was effectively equivalent to administering methylmercury at 1 mg/kg of a cat's body weight, (WHO, 1991).

Over the next 20 years, the number of people known to be effected increased to thousands. In time the disease was recognised to result from methylmercury poisoning and fish were subsequently identified as the source of methylmercury. As is often the situation with epidemics, the first cases noted were severe. Deaths occurred among both adults and children. It was also recognised that nervous system damage could occur to the fetus if the mother ate fish contaminated with high concentrations of methylmercury during pregnancy. The nervous system damage of severe methylmercury poisoning among infants was very similar to congenital cerebal palsy. In the fishing villages of this region the occurrence of congenital cerebal palsy due to methylmercury was very high compared to the rest of Japan. At the height of the mercury contamination, mercury concentrations in fish were between 10 and 30ppm. After the source of mercury was identified. Efforts were made to reduce the mercury into the bay. After 1969, average mercury concentrations in fish had fallen below 0.5ppm (US EPA,1997).

The first patients detected with mercury poisoning from Minamata were considered to be cases of acute and subacute poisoning. Of the 34 patients diagnosed initially, 16 died within 3 months of the onset of disease. Within 6 months of the onset, an additional 4 died, which demonstrated that the poisoning advanced rapidly. Pathological findings demonstrated a number of common features namely damage to the central nervous system, that is the cerebellar cortex. All patients had common symptoms, including constriction of the visual field, sensory disturbances, muscular tremors and poor co-ordination, speech and auditory disturbances. However, some bias in early diagnosis may have occurred due to the fact that only serious cases manifesting all these symptoms were diagnosed as having the disease and, therefore, the actual number of cases was probably higher (WHO, 1991).

Soon after the official discovery of Minamata poisoning incident, it also became clear that a considerable number of children were born with congenital cerebral palsy. These patients had the common symptoms of the chronic conditions already mentioned. However, symptoms also included mental retardation, disturbances in physical development and nutrition, strabismus and excessive salivation. All of the above symptoms were common to all patients. However, the WHO study on this incident pointed out that such extensive damage to the brain is, of course, not limited to the symptoms of mercury poisoning. Without data on mercury contamination, individual diagnosis is often near impossible, but group diagnosis or diagnosis in terms of epidemiological data is possible (WHO, 1991). While mothers were at first thought to be asymptomatic, subsequent, detailed examinations revealed a high incidence of mild symptoms of mercury poisoning. Mothers generally suffered from sensory disturbances common to chronic poisoning. However, the degree of their symptoms were much milder than those of babies (WHO, 1991).

In 1965, an additional methylmercury poisoning outbreak occurred in the area of Niigata, Japan. As in Minamata, multiple chemical plant sources of the chemical were considered. Scientific detective work identified the source again to be a chemical factory releasing methylmercury into the Agano River. The signs and symptoms of the disease in Niigata were those of methylmercury poisoning and strongly similar to the disease in Minamata. The abnormalities in the human brain that result from methylmercury poisoning are well described. There is an extreme high level of scientific certainty that methylmercury causes these changes. Similar pathology has been identified in other countries where methylmercury poisoning has occurred. methylmercury contamination of other food products (including grain and pork) has resulted in severe methylmercury poisoning with pathological changes in the nervous system and clinical disease virtually identical to Minamata Disease (US EPA, 1997).

Methylmercury poisoning occurred in Iraq following consumption of seed grain that had been treated with a fungicide containing methylmercury. The first outbreak occurred prior to 1960 and resulted in severe human poisoning. The second outbreak of methylmercury poisoning from grain consumption occurred in the early 1970s. Imported mercury treated seed grain arrived after the planting season and was subsequently used as grain to make flour that was used to bake bread. Unlike the long-term exposure in Japan, the epidemic of methylmercury

poisoning in Iraq was short in duration, but the magnitude of the exposure was high. Because many of the people exposed to methylmercury lived in small villages in very rural areas, or were nomads, the number of people effected is not known. The number of people admitted to hospital with symptoms of poisoning has been estimated to be approximately 6500 with 459 fatalities. As in the Japanese poisoning epidemics the signs and symptoms of the disease were predominantly of the nervous system. That is, difficulty with peripheral vision or blindness, sensory disturbances, lack of coordination, impairment of walking, slurred speech, and in some cases death. Children were affected as well as adults. Of great concern was the observation that infants, born of mothers who had consumed the methylmercury contaminated food, could show nervous system damage even though the mother was slightly affected herself (US EPA,1997).

Similar observations were also made in the methylmercury contamination incidents of New Mexico. Mercury levels from mothers were analysed only 5 to 8 years after having given birth and the mercury content of their hair was lower then the congenital patients (WHO, 1991). Generally, infantile methylmercury poisoning is only noted or diagnosed many years after birth. However, in the case of the Minamata incident, diagnosis took place much sooner because people in this region of Japan have a custom of preserving the umbilical cords of new borne babies (Harada, 1995).

Of interest is the survey carried out by Myers *et al.* (1995) where comparisons were made on prenatal methylmercury exposure and on neuro-development in studies carried out in various countries. Initial studies from Canada and New Zealand and more recently from the Faroe Islands, have supported the Iraqi conclusions. However, studies from Peru and the Republic of the Seychelles have not found adverse associations. The studies have varied in multiple ways including the end points evaluated. The above findings are given in Table 2.7 below. As can be seen there is no consistent pattern between prenatal methylmercury exposure and neuro-development in the reported studies conducted in these various countries. Therefore, Myers *et al.* (1995) does not support the hypothesis that consumption of even large amounts of fish during pregnancy places the fetus at neuro-developmental risk from methylmercury exposure, moreover, fish is an important nutritional source in many parts of the world as it provides important components for brain development.

Table 2.7 Categories of tests used to detect an association between prenatal methylmercury exposure and neuro-development in reported studies. (Myers *et al.*, 1995)

Testing category	Iraq	Canada	New Zealand	Peru	Faroe Islands	Seychelles main	Seychelles pilot
neurologic	+	+	-	-	-	-	-
dev. milestones	+			-	-	-	
dev. screening	-	+			-	-	+
phycological			+		+	-	+
educational			-			-	-
behavioural						-	+
neuro-psychologic					+	+	
neurophysiological					+		

+ studies in this category were done and an association with prenatal methylmercury was reported by the authors;
- studies in this category were done and no association with prenatal methylmercury exposure was reported by the authors.

Myers *et al.* (1995) reiterated the importance of traditional lifestyles, such as fishing, to the social, cultural and economic well-being of indigenous people can not be dismissed. In addition Myers *et al.* (1995) pointed out that there is growing evidence that fish consumption has cardiovascular protective benefits for adults. Concern about fetal exposure to methylmercury from fish should be tempered by it's importance to brain development and other benefits.

In the study area (Valley of a Thousand Hills) visual observations suggest that the people are generally very poor and do not have many opportunities for employment in the region. Most families survive as subsistence farmers and food in the region is a scarce resource. It was observed that children swim and fish in the river and dam, and consume fish on a daily basis. Fish is therefore an important source of protein in the community, particularly among young boys. As such the fish supply needs to be monitored and protected from contamination. Although the currently available data on developmental effects in chronically exposed children appears to be inconclusive, there is still the possible potential threat to child development, which raises concern regarding exposures. The (US EPA, 1997) verifies that children may be higher at risk of methylmercury exposure than adults because they appear to have a greater exposure per kilogram body weight and therefore may be more sensitive than adults given the developmental state of the nervous system. However, whether or not children differ from adults in sensitivity to methylmercury neurotoxicity is not known. In the

Valley of a Thousand Hills, children are the most likely group to consume the largest quantity of fish and are, therefore, deemed to be at a "higher" risk than other members of the community.

2.11 THE REFERENCE DOSE (RfD)

The US EPA defines the Reference Dose (RfD) is an estimate of the daily exposure to a chemical that the human population (including sensitive subgroups) can be subjected without an appreciable risk of deleterious effects during a lifetime. RfD's are reviewed by US EPA scientists for accuracy, appropriate use of risk assessment methodology, appropriate use of data and other scientific issues. When consensus has been reached, information on the RfD is made available to the public through a US EPA database, namely, The Integrated Risk Information System (IRIS). The RfD is based on the best available data that indicate a "critical effect". This is generally the first indicator or most subtle indicator of an adverse effect in the species under study. In calculating RfD's, the US EPA generally uses a "no-observed effect level" (NOAEL). This is determined by either inspection or modelling of dose-response data on the critical effect. It is a means of estimating the threshold for effect in the reported study. The NOAEL is most useful when it is from a study from which a determination of the "lowest-observed-adverse-effect level" (LOAEL) can also be done. The LOAEL is the lowest tested dose at which the critical effect was seen in the species under study. In calculating the RfD the US EPA divides the NOAEL or LOAEL by a series of uncertainty and modifying factors in order to extrapolate to the general human population. The uncertainty factors that should be considered are as follows: extrapolation of data to sensitive human sub-population; extrapolation from animal data to conclusions for humans; lack of chronic data; lack of certain other critical data; and the use of a LOAEL in the absence of a NOAEL. The RfD is used for risk assessment judgements dealing with evaluations of general systemic toxicity. It is intended to account for sensitive (but not hypersensitive) members of the human population. The rationale is that if exposure to the RfD is likely to be without appreciable risk for sensitive members of the population, then it is without appreciable risk for all members of the population.

The RfD is generally applicable to men and women and to adults, to children and to the aged, unless data support the calculation of separate RfD's for these groups. The RfD is a quantitative estimate of levels expected to be without effect even if exposure persists over a lifetime. It is not intended to be compared with isolated or one time exposures. Exceeding the RfD does not necessarily mean that risk will be present. Acceptability of uncertain risk is a risk management decision. Risk management decisions may consider the RfD, but will take into account exposures, other risk factors and non-risk factors as well. At the RfD, or below it, exposures are expected to be safe. The risk following exposures above the RfD is uncertain, but risk increases with increasing exposures (US EPA, 1997).

2.11.1 Methylmercury RfD.

Numbness or tingling in the hands and feet (paraesthesia) also experienced around the mouth, in adults, was used as the basis for US EPA's methylmercury RfD up to the 1980's. However, paraethesis was identified as not being reliable endpoint for dose response assessment, in that it is a subjective response relying on a patients recognition of these effects. There are still uncertainties remaining on the current RfD, based on developmental effects from methylmercury poisoning in children exposed *in utero*. There are difficulties with reliability in recording and classifying events like late walking in children, especially as the data were collected approximately 30 months after the child's birth. It should be noted, however, that the endpoints used, represented substantial developmental delays. For example, a child's inability to walk two steps without support at the age of 2, inability to talk (based on the use of 2 or 3 meaningful words) by 2 years, or the presence of generalized convulsive seizures. There is uncertainty in the physiological factors which were used in estimating the ingested mercury dose (US EPA, 1997).

Information on the amount of methylmercury exposure producing particular combinations of signs and symptoms in people has been analysed to yield what are called quantitative dose-response assessments. Both the Japanese and Iraqi epidemics are important in understanding how methylmercury, from food, produces neurological disease in humans. In the epidemics of Minamata and Niigata, the exposures were long-term, and the tissues of fish and shellfish were the sources of methylmercury exposure. Therefore, there appears to be

strong evidence exhorting that methylmercury in fish, can produce human disease. A limitation to these data is that many patients were severely affected. The extent of methylmercury poisoning was so severe that identifying subtle indications of disease was difficult. Nevertheless, it showed that the mercury caused the poisoning. Subtle indicators of poisoning are important for estimating the level of exposure that will not cause adverse effects, (US EPA, 1997).

The threshold levels of methylmercury at which the developing brain is affected have been determined in several exposed populations (Kjellstrom *et al.*, 1989). However, Kjiellstron *et al.* (1989) study of *in utero* exposure provided an unambiguous basis for threshold levels. However, a similar quantitative conclusion given by Choi (1989) stated that 10 μg Hg/g maternal hair, corresponds to a methylmercury ingestion level of 0.7 μg/kg/day, and therefore, this may be considered as the LOEL for neurological effects in the developing brain. The nature and severity of the potential nervous system changes vary according to the duration and intensity of exposure, and the gestational stage at which the exposure occurred. Observation of children affected by prenatal methylmercury exposures from Japan and Iraq suggest that the most critical periods for methylmercury exposures during pregnancy appear to be the late embryonic and fetal periods after the seventh week of gestation (Choi, 1989).

2.11.2 Methylmercury Exposure Guidelines Published.

Table 2.8 gives a synopsis of the various agencies that have published methylmercury exposure guidelines or statutory levels. In order to understand how these parameters were determined, each level is described in the table to provide more detail on each. The most significant parts to note in Table 2.8 in terms of this study are the US Food and Drugs Administration (FDA) levels and the SA Foodstuffs, Cosmetics and Disinfectants Regulations These two values are considered to be the most appropriate in that they can be compared to the data obtained in this study. Additional data in terms of fish consumed and weight of adult fish eating population would have been required for the US EPA (1997)and WHO (1991) values which is beyond the realms of this study.

Table 2.8 Various methylmercury consumption limits of fish set by regulatory agencies.(SA FCD Reg 1518,1994: US EPA 1997: WHO 1991)

Regulating agency	RfD or Allowable daily intake (ADI)	Based on	How used
Food, Cosmetics & Disinfectants Reg 1518;1994 (South Africa)	0.5 mg/kg in fish as methylmercury	Greater than indicated deemed to be contaminated, harmful or injurious to human health.	.Determine acceptable levels of mercury in food.
FDA	0.47 μg / kg of body weight / day Action level of 1.00 ppm as methylmercury	The health effects of mercury, how much fish the average person consumes, the variety of fish that people consume, and how often they eat fish.	Regulating the mercury levels of fish sold in commerce.
US EPA	Interim safe RfD for consumption > 10 grams fish having mercury between 0.1-0.15ppm for adults only.	The health effects of mercury, Determined by quantity of fish consumed and / or level of mercury in fish. RfD still uncertain, particularly concerning high risk groups and is dependent on further research.	Used to determine if fish advisories are required for fish consumption.
WHO / IPS (WHO 1991)	0.48 μg Hg/kg body weight per day	Standards based on clinical observable neurological changes as the indicator of effect to exposure to mercury	As a preventative measure in adult populations who consume large amounts of fish. Levels in excess of stated value may result in incidence of paraethesia

2.11.3 WHO International Programme on Chemical Safety (WHO/IPCS)

Reference values for mercury concentrations (expressed as total mercury) in biological materials commonly used to indicate human exposures to mercury were published in 1990 by the WHO/IPCS. The recommendations of WHO/IPCS are based on clinically observable neurological changes as the indicator of effect. In addition to their recommendations of mercury concentrations WHO/IPCS recommended that as a preventative measure, in a sub population that consumes large amounts of fish (100 grams per day was given as an example women of child-bearing age should be monitored for methylmercury. The WHO/IPCS (1991) estimated that a daily methylmercury intake of 0.48 μg /kg body weight will not cause any adverse effects to adults as stated in Table 2.8 above. However, a methylmercury intake of

3 to 7 μg/kg body weight/day would result in a <5% increase in the incidence of paraesthesia in adults (WHO 1991).

2.11.4 US Food and Drugs Safety Administration (FDA)

In 1969, in response to the poisonings in Minamata Bay and Niigata, Japan, the US FDA proposed an administrative guideline of 0.5 ppm for mercury in fish and shellfish. This limit was, however, converted to an action level of 1.0 ppm in 1974 in recognition that exposure to mercury was less than originally presumed as reflected in Table 2.8. In 1984, the 1.0 ppm action level was converted from a mercury standard to one based on methylmercury (US EPA, 1997). FDA's action level is based on consideration of the tolerable daily intake. The tolerable daily intake is the amount of methylmercury that can be consumed daily over a long period of time with a reasonable certainty of no harm to adults. This equates to a tolerable daily intake per week of approximately 230 μg/week for a 70 kg person or 33 μg per person per day. The tolerable daily intake was calculated from data developed in part by Swedish studies of Japanese individuals poisoned in the episode of Niigata which resulted from the consumption of contaminated fish and shellfish and the consideration of other studies of fish-eating populations (US EPA, 1997).

Based on observations from the poisoning event later in Iraq, the US FDA has acknowledged that the fetus may be more sensitive than adults to the effects of mercury. In recognition of these concerns, US.FDA has provided advice to pregnant women and women of child-bearing age to limit their consumption of fish known to have high levels of mercury as stated in the US FDA Consumer Register 1994 (US EPA, 1997). US FDA believes, however, that given existing patterns of fish consumption, few women (less than 1%) eating fish with such high levels of mercury contamination will cause slight reductions in the margin of safety. However, due to the uncertainties associated with the Iraqi study, US FDA has chosen not to use the Iraqi study as a basis for revising its action level. Instead, the US FDA has chosen to wait for findings of prospective studies of fish-eating populations in the Seychelles Islands and the Faroe Islands[1].

2.11.5 South African Foods, Cosmetics and Disinfectants Regulation, Metals in Foodstuffs, Government Notice R. 1518 of 1994.

This Food, Cosmetics and Disinfectants Regulations, Metals in Food stuffs, Regulation R1518 is the statute for the control of contaminants for various constituents and ingredients of food stuffs in South Africa (1994). In terms of Regulation R. 1518 / 1994, as framed under the Food, Cosmetics and Disinfectants Act number 54 0f 1972, the levels of metals in foodstuffs are prescribed. Levels which exceed the stated dose as stated in Table 2.8 are deemed to be contaminated, impure or injurious to human health in terms of food offered for sale to the public. Therefore, it is an offence to offer for sale food that has methylmercury levels in excess of those levels as stated in these regulations (FCD Reg,1994). There is no reference in the legislation to suggest how the regulated level was determined.
Regulation R.1518 (1994) does not specify tolerable daily intake levels for the consumption of methylmercury in fish. All mercury levels for fish and fish products were expressed as methylmercury. This equates with the findings of Wagemann *et al.* (1997) and the US EPA recommendations that mercury is present as methylmercury in order to be most protective to the consumer[3].

2.11.6 United States Environmental Protection Agency.

In 1999 the US EPA stated that in terms of their previous report to Congress in 1997 consumers who eat less then 10 grams of fish per day with mercury levels ranging from 0.1 to 0.15ppm levels would be considerably lower then the present acceptable RfD for methylmercury (see Table 2.8)[3]. However, concern was expressed on the risk to developing fetus should these levels be exceeded and a more conservative approach should be considered. Level of exposure to methylmercury was dependent on either the quantity of fish consumed or the level of methylmercury present. Those who consume approximately 50 grams of fish per day containing between 0.1 to 0.15 ppm mercury run the risk of slightly exceeding the RfD to levels reaching twice the RfD. Whereas those who consume levels of 0.5 ppm mercury but ate less then 10 grams of fish per day are likely to have mercury exposure near the RfD. Those who, however, consumed 40 to 70 grams a day are likely to

exceed the RfD by as much as six times. The US EPA has calculated consumption limits in terms of methylmercury in fish to allowable fish meals per day, which should not be exceeded[3]. These are indicated in Table 2.9 below and were based on the following assumptions:

- Adult body weight 72 kg
- Average fish meal 227grams
- Time averaging period 30.44 days
- US EPA interim reference dose for methylmercury (1x10 -4 mg/kg)[3]

Table 2.9 Monthly fish consumption limits of methylmercury [3]

Maximum allowable Fish Meals per Month	MeHg Concentrations (ppm MeHg in fish, wet mass)
16	>0.03 - 0.06
12	>0.06 - 0.08
8	>0.08 - 0.12
4	>0.12 - 0.24
3	>0.24 - 0.32
2	>0.32 - 0.48
1	>0.48 -0.97
0.5	0.97 - 1.9
No meals	>1.9

When comparing the SA Foodstuffs, Cosmetics and Disinfectants regulated methylmercury levels in fish (0.5mg/kg) (FCD R1518, 1994) to the levels as given in Table 2.9 fish consumption should be restricted to only 16 fish meals per month. This may be problematic in those communities where fish is a major part of their diet and who may consume fish on a daily basis. In terms of risk assessment evaluations, Table 2.9 appears to be realistic in terms of general exposure as opposed to relying purely on single dose exposure.

The US EPA have reiterated that the RfD is not an exact determination between safety and toxicity and, therefore, tolerable methylmercury levels for consumption are difficult to determine, and therefore, should be considered as interim RfD values. As a precaution, certain states within the U.S issue advisory warnings of ' no consumption' to 'restricted consumption' for sensitive population groups such as pregnant and nursing mothers and young children. Despite these precautionary warnings exact harmful effects to children *in utero* are still unclear[3]. Recent studies examined populations that are exposed to lower levels of methylmercury as a consequence of routine consumption of fish and marine mammals around the great lakes and in New Zealand, the Amazon basin , the Seychelles Islands and the Faroe Islands. The last two studies were of large populations of children presumably exposed to methylmercury in utero. Very sensitive measures of assessing developmental neurotoxicity in these populations are still being analysed and published. A recent workshop discussed these studies and concluded that they have provided valuable new information on the potential health effects of methylmercury. Significant uncertainties still remain, however, because of issues related to type of exposure, neuro-behavioral endpoints, confounders and statistics as well as study design[3].

The US EPA (1997) and Boischo and Henkell (1996) also consider other parameters to evaluate the risks of methylmercury exposure in terms of exposure modelling. However, exposure modelling other than as discussed in the above synopsis is considered beyond the requirements of this study. In brief, the US EPA (1997) states that there are various ways available to assess the risk to populations from methylmercury exposure, namely, the following:

i) Increases in methylmercury concentrations in fish due to anthropogenic emissions and exposure levels of human populations are predicted, allowing for the quantification of risk.

ii) The use of dietary surveys to identify the amount and type of fish consumed by populations.

iii) The use of hair mercury levels as a method of determining whether members of a population are at risk. Methylmercury exposures for general populations are reflected by hair mercury levels. This type of assessment is an appropriate measure of actual mercury exposure since biological samples are utilized (US EPA, 1997).

2.11.7 Environmental Control in South Africa in Terms of Mercury.

In South Africa there are primarily two sets of legislation that can be used to control and prevent environmental pollution as a result of mercury. These are the Water Act, Number 36 of 1998 and the National Environmental Management Act, Number 107 of 1998 (NEMA)(Water Act,1998) and (NEMA, 1998). In terms of the General and Special Standards, which were laid down under the previous Water Act, Number 54 of 1956, a maximum level of 0.02 mg/litre mercury can be discharged into receiving waters (DWF, 1996). This is the only statutory requirement specific to mercury, which is still in force. Although the new Water Act (1998) has made provision within the Act to promulgate new criteria governing discharges of pollutants into water, however, this has still to be accomplished. The new Water Act (1998) also has procedures in place to deal with the prevention and remediation of pollution incidents. The Water Act (1998) is specific in placing responsibility on the owners of land where a pollution incident may have occurred. Owners are required to prevent incidents of pollution and where they have occurred to institute procedure to eliminate, remedy or comply with prescribed procedures to deal with such pollution incidents. Should a land owner default the controlling authority (Catchment Management Agency) may then take measures to attend to the pollution incidents and any costs that may occur will be recovered from the land owner. A Catchment Management Agency could be established for a specific water management area such as the Valley of a Thousand Hills, after public consultation with and through the initiative of the community and stakeholders present (Water Act,1998). Due to the Act only being recently promulgated it could not be established if a Catchment Management Agency had been established for the Study Area. Because Umgeni Water are the water providers for various regions of Kwa Zulu Natal they are obliged to routinely sample and analyse for

mercury in water along various points of the Umgeni River and Inanda Dam to protect their water resources[1].

The NEMA (1998) is not as specific, but has powers to attend to the care and remediation of environmental damage. As for the Water Act (1998) the obligation is placed on the owners of land on which the pollution incident may have occurred. They are required to satisfactorily abate or remedy a pollution incident and be responsible for any costs so incurred. The NEMA (1998) also confers powers on the Minister of Environmental Affairs to direct investigations, evaluations or assess the impacts of specific activities involving pollution of the environment. Such investigations can include other government departments such as the Department of Water Affairs and Forestry or the Department of Health, through the formation of a committee who are empowered to report or co-ordinate investigations (NEMA, 1998).

2.12 LABORATORY ANALYSIS OF MERCURY.

Wagerman *et al.* (1997) found a difference in results when using two different analytical procedures to determine mercury levels. The two methods employed by Wagerman *et al.* (1997) were the cold vapour atomic absorption spectrometer and gas liquid chromatography. These two methods produced differing results with higher levels being obtained by the cold vapour atomic absorption spectrometer. Wagerman *et al.* (1997) also established that when using three different calculation methods , only one of them, the linear regression analysis produced acceptable results. In South Africa the Laboratory Services of Umgeni Water utilise cold vapour atomic absorption spectrometer to analyse heavy metals primarily in water and sewage samples (Umgeni, 2000). In terms of South African criteria the Laboratory Services of Umgeni are accredited in terms of the South African National Accreditation System and they apply method 34 for the analysis of mercury. This method has also received accreditation in terms of the South African National Accreditation System (Umgeni ,1998).

CHAPTER 3

METHODS

3. SAMPLING METHODS.

3.1 INTRODUCTION

In order to quantify the extent to which mercury has become mobilized in the study area and to identify possible pathways of exposure to the community, samples of sediment, algae, cattle hair and fish were collected from an area located between Thor Chemicals and Inanda Dam. The samples were compared with those taken in a control area as indicated in figure 3.1. Mercury concentrations in fish were also compared to methylmercury consumption limits set by regulatory agencies. An outline of the generic sampling strategy applied for this study is detailed below in Sections 3.2 to 3.2.3.

3.2 AN OUTLINE OF THE GENERIC SAMPLING STRATEGY.

The sampling strategy adopted for this study was based on studies carried out by Jackson (1988), Jackson (1993), US EPA (1997) and Povari (1998). This strategy provides guidance for establishing the size of the study area, the selection of the types of samples to include in the study and the criteria to follow when collecting sediment and fish samples. In order to reduce contamination and to ensure accuracy of mercury results the methods for collecting trace elements in river beds recommended by Shelton and Capel (1998) and Porter *et al.* (1998) were adopted. These methods were either developed or modified to suit prevailing local conditions. The above methods were accepted because they are considered to be the most suitable in terms of reducing the loss of mercury from the samples (sediment, algae, cattle hair and fish) due to volatisation and contamination. In addition these procedures were used to reduce costs, lessen local scale variability and to obtain results more representative of the average contaminant levels within a sample site from where samples were collected (Shelton and Capel, 1998; Porter *et al.*, 1998).

In terms of the literature reviewed and initial observation of the Valley of a Thousand Hills the following specimens were collected for the reasons as stated:

- Sediment and algae specimens were selected since they are considered to be the most suitable indicators of mercury biomagnification within a river system (Porter *et al.,* 1993; US EPA, 1997).
- Algae was also identified as the most abundant aquatic plant in the Umgeni River.
- Cattle hair, which is considered to be a reliable indicator of mercury mobilization were included in order to ascertain the extent of bio-accumulation that may be taking place in the area (Burger *et al.*, 1994; Palherta and Taylor, 1995).
- Because fish are effective accumulators of mercury and are consumed by humans, the inclusion of fish samples was considered crucial to this study (Jackson, 1988; WHO, 1993; US EPA, 1997; Park and Curtis,1997 and Kannan *et al.*, 1998).

A total of ten sample sites were selected and were identified alphabetically from A to J. The specific methodology applied to obtain each of the sample groups is detailed in sections 3. 3 to 3.6 below. In order to predetermine the approximate position of sampling sites and to establish access in terms of the terrain and roads within the area, two 1:50 000 topographical maps were obtained from the Land Surveyors Office, Cape Town. The area maps are identified as 2930DA Cato Ridge: third edition 1989 (Cato Ridge: 2930DA) and 2930DB Inanda: fourth edition 1989 (Inanda: 2930DA), see Annexure A. The first sampling site was identified as being approximately 500 metres from the boundary fence of Thor Chemicals at co-ordinates 30°43" 00'S and 29°37" 30'E, and was marked on the Cato Ridge: 2930DA map with a red dot and the letter A. The final sampling site was taken at the top end of the Inanda Dam, approximately 200 metres above where the Mshazi Stream enters the Umgeni River, at co-ordinate 29°40"85'S and 30°48"80'E, and was marked on the Inanda:2930DB map with a red dot and with the letter J. This identification procedure was applied to all sampling sites. The remaining eight sample sites were selected from between the above two points on the two maps as described above. These sites extend along the Mngceweni River (tributary) and Umgeni River at intervals ranging from 3 to 5 kilometres from each other. The maps Cato Ridge: 2930DA and Inanda: 2930DB were used to assist to identify access points to each sample site. Figure 3.1 indicates the general position of the sample sites A to J in the study area.

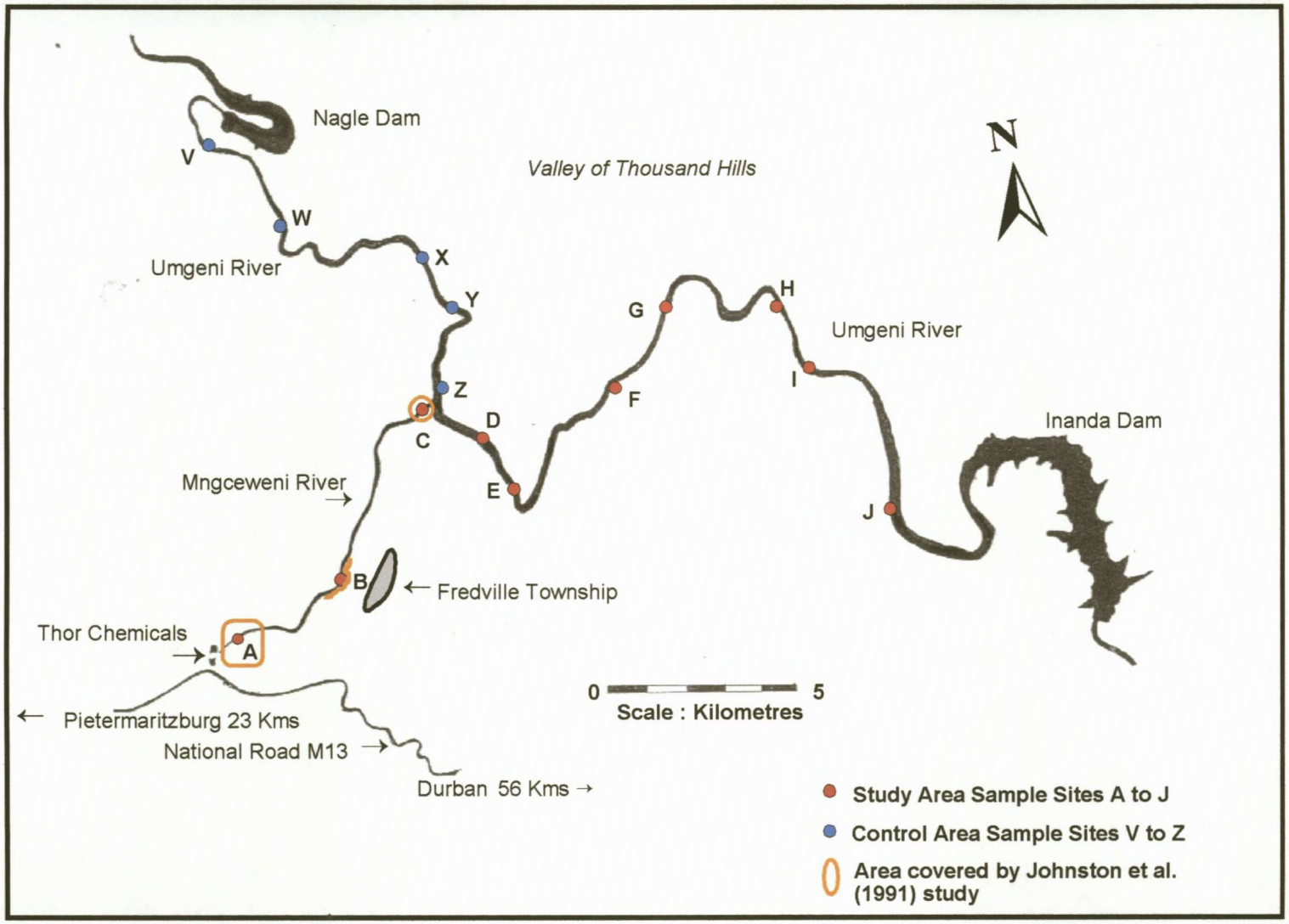

Figure 3.1 Sketch of Study Area and Control Area Indicating Locality of Sample Sites (A to Z) in Relation to Thor Chemicals at Co-ordinates 30°43'08" 29°37'20"E in The Valley of a Thousand Hills, Kwa Zulu Natal

To improve accessibility, a 2 x 4 vehicle was used to transport equipment and personnel into the area. At each sample site the sediment, algae and fish samples were collected in terms of the methods described below. Cattle hair was obtained from cattle in the immediate environment of the sampling site. These samples were obtained between November and December 1998 and in the case of fish samples from Inanda Dam between December 1998 and June 1999. The methodology pertaining to personnel equipment and sample identification is described under sections 3.2.1 to 3.2.3 below.

3.2.1 Personnel Sampling Equipment.

During the sampling period all sampling personnel wore clean cotton clothes and gumboots and un-powdered vinyl gloves in accordance with the procedures as recommended by the US Water Quality Assessment Programme (Shelton and Capel, 1998) and (Porter *et al.*, 1998).

3.2.2 Sample Identification for Sediment, Algae, Cattle hair, Catfish and Carp.

All samples (sediment, algae, cattle hair, catfish and carp) were identified numerically starting with the numerical figure 1 followed by the specific name of the sample being collected (e.g. sediment). Further each sample site was identified alphabetically starting with the letter A, which identifies the first sample site, see Fig 3.2 below. When additional or sub-samples were taken for individual analysis from the same sample site these were further identified by using lower case alphabetical letters, in brackets, after the sample number e.g. 1 (a); 1 (b) etc.

Sample No: 1(b)
Type of Sample: Sediment
Sample Site: A

Figure 3.2 Indicating a typical sample identification label. Label for sediment sub-sample 1 (b) taken at the first sample site being A, situated approximately 500 metres below Thor Chemicals.

In the cases where samples of carp and catfish were obtained from Inanda Dam, the sample site was identified as Inanda Dam.

3.2.3 Sample Collection and Dispatch (sediment, algae, cattle hair and fish).

All samples (sediment, algae, cattle hair and fish), immediately after collection, were placed in Styrofoam insulation boxes, which were packed with ice, in order to reduce the temperature as rapidly as possible so as to decrease volatisation of the mercury (Shelton and Capel, 1998; Porter *et al.*, 1998). The samples were dispatched to the South African National Accreditation System (SANA) approved laboratory of Umgeni Water, Pietermaritzburg, on the day of sampling. On occasions when samples could not be dispatched, for example when collecting samples after hours, they were kept frozen at - 15°C until delivered to the laboratory for analysis.

3.3 SEDIMENT SAMPLE COLLECTION.

As previously stated in 3.2 a total of 10 sample sites were selected from within the study area from which sediment samples were obtained. The methodology as defined in the US Geological Survey National Water Quality Guidelines for collecting stream bed sediments was accepted (Shelton and Capel,1994). Samples were collected from depositional zones where sediment was likely to be deposited along the river course. These areas were located on the inside bend of the stream or areas downstream from obstacles, such as boulders,

islands, sand bars, or simple shallow waters near the shore. Only wadeable depositional zones were chosen in that they were easy to visually identify and sample. Each sample site extended approximately 100 meters in length along the river. The length of the sampling site was determined by the streams geomorphology in terms of the extent and access to the sediment bed. Figure 3.3, below, illustrates a typical stretch of river, showing the natural deposition zones and possible sample points, from where sediment samples were removed from the river bed.

The sample point was visually examined to identify areas of the river bed that appeared to include only fine grained sediments (<20 μ m fraction) which have a high organic loads. Such sediments would include those that contain clay and silt particles, as these properties are considered to be natural accumulators of mercury (Shelton and Capel, 1994). If the sediment appeared to be of a higher fraction, that is containing high levels of grit or sand, the immediate area of the river bed was regarded as being unsuitable for sampling and was bypassed. At this stage the low fraction sediments were selected purely on visual inspection of the river bed. The actual 20 μ m fraction was to be removed later by the analytical laboratory at Umgeni Water.

At each sample site, 5 to 8 sub-samples were collected to make one single sample which was considered to be representative of the entire sample site (Shelton and Capel, 1994). This single sample was obtained by a process known as coning where the sub-samples are homogenised and combined to form a composite sample. The actual coning of the sub-samples to make one representative composite sample was carried out in the Umgeni Water's Analytical Laboratory. The objective and method of taking these sub-samples for coning is described further in Section 3.5.

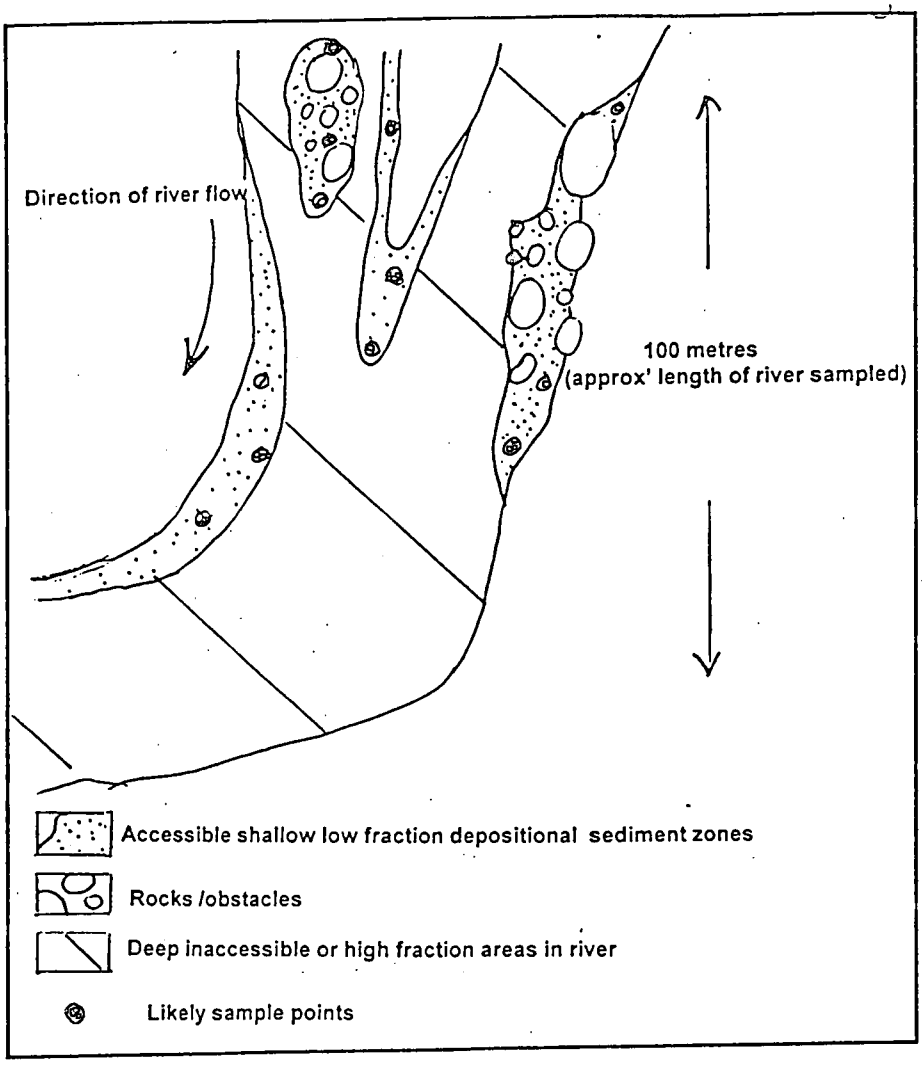

Figure 3.3 Representation of typical river to indicate likely areas for sediment sample collection in terms of access to high fraction depositional zones and wadeable areas in a river as recommended by the US Geological Survey Report , Guidelines for collecting samples from a stream bed for trace elements and organic materials (Shelton and Capel, 1994).

3.3.1 Sampling Procedure.

Upon arrival at a sampling site the actual site was marked in red on the appropriate 1: 50 000 maps, shown in a reduced form in figure 3.1. Sampling personnel wearing rubber boots, clean cotton clothing and un-powdered vinyl gloves removed the following equipment from

the sampling container: sterile plastic bags for containing the sediment sub-samples, 30 cm PVC coring sampler, with two air tight plastic bungs inserted at either end and a heavy duty plastic scoop for the actual removal of the sediment. Tie on labels and a water proof pen were also removed and set aside on the river bank in preparation for labeling as specified in 3.2 2 above.

The sample site was approached from downstream in order to reduce the disturbance of the sediment which could result in contamination of the sample. The plastic bungs were removed from both ends of the corer. The corer was then inserted into the river bed to a depth of approximately 10 cm in order to draw up a sediment sample. Prior to removing the corer from the river bed, a plastic bung was inserted into the top opening of the corer, so as to retain the sub-sample within the corer. Only after the bung was securely in place was the corer lifted from the river bed. However, before removing the corer from the water, the second bung was firmly inserted to seal the corer containing the sub- sample. The corer containing the sub-sample was then taken to the river bank. The top bung was removed and the excess water drawn off by tilting the corer carefully so as not to loose any of the sediment trapped within the corer. Finally the sediment sample was emptied into a sterile plastic sampling bag. The sediment sample was again inspected to visually determine if it contained primarily fine fraction (20 μm) organic material and that there was sufficient amount of sediment for analysis, being not less then 500 grams. If the sub-sample appeared to contain only high fraction sediments or was less then 500 grams it was rejected and discarded. Tie on labels were then firmly attached to the bags containing the sub-samples considered suitable for analysis. The sample identification particulars as described in 3.2.2 above were written on the label with a water proof pen. The bagged and labelled sub-sample was immediately placed into the cooler box containing ice in order to reduce the loss of mercury due to volatisation from the sediment.

In areas where the sediment bed was not sufficiently deep, or in the shallow pool areas, sediment was removed by scooping up 500 grams, or more, of sediment. The same procedure as described above was applied with respect to the suitability of the sub-sample and its labelling and containment in the plastic bags. This process was repeated until five

to eight sub-samples had been collected from each sample site depending on the availability of suitable sediment being sampled.

3.3.2 pH and Temperature Readings.

In order to determine the potential of the river water to reduce inorganic mercury to methylmercury, water temperature readings (°C) were taken at each point from where the sub-samples of sediment were removed. Simultaneously pH readings were also taken to determine the potential for mercury to leach from the sediment and therefore become mobilized to be taken up into other trophic levels within the ecosystem. Both readings were taken using a Beckman 200 pH and temperature metre. The instrument was calibrated prior to sampling with buffers of pH 4 and pH 10. The probes were placed in the river water and once the readings were stabilised they were recorded. An average for each of the pH and temperature readings were calculated and was considered to be representative for the sample site from where they were obtained.

3.4 AQUATIC MICROPHYTES (ALGAE)

Depending on availability, algae samples were collected at the same sample sites as for the sediment, in accordance with the methodology detailed in the US Geological Survey for the collecting of algae samples (Porter *et al.*, 1998). The collection of algae only took place after the sediment sub-samples had been obtained in order to reduce stirring or contaminating the sediment within the river. Algae samples were collected from within the sampling site area and the number of samples obtained depended on access and availability of the algae. A minimum of 5 and a maximum of 8 sub-samples of algae were obtained from each sample site. Sub-samples were collected by hand, using un-powdered vinyl gloves, in wadeable areas only. Where algae adhered to the substrate and, as such, could not be removed by hand, the heavy duty plastic scraper was used to dislodge the algae. Care was taken not to contaminate the sub-samples with substrate particles. Immediately after the sub-sample was obtained it was placed in a sterile plastic bag and removed to the river bank where it was labelled in accordance with the methodology as described in section 3.2 and 3.3.1 above.

Thereafter the bag containing the algae was firmly sealed and placed in the cooler box along with the sediment sub-samples. As for the sediment samples, sub-samples of algae were collected at each site and were composited through the procedure known as conning as described in section 3.5.

After all of the sediment and algae samples had been labelled and placed in the cooler boxes the sampling personnel and their assistants removed their gumboots and un-powdered vinyl gloves and washed them in the river in order to limit any form of contamination of future samples to be taken at other sample sites. These were retained until the next sampling site was reached.

3.5 THE CONING PROCEDURE FOR COMPOSITED SEDIMENT AND ALGAE SAMPLES.

As stated above, at each of the 10 sample sites, five to eight sub-samples of sediment and algae were collected. The number of sub-samples was based on the size of the sample site and access to suitable sediment and algae. Each of the sub- samples were bagged, labeled and placed in cooler boxes as described in section 3.2.2 and 3.3.3, prior to removal to the Umgeni Water's Analytical Laboratory. The Umgeni Water's Analytical Laboratory applied the same procedure for sediment and algae samples. That is, the sub-samples for either the sediment or algae were combined, mixed well and homogenised to form one sample. From this one sample, a cone was formed and separated into quarters. The bottom left and top right was discarded. The remaining quarters were mixed well and again a cone was formed. This cone was also separated into quarters. The bottom right and top left was discarded. The remaining sample was again mixed well and a cone formed . The procedure of discarding the top right and bottom left in the first instance and in the second instance of discarding top left and bottom right was repeated twice again. The remaining portion of the sample was then considered to be a composited sample and was analysed. As stated this procedure was carried out by Umgeni Water's Analytical Laboratory.

In order to ascertain the validity of the coning technique used by the laboratory one sample site was selected randomly, i.e. sample site C, see figure 3.1. Sediment and algae sub-samples obtained from this sample site were analyzed individually after each of them were throughly mixed and homogenised. The composited sample was then formed by removing a potion of the homogenised material from each of the sub-samples. These individual potions were also combined, mixed well, homogenised and coned as described above. The Wilcoxon Scores Two Sample t Test was used to statistically validate this technique by comparing the mean of the individual sub-samples to the composited sample result for both sediment and algae. The compositing technique would only be accepted if the mean of the individual samples were comparable to the composited sample at the 95% confidence level. The statistical analysis and results are described below.

3.5.1 Sediment

The results for the individual sediment sub-samples and the composited sample from site C are given in Table **3.1** below. Sample numbers Ca to Cg are the individual sub-sample results which gave a mean result of 0.73 μg/gram. The composited sample, made up of the combined sub-samples, was analyzed and a reading of 0.86 μg/gram was obtained. No significant difference was found between the mean of the individual sub-sample results (0.73) and the composite result (0.86) at the 95% confidence level ($p = 0.16$). Therefore the compositing technique, as carried out by the Umgeni Water's Analytical Laboratory, can be considered to be statistically acceptable.

Table 3.1 Mercury levels of individual sediment samples taken at Sample Site C and the composited sample (homogenised individual samples) in order to verify the technique of compositing conducted within the laboratory.

Sample No	mercury (μg/g)
Ca	0.63
Cb	0.83
Cc	0.52
Cd	0.57
Ce	1.109
Cf	0.72
Cg	0.78
Composite:	**0.86**
Mean (Ca to Cg):	**0.73**

3.5.2 Algae

All the mercury levels for both the individual sub-samples and the composited sample were below detectable limits (<0.5 μg/liter). Therefore it was not statistically possible to compare the mean of individual sub-samples to the composited sample. As a result the coning method as applied to the algae cannot be validated statistically.

3.6 CATTLE HAIR

Cattle in the area are only penned at night and during the day they graze freely in the study area and consume water from the Umgeni River. Cattle also have a habit of wading into the water when drinking, thereby stirring up sediment, which increases the likelihood that they could be consuming deposited mercury.

Cattle's hair could not be collected during the day because the cattle graze freely in the veld. The local people from the community were therefore approached to assist in obtaining

samples of hair from their animals when they were penned at night. Due to the difficulty of obtaining samples during the day, a relationship was established with the owners to ensure that the appropriate samples were collected by them from their cattle. Only cattle that drank from the Umgeni River and had been residing in the area for more then three years were selected for sampling purposes. Cattle were not found in the vicinity of the Mngcweni River and therefore cattle hair samples were not obtained from this source. Sampling was restricted to the area below the confluence of the Mngcweni stream along the Umgeni River up to the Ndunaizi Village, due to the resistance of local farmers to allow samples of hair to be taken from their cattle, see Cato Ridge: 2930DA map, Annexure A for the location of the area discussed above. No distinction was made between the various breeds and sexes of cattle.

3.6.1 Methodology for Collecting Cattle Hair Samples.

Local inhabitants were interviewed and their permission was obtained prior to any samples being taken. They were remunerated for obtaining the hair samples. The owners of the cattle were requested to complete a short questionnaire, as indicated below, in order to verify that the animals were suitable. All instructions were conducted through interpreters so as to prevent any misunderstandings. The prevention of contamination of the sample was strictly emphasised and owners were required to wash their hands throughly prior to collecting the sample and again, if a further sample was to be obtained that same evening. The cattle owners were provided with stainless steal scissors and were requested to cut approximately a handful of hair from the tail of the animal. The hairs were placed in a plain white envelope and sealed immediately after collection. The completed questionnaire was attached to each envelope. Sample area identification and numbering for each hair sample was determined from the information derived from (b) in the questionnaire below. The hair from cattle which resided closest to the equivalent sample site from where sediment / algae samples were collected, were given the identical sample site number and were labelled in accordance with the methodology as stated in section 3.2.2.

Questionnaire given to cattle owners:

a Name of owner:

b. Kraal name and chief of the area.

c. Length of time residing in the area.

d. When was the sample animal obtained ?

e. Where was the sample animal obtained ?

f. Food source

Sample No. (to be completed by researcher)

3.7 FISH

Since Inanda Dam is deemed to be the major receiver of sediment deposition from the study area, the sampling of large fish from this source was considered to be of great importance. Figure 3.1 indicates the locality of Inanda Dam to the study area. Sharp Toothed Catfish and Carp of between 3 to 5 kg in weight, or between 30cm to 40 cm in length, were caught from Inanda Dam which is situated approximately 35 km downstream from Thor Chemicals. These species and sizes were considered the most suitable in terms of indicators of mercury bio-accumulation, as described under Chapter 2 section 2.6.

Along the Umgeni River, in both the study and control areas, Catfish and Carp of this size could not be obtained. However, local fishermen were observed catching and reported consuming a large number of Carp and Catfish from the area, all of which were under size, ranged between 15 cm to 20 cm in length and approximately 600 grams in weight. Due to the fact that these were the most prevalent size and types of fish caught and consumed by the people in this area, in particular by small boys, it was considered appropriate to include them in the study, despite their small size. Seven fish of this nature were purchased directly from the local fishermen and immediately weighed and measured before placing the sample into a sterile bag. The fish samples were labelled in accordance with the methodology as described in section 3.2.2. They were then immediately placed within the cooler boxes,

containing ice, prior to removal to Umgeni Laboratory on the same day of collection. Those samples that could not be delivered to the Laboratory were placed in a deep freeze.

3.7.1 Methodology for collecting fish samples.

A local fisherman in the area was approached to assist in the collection of fish samples from Inanda Dam. These were caught with fishing rods using earth worms, maize meal and bread as bait. The fisherman was instructed to, upon landing the fish, to immediately place the specimen in one of the sterile bags provided. The fisherman was required to complete the questionnaire as indicated below and attached it to the bag containing the specific sample. The fish was then placed within a cooler box containing ice in order to reduce the temperature as rapidly as possible. Upon returning home the fisherman was required to place the samples in a deep freeze at -15°C. He was instructed to ensure that the fish were kept frozen at all times. The fish remained within the cooler boxes until placed in the freezer on the same day as the fish were caught. The fish were collected from the fisherman within 30 days. The samples were identified and labelled as follows. All the fish were identified according to their species. Those fish obtained from Inanda Dam were allocated a sample number starting with numeral 1, for example: Inanda Dam; Carp 1. The small fish obtained from Umgeni River were identified in the same way as for the hair samples, see 3.6.1. The samples were immediately delivered to the Umgeni Water Laboratory within one hour of collection in order to ensure that the samples remained frozen until analysed.

Questionnaire given to fisherman:

a. Name of fisherman and address.
b. Site and location were fish was caught.
c. Date and Time fish caught by fisherman.

To be completed by researcher:

a. Date and Time fish obtained from fisherman

b. Weight of fish.

c. Length of fish.

d. Sample No.

3.8 CONTROL SAMPLES

3.8.1 Location of the Control Area

The control area was chosen due to its similarity to the study area in terms of its geographic location, for example the majority of the samples were taken from the same river, and that other possible mercury pollution sources, such as air pollution would affect both areas similarly. The five control sample sites (V to Z) were identified along the Umgeni River north, upstream and above the watershed from Thor Chemicals and the Mngceweni Stream. The first sampling site was identified at the last bridge prior to entering the picnic site at Nagle Dam at co-ordinates 29°35"92'S and 30°37"72'E and the final sample site was identified on the left bank approximately 100 metres north of the bridge to Egugwini Village at co-ordinates 29°39"00'S and 30°41"03'E, approximately 17 kilometres from Nagle Dam. The remaining three sample sites were situated at a distance of 3 to 5 kilometres distance from each other, depending on accessibility. As for the study area the samples were collected from each site by referencing the Cato Ridge: 2930DA map in order to determine suitable access points in terms of the terrain, roads and general lay of the river. The sites were marked on the Cato Ridge: 2930DA map in blue in order to distinguish the study group sample sites from the control group sample sites. Fish samples were obtained from Nagle Dam situated approximately 16 kilometres linear distant from Thor Chemicals. Figure 3.1 indicates the location of the control area to the study area.

3.8.2 Sampling Strategy for the Control Area.

The procedures, protocols and methodology employed in the collection of control samples was identical to that described above for the study area. The following control samples were collected:

i) Sediment: (5 composite samples, consisting of between 5-8 sub-samples)
ii) Algae: (4 composite samples consisting of between 5-8 sub-samples)
iii) Cattle hair: (7 samples)
iv) Fish: (10 samples from Nagle Dam)

3.9 LABORATORY ANALYSIS OF SAMPLES.

All samples were transported to the Umgeni Water laboratory immediately after collection, or frozen at -15°C, (except hair) until they could be taken to the laboratory. Umgeni Water Laboratory is accredited in terms of South African National Accreditation System (SANAS) (see Appendix B). Method 34 which is also accredited in terms of SANAS was used to analyse all the samples for total mercury and is described in greater detail in Appendix C. Essentially, Method 34 is used to quantify trace quantities of mercury in water and waste waters. Although Method 34 was used to analyse all the specimens, certain of the procedures were modified where necessary. In the case of sediment algae and hair, the specific procedure is detailed in Appendix C section 4.1. Both sediment and algae were required to be coned to comply with the recommendations as given by (Shelton and Capel, 1994). The procedure adopted for coning these samples by the laboratory is described in Appendix C section 4.3. Muscle tissue from the area adjacent to the dorsal fin of the fish was selected for analysis because the affinity of mercury to be absorbed into fish muscle (WHO, 1993); (US EPA, 1997) and (Kannan *et al.*, 1998).

Possible sources of error of measuring mercury in terms of Method 34 are listed in Appendix C Section 5. However the analysis methods were subjected to standards and strict analytical

quality control pre-treatment procedures in order to minimise any sources of error, see Appendix C sections 2.2 and 3.3. In addition, the atomic absorption spectrometer was also calibrated prior to analysis, as described in Appendix C section 3.4. In order to determine as accurately as possible the mercury levels in the sediment, duplicate samples were analysed and the final result was calculated from the mean of the two results. Due to the limited sample mass, however, duplicate specimen samples could not be analysed for algae and cattle hair as stated in Appendix C section 4.1. Finally all glass ware and bottles used in the analysis were soaked in a dichromate/ nitric acid bath solution to reduce contamination as described in Appendix C section 2.1.

3.10 UNIT OF MEASUREMENT

The measuring of all the samples (sediment, algae, cattle hair and fish) for mercury was determined by the Umgeni Water's Atomic Absorption Spectrometer which provides readings in μg/ litre. Sediment, algae and cattle hair readings were based on the dry mass of the sample and in the case of the fish it was based on the wet mass of the sample. In order to compare mercury levels to various regulatory standards and findings from other studies, the sediment and fish results were converted to μg/gram. Mercury levels detected in algae and cattle hair were also given in μg/litre, but there was insufficient sample material to convert from μg/litre to μg/gram, as explained in Annexure C section 4.1. The conversion to μg/litre to μg/gram was achieved by multiplying the mercury value in μg/litre by 0.1 and dividing this result by the weight of the sample to give a reading in μg/gram. For example the weight of a sediment sample was 5.83 grams. The Atomic Absorption Spectrometer gave a reading of 18 μg/litre. 18 μg/litre multiplied by 0.1 and divided by 5.83 (weight of sample) equals 0.31 μg/gram. None of the sediment and fish samples collected had the same weight. However, it is also important to note that the Atomic Absorption Spectrometer was limited to give readings no lower than 0.5 μg/liter. Where values may have ranged between zero and 0.5 the Atomic Absorption Spectrometer would only display a reading of < 0.5, thereby indicating that the mercury level is below detectable limits. All readings that had a value of < 0.5 μg/liter are, therefore, in effect are fixed values. The conversion to μg/gram in such cases is entirely dependent on the weight of the sample. These values (μg/gram) are represented in **bold** in

the results and should also be considered as below detectable limits and not as true values, other than when discussed separately in chapter 4.

3.11 LIMITATIONS OF THE STUDY

In any study there are certain limitations that are identified and these need to be highlighted as they may influence the validity of the findings. The following limiting factors were identified in this study.

i. Due to the geographical nature and extent of the study area as well as budgetary constraints, a limited number of environmental samples could be taken. A sampling technique described as compositing was used to optimize the representativeness of sediment and algae samples. In addition only 10 and 5 sample sites were selected for the study and control areas respectively.

ii. The number of algae samples collected from for this study were limited due to negligible amounts of the plant in certain parts of the river in both the study and control areas

iii. Obtaining permission from the local people to collect cattle hair samples proved to be difficult due to the superstitious beliefs, by them ,regarding the use of animal parts to perform witchcraft. Therefore samples could only be obtained between sample points D to E. It is noted however, that the most problematic areas, in terms of obtaining samples, were some distance from the Thor Chemicals plant on the periphery of the study area.

iv . The Umgeni Water's Analytical Laboratory was unable to isolate the <20μm sediment fraction as initially requested, which may result in lower mercury levels readings in the sediment samples. Mercury content in sediments tend to be higher in those sediments that have a fraction size of 20μm or less.

v. The Atomic Absorption Spectrometer used at Umgeni Water's laboratory could not analyse mercury lower than 0.5μg/ litre in all the samples analysed (sediment, algae, cattle hair and fish). Consequently all mercury concentrations below 0.5μg/ litre could not be determined, which restricted the available data for statistical analysis.

CHAPTER 4

RESULTS

4. INTRODUCTION.

The objectives of this study are to investigate the concentrations of mercury in sediment, algae, cattle hair and fish recorded at each site in the study area to ascertain whether mercury is being transferred in the environment and if bio-accumulation is taking place. Of particular significance in this regard are the mercury levels found directly below Thor Chemicals, at the confluence of the Mngceweni and Umgeni River and the mercury levels found in the fish obtained from the Inanda Dam, as discussed below. In addition comparisons are made between the sediment results obtained in this study to the data collected by Johnston *et al.* (1991) in order to ascertain likely trends in mercury concentrations that may have taken place in the intervening eight years.

4.1 ENVIRONMENTAL MERCURY LEVELS.

4.1.1 Sediment.

The first step in the study was to ascertain the levels and the state of mercury in the sediment of the Mngceweni and Umgeni Rivers. The second step was to determine if the mercury had become mobilised and thereby be made available to be taken up by the algae, cattle and fish within the study area. In order to quantify this the concentration of mercury in the sediment was initially obtained. The results of the mercury in the sediment are given in table 4.1 below. The levels of mercury within the sediment at site A, located at the source of the Mngceweni River which begins approximately 200 metres below Thor Chemicals, was found to be the most meaningful. Mercury concentrations in sediment at sample site A was considerably higher (54 μg/ gram) than all the other mercury levels detected in the sediment at the remainder of the sample sites in the study area. Mercury levels within detectable limits

were only found at 5 sample sites, being B, C, E, H, where a mean value of 0.41 μg/gram for these sample sites was calculated. This can be regarded as a 99 % reduction in mercury concentrations in sediment downstream of sample site A. Mercury levels in sediment below detectable limits (< 0.5 μg/ gram) were recorded in the remainder of the sample sites, being D, F, G, I and J, all of which are on the Umgeni River. This suggests that once the Mngceweni River enters the Umgeni River, which is directly below sample site C, there is a substantial dilution of mercury concentration in the sediment. This can be demonstrated by comparing the mean detectable mercury values (0.53 μg/ gram) at sample sites B and C on the Mngceweni River, to the detectable mercury values (0.23 μg/ gram) at sample sites E and H on the Umgeni River, which is 50 % reduction in mercury in the sediment between the two rivers. The concentration of mercury in the sediment appears to reduce even further at 18 kilometres downstream of Thor Chemicals (Sample Site F). From this site to Inanda Dam, only one site (Sample Site H) was within detectable limits as recorded by the Atomic Absorption Spectrometer. Nonetheless, the mercury concentration of 0.09 μg/ gram in the sediment, at sample site H, is substantially lower when compared to the mean value of 0.41

Table 4.1 Mercury levels (μg/g) in composited sediment samples (consisting of 5 to 8 sub-samples) obtained directly below Thor Chemicals (Sample Site A) to Inanda Dam (Sample Site J), in 1998, and mercury in sediment results obtained by Johnston *et al.* (1991) at Sample Sites A, B and C, and respective distance (kilometres) of each site from Thor Chemicals to each Sample Site A to J.

STUDY AREA Sample sites	**UNITS: mercury concentrations (μg/g: dry mass) 1998**	**Mercury (μg/g: dry mass) Johnston *et al.* (1991)**	**Approximate Distance of site from Thor Chemicals (kilometres)**
A	54.00	49.6	1
B	0.19	0.26*	4
C	0.86	0.017	9
D	**<0.12**		12
E	0.48		15
F	**<0.07**		18
G	**<0.01**		21
H	0.09		26
I	**<0.20**		30
J	**<0.10**		34.5
K			
Mean values of B,C,E & I	0.41		

* The exact location of this Johnston *et al.* (1991) sampling site to Sample Site C (Fredville Township) cannot be established.

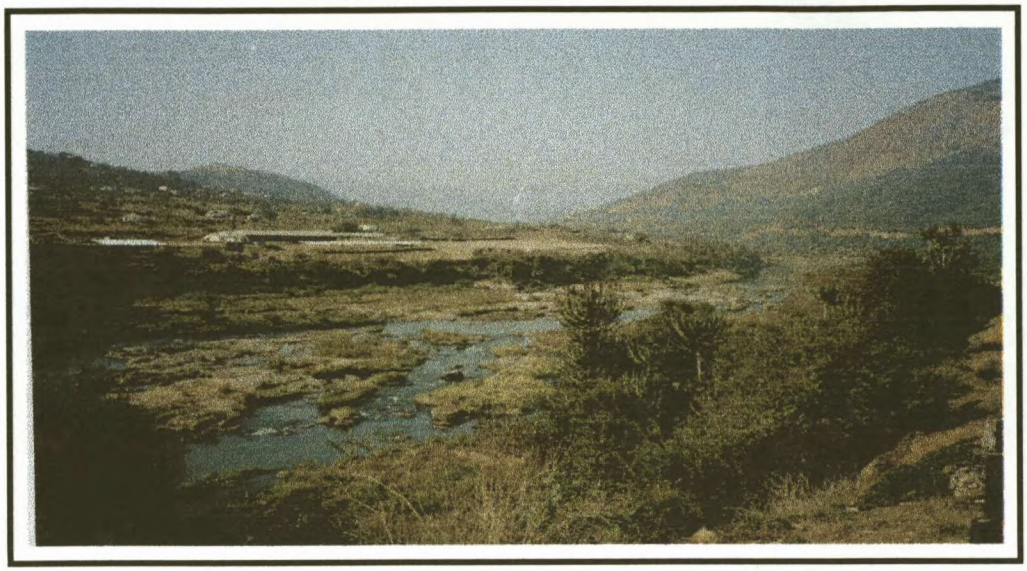

Plate 4.1 **The Umgeni River looking downstream to where the Mngceweni River enters the Umgeni taken in December 1998.**

Plate 4.2 **Sample Site C on the Mngceweni River approximately twelve kilometres from Thor Chemicals and directly above the point where it enters the Umgeni River in December 1998.**

Table 4.2 Mercury levels (μg/g) in composited sediment samples (consisting of 5 to 8 sub-samples) obtained from the control area from sample sites V, at the bridge to Nagle Dam, to sample site Z, at the bridge to Egugwini Village.

Control Area Sample Sites.	**UNITS: mercury (μg/g)**
V	**<0.006**
W	**<0.100**
X	0.4700
Y	0.0300
Z	0.3000
Mean values of X,Y& Z	0.27

When comparing mercury in sediment levels from this study to those obtained by Johnston *et al.* (1991) eight years previously, an interesting scenario appears. Both sets of results are given in Table 4.1. The mercury level in sediment measured at Sample Site A in 1998 (56 μg/ gram) compare well with mercury in sediment taken from the same area by Johnston *et al.* (1991). This indicates that there has been a slight increase (8.8%) in the amount of mercury below Thor Chemicals. The fact that mercury levels in this area are still relatively high may support the theory that mercury can exist in stream sediments for decades (US EPA, 1997). However, the possibility that continuous leaching from the slimes dams situated within the factory complex of Thor Chemicals into the Mngceweni River cannot be discounted as a cause for the steady levels of mercury in the sediment over this period. Although Johnston *et al.* (1991) also took sediment samples from the Mngceweni River in the Fredville area, as in this study (Sample Site B) the exact location of Johnston's site could not be established. Figure 3.1 shows the approximate location of the Johnston *et al.* (1991) sample sites with respect to the samples for this study. Therefore, comparisons between Sample Site B and Johnston *et al.* (1991) were not ascertained. This was not the case for sample sites A, as discussed above and C which is discussed below.

Of particular interest was the level of mercury in sediment at Sample Site C. When comparing the values of the Johnston *et al.* (1991) study to the results obtained in 1998 from the same area the mean value of mercury in sediment increased from 0.017 μg/ gram in 1991 to 0.860 μg/ gram in 1998. This is an increase of 98.11% of mercury levels in the sediment at this site over a period of eight years. This may support the theory that some of the mercury is being assimilated into the sediment due to microbial activity and temperature (Jackson, 1993 and others). However, this increase in mercury values could also be attributed to several other factors. For example, no recorded information could be obtained to determine any events that may have occurred at Thor Chemicals or within the Mngceweni River over the last seven years, which could have affected the movement of mercury in this region. In addition, this section of the Mngceweni River, at Sample Site C, levels out into a flat alluvial plain and could become a natural sink for mercury deposition from either Thor Chemicals or even from natural deposition from the surrounding area. See Plate 4.2 which is photograph taken of sample site C indicating the layout of the Mngceweni River at this point. Further the precise sampling and analytical procedures adopted by Johnston *et al.* (1991) cannot be established from the literature. Therefore, there may be fundamental differences between the procedures adopted in this study to those adopted by Johnston *et al.* (1991). Wagermann *et al.* (1997) reported that there are inherent limitations when measuring mercury, in terms of accuracy, due to possible contamination of the sample and different methods of analysing and calculating mercury, see Chapter 2 section 2.12. The subject concerning different sampling and analytical procedures to determine mercury levels in sediment can be further demonstrated by referring to Johnston's *et al.* (1991) study where only those sediments with a low fraction level (<65 μm) were analysed for mercury. As discussed in Chapter 2, sediments with a lower fraction tend to have higher mercury concentrations. One of the limitations of this study (Chapter 3 Section 3.11) is that the Umgeni Water's Analytical Laboratory were unable to isolate the <20μm fraction from the sediment. As a result the mercury sediment levels could have been higher or lower if the <20μm fraction had been removed by Umgeni Water's Analytical Laboratory.

An important aspect of this study is the comparison between mercury in sediment levels, recorded within the study area, to those measured in the control area, see Table 4.1 and 4.2. The limitation of not being able to analyse the <20μm fraction could influence the comparison

of mercury levels in sediment between the study and control areas. This crucial factor is considered important in terms of statistically comparing the two areas to determine the possible effects of mercury pollution from Thor Chemicals. The probability that the mercury concentrations may have been higher in the low fraction sediments cannot be disregarded. In addition the Atomic Absorption Spectrometer was unable to give readings for mercury below 0.5μg/litre (see Chapter 3 Section 3.10), which affected the quantity of meaningful data available to statistically compare the two groups. In such cases where the Atomic Absorption Spectrometer could not give readings these levels where considered to be below detectable limits. However in order to compare the mercury in sediment concentrations with other studies it was necessary to convert the values from μg/litre to μg/gram. The methodology pertaining to the conversion from μg/litre to μg/gram is discussed in detail under Chapter 3, Section 3.10. In such cases where the Atomic Absorption Spectrometer gave a reading of <0.5μg/litre (below detectable limits) the same calculation was performed using the 0.5μg/litre value as the concentration of mercury. Because none of the sediment samples were of similar weight all of the 0.5μg/litre values would be different once they were converted to μg/gram. All of these conversions, using the 0.5 μg/litre values, are indicated in bold in Table 4.1.and 4.2. However, in consideration that mercury levels in the sediment could have been higher, for the reasons indicated, it was considered statistically acceptable to also include the less than value (< 0.5μg/litre) when comparing the study area to the control. Because of the unreliability of including all the results as furnished in Table 4.1 and 4.2, two Wilcoxin Two Sided t Tests were conducted as follows:

i) The Two Sided t Test was conducted on all mercury levels in the sediment samples. That is levels within delectable limits and those in **bold** which are considered to be below delectable limits, in consideration that these levels may have been higher as explained above.

ii) The same statistical method was carried out a second time on those values which were considered to be true values. That is excluding those values below detectable limits which are indicated in bold in Table 4.1 and 4.2.

From the results of these two separate statistical analysis it was considered admissible that if both tests gave equally corresponding results it would be considered to be highly significant. Or, if the results from the analysis were different, then any distinction between the study and control areas would remain inconclusive.

When comparing all of the mercury in sediment values from the study area (Sample Sites B to J, excluding site A, which is considered an outlier) to the control area (Sample Sites V to Z) it was found that there is no significant difference at the 95% confidence level. The same was found when comparing only the true values, where p=0.53. It appears that mercury discharges from Thor Chemicals have not had any significant effect on the mercury levels in sediment of the Mngceweni and Umgeni Rivers within the study area, other than that area directly below Thor Chemicals (Sample Site A).

4.1.2 pH and Temperature.

Important factors which may influence the concentration or the state of mercury in the sediment are the temperature and pH of the river water from where the sediment samples were collected, see Table 4.3. The mean temperature of the river water at sample sites A to J ranges between 27.7 °C and 31.5 °C. These values were obtained by averaging between 6 to 8 readings taken at each sample site in November 1998. There is little difference in temperature between each site, including the control sites (Table 4.3). The similarity in temperatures can be attributed to the fact that all the sites in both the study and control areas are all comparatively close (one to 20 kilometres apart), that water heats and cools relatively slowly and that the readings were all obtained within a few days of each other. These temperatures are typical for that time of the year (SAWB, 1990), the total average being 29.25 °C. It is expected that such high water temperatures may influence the rate of methylations at theses sites (Hintleman and Wilkelman, 1995), especially where mercury concentrations in the sediment is highest at sample site A. It is highly probable that the majority of the mercury in the sediment at sample site A is methylmercury in accordance with studies conducted by Park and Curtis (1997) and others.

Table 4.3 Mean pH and Temperature readings taken over two days in November 1998 of the river water within the study area from sample sites A to J and the Control Area (shaded) from sample sites V to Z.

Study Area. Sample Site	Number of readings of both pH and temperature taken at each sample site	Mean pH	Mean Temperature °C
A	6	7.0	27.8
B	8	7.7	31.5
C	7	7.8	31.3
D	6	7.5	29.3
E	7	7.9	29.5
F	6	8.3	29.4
G	6	8.3	27.7
H	7	8.2	28.3
I	8	8.2	29.5
J	6	7.9	28.3
Total averages for A to J (Study Area)		7.9	29.26
V	8	7.2	30.1
W	6	7.9	29.8
X	6	7.7	28.5
Y	8	7.8	28
Z	6	7.9	29.5
Total averages for V to Z (Control Area)		7.7	29.18

A further factor to consider, with respect to mercury availability in the environment, is the pH of the river water at each sample site. As for temperature the pH of the river water was measured at each point where the sediment samples were taken. These readings are given in Table 4.3. Once again the pH readings, as for temperature, at sites A to J are similar. They range between 7.0 and 8.3, with the total average being 7.9. According to studies conducted by Panda *et al.* (1990) it would appear that the movement of mercury is hampered by the pH found within the study area. Panda *et al.* (1990) have shown that pH levels ranging between

2 to 6 in river waters results in the leaching of mercury from the sediment and that this action is accelerated with decreasing pH. According to Panda *et al.* (1990) mercury will be bound to sediments where the pH is above 6, which may explain why mercury levels are high at site A in comparison to the mercury levels found in the remainder of the sites B to J. The mercury may, therefore, be bound to the sediment at site A preventing it leaching from the sediment and being transferred further downstream. The presumed increase of mercury at site C, when comparing this study to Johnston *et al.* (1991) could again be attributed to pH of the river water. Slow leaching of mercury from the sediment at site A may have occurred over time (8 years) when the pH could have been sufficiently low allowing the mobilization of mercury from the sediment to take place. Unfortunately, it appears that Johnston *et al.* (1991) did not measure pH or temperature in their study, so there is no data available for comparison which may help to shed light on this. As mentioned previously it is possible that there are several other factors that could account for the difference in mercury concentrations at site C.

In summary the only significant levels of mercury in sediment appear to be at site A. Despite the difference in mercury concentrations at site C, which is apparent only when comparing them to Johnstone *et a.l* (1991) study, all of the mercury values in the sediment, from sites B to J, are low. However, since there are no other reported studies since Johnston *et al.* (1991) study, it was considered necessary to investigate the movement of mercury in the environment by examining whether biological material would show evidence of mercury absorption and bio-accumulation. In order to achieve this, samples of algae, cattle hair and fish were taken from both the study and control areas.

4.1.3 Algae.

Unfortunately, the results of the analysis of the algae samples was inconclusive, see Table 4.4. All of the levels were below detectable limits, other than at site B. Despite the fact that algae are deemed to be good indicators of mercury pollution, the levels found in the algae in both areas were not significant. A confounding factor may be that there was insufficient algae in both the study and control area to acquire significant results or that low enough readings could not

be obtained to determine if there was any trend towards the mobilization or bio-magnification of mercury. There were also no other suitable aquatic plants in abundance in either the study or control areas. Despite its limited quantity algae was the most prevalent aquatic plant available. These results, as shown in Table 4.4, must further be considered tenuous in that the laboratory was unable to conduct duplicate analysis in order to substantiate the results they obtained. Therefore, to quantify mercury in algae it appears that large sample masses must be collected.

Table 4.4 Average mercury concentrations in μg/litre in algae samples obtained from the study area taken directly below Thor Chemicals downstream to Inanda Damn (sample site A to J) and from the Control Area which extends north and upstream along the Umgeni River to Nagle Dam (sample sites V to Z). The average concentration of mercury was obtained by compositing 5 to 7 sub-samples at each site.

STUDY AREA Sample Site	**Number of sub-samples taken at each site**	**mercury (μg/litre)**
A	0	No algae
B	5	2.1
C	7	**<0.5**
D	6	**<0.5**
E	6	**<0.5**
F	7	**<0.5**
G	5	Insufficient algae
H	0	No algae
I	0	No algae
J	0	No algae
V	5	**<0.5**
W	0	No Algae
X	0	No Algae
Y	6	**<0.5**
Z	6	**<0.5**

Notwithstanding the above, the fact that the mercury may be bound to the sediment because of a relatively high pH levels in the river water could be considered as a possible reason for the low mercury levels in algae below site A.

4.1.3 Cattle Hair

The analysis of the cattle hair taken from the tails of the cattle in both the study and control areas revealed that the levels were all below detectable limits other than one sample obtained from the control area, which suggests that mercury has not accumulated in the cattle tissue. The results are given in Table 4.5 below.

Table 4.5 Cattle hair mercury concentrations (μg/litre) obtained from the Study Area at sample sites D and E along the Umgeni River and from the Control Area (shaded) at sample site W near to Nagle Dam.

STUDY AREA Sample number	Hg (μg/liter)	CONTROLS Sample number	Hg (μg/liter)
D a	<0.5	W a	<0.5
D b	<0.5	W b	<0.5
D c	<0.5	W c	<0.5
D d	<0.5	W d	<0.5
D e	<0.5	W e	0.6
D f	<0.5	W f	<0.5
D g	<0.5	W g	<0.5
E a	<0.5		
E b	<0.5		
E c	<0.5		

4.1.4 Fish (Carp and Catfish)

Carp and Sharp Toothed Catfish were also collected for this study. Fish were taken from Inanda Dam (study area) and from Nagle Dam (control area) as they were considered to be the most prevalent fish in both areas (Skelton 1993). In terms of sampling, it was difficult to determine which of these species of fish were preferred for consumption by the local community. However, from discussions with the local fisherman conducted during the collection of samples it appeared that the people ate whichever fish they caught, although this is not necessarily conclusive indication of local trends.

Before reviewing the concentration of mercury (Table 4.6) in fish it is considered significant to point out that due to the limited number of samples analysed it was statistically preferable to combine both species as opposed to comparing them separately. In order to validate this approach the sizes of the fish were statistically compared using the Wilcoxin Scores for variations between the two species. In terms of size there was no significant difference between the Sharp Toothed Catfish and the Carp from Inanda Dam at the 95% confidence level, and the same was evident for Nagle Dam, where there was no significant difference between the species ($p=0.1$). As it was established that there was no significant difference between the species, in terms of size the two species were combined as a single group.

As can be seen from Table 4.6, the concentration of mercury in fish is fairly low. The mercury levels in fish were compared between the study area (Inanda Dam) and control area (Nagle Dam) in order to investigate whether mercury being discharged from Thor Chemicals into the two river systems is having any effect on the fish in Inanda Dam. Comparisons of mercury concentrations were made between the mercury levels expressed in μg/litre. Using the Two Sample t Test it was found that there is was statistically no significant difference between the fish caught in the two dams, where a 'p' value of 0.08 was found. A 'p' value of 0.05 or less was considered to indicate a significant difference. Nevertheless, despite the statistics, recognition has to be given to the fact that there is a 1 in 12 probability of a biological difference, when defining the result of this 'p' value (0.08) further. Despite this uncertainty, in the statistical significance of the mercury levels, it is important to note that all actual concentrations of

mercury in fish in Inanda Dam were within detectable limits whereas in Nagle Dam only 40% of the concentrations measured in fish were within detectable limits. This suggests that a degree of bio-accumulation may be taking place within the Inanda Dam, possibly due to discharges from Thor Chemicals. However, as stated, this assumption cannot be statistically verified. Again this reiterates the need to obtain further data to obtain a true reflection of mercury pollution in the study area.

Table 4.6 Mercury concentrations (μg/litre and μg/gram) and sizes in centimetres for Carp and Catfish caught in Inanda Dam (Study Area) and Nagle Dam (Control Area, shaded)

Inanda Dam (study)				Nagle Dam (control)			
Sample No	**Size cm**	**mercury μg/litre**	**mercury μg/gram**	**Sample No**	**Size cm**	**mercury μg/litre**	**mercury μg/gram**
carp 1	30	0.5	0.05	carp 1	31	0.7	0.10
carp 2	28	1.0	0.10	carp 2	33	0.6	0.10
carp 3	27	0.8	0.07	carp 3	33	<0.5	<0.55
carp 4	31	0.9	0.08	carp 4	35	<0.5	<0.66
carp 5	30	2.6	0.25	carp 5	30	<0.5	<0.44
Mean Values Carp	**29.2**	**1.16**			**32.4**	**0.65**	
catfish 1	35	2.7	0.19	catfish 1	35	<0.5	<0.05
catfish 2	30	2.4	0.21	catfish 2	34	1.0	0.24
catfish 3	34	2.5	0.20	catfish 3	34	<0.5	<0.13
catfish 4	35	2.3	0.20	catfish 4	34	<0.5	<0.08
catfish 5	36	2.0	0.20	catfish 5	32	1.8	0.20
Mean Values Catfish	**34**	**2.38**			**33.8**	**1.4**	
Mean Values Carp & Catfish (Combined)	**31.6**	**1.77**			33.1	1.03	

When comparing the concentration of mercury (μg/litre) in Carp and Catfish, in the study area, as shown in Table 4.6, an interesting trend emerges between the mean mercury concentration of 2.38 μg/litre for the Catfish and the mean value of 1.16 μg/litre for Carp. The mean concentration of mercury for Catfish is twice (2.38 μg/litre) that of the Carp (1.16 μg/litre). This implies that the Catfish are taking in greater amounts of mercury since they were all similar size.

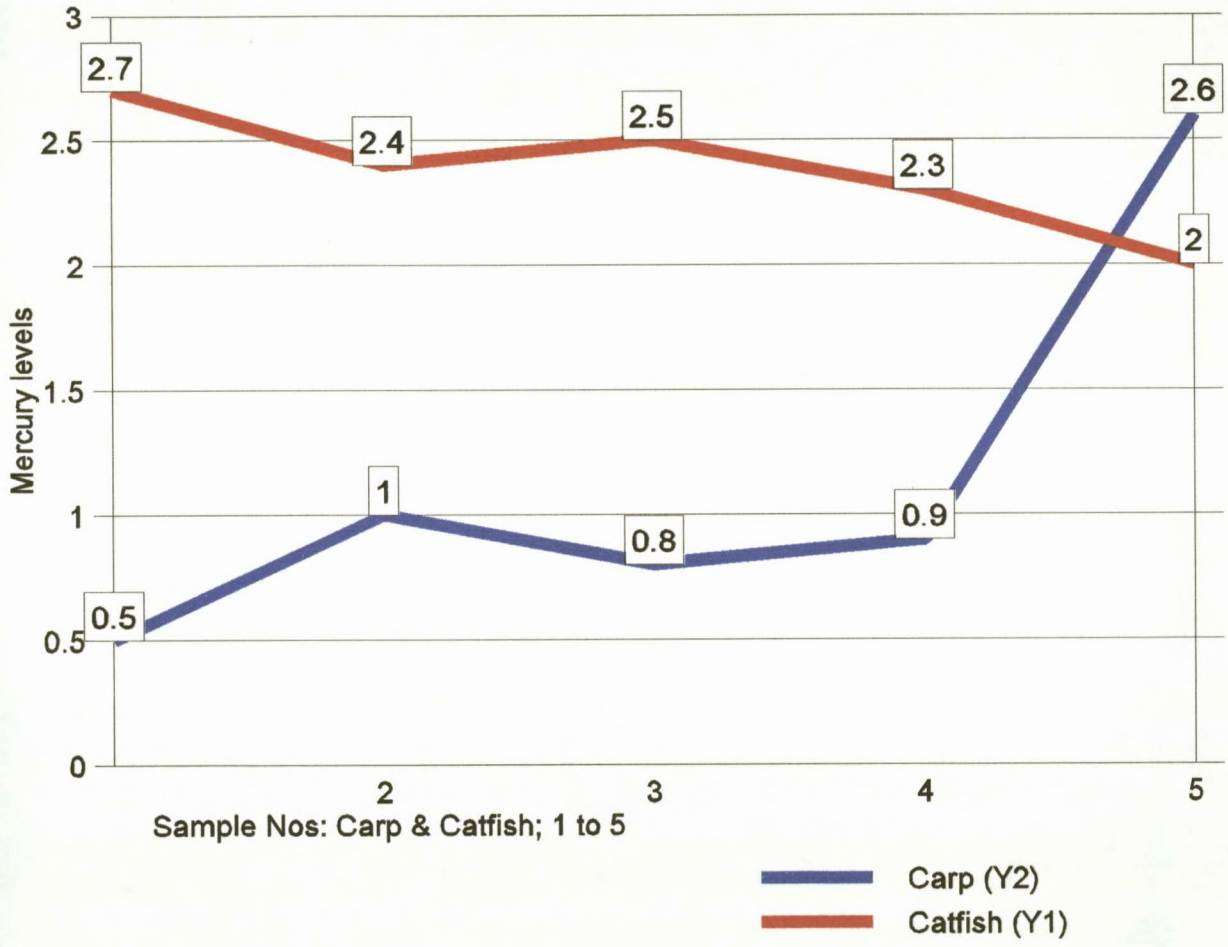

Figure 4.1 Mercury concentrations in (μg/litre) between Carp and Catfish caught in the Inanda Dam (Study Area).

The graph figure 4.1 clearly demonstrates the difference in mercury concentrations between the species. The Two Sample t Test confirms that there is a significant difference between the mercury concentrations in Catfish and the Carp in the study area at the 95% confidence level ($p=0.014$). The higher concentrations of mercury in the Catfish may be explained by the fact that they are bottom feeders and may ingest sediment and mercury while feeding (Skelton, 1993 and others). In addition, Catfish are also predators and could be ingesting mercury from other organisms as well, unlike the Carp that are predominantly omnivores only (Skelton, 1993). These findings are confirmed by studies conducted by Holsbeek *et al.* (1991) and Bioschio and Henshel (1991) who found that the greatest degree of mercury biomagnification took place in piscivores as opposed to other species lower down the food chain such as omnivores.

It is noteworthy to consider Kannan *et al.* (1998) findings where concentrations of mercury in sediment were found to be positively correlated with mercury levels within two different species of Catfish. Although mercury levels in the sediment were low throughout the Umgeni River, sediment samples were not taken below the deep waters of Inanda Dam. Therefore, mercury levels in these sediments remains unknown. Furthermore, consideration must be given to the fact that discharges from Thor Chemicals allegedly occurred 8 years ago. The status of mercury in the sediment beds could have altered substantially since then, and could have been relatively high in concentration soon after the discharges from the plant took place.

Although the initial study design plan was to obtain older larger fish from Inanda Dam and to compare these to fish obtained from the control area, additional smaller younger fish were also collected from the Umgeni River. These samples were collected because while conducting the study it was noted that smaller, younger fish, caught in the river formed an important part of the diet of people living along the river banks. In particular it was found that young boys net and consume young fish from the rivers daily. In terms of assessing all possible impacts on those residing in the area it was decided that young "river" fish would also be included in the study. As indicated in Table 4.7 all of the fish analysed contained mercury levels below detectable limits. It therefore appears very probable that these fish have sufficiently low levels of mercury not to pose a threat to the community who consume them. These results are consistent with the findings

of the Holsbrook *et al.* (1996) and others that mercury tends to accumulate in the larger older fish. The fish obtained in the Umgeni River were of an average size of 17.14 cm, considerably smaller then the fish collected in the Inanda Dam with an average size of 31.6 cm. Therefore, it appears that these relatively small and younger fish may have not been exposed to a source of mercury for a sufficient period of time, to accumulate mercury. These results are also in agreement with the findings of Holsbrook *et al.* (1996) and Biodone *et al.* (1997) who reported that older and larger fish are likely to accumulate mercury due to a longer exposure period. Nevertheless to obtain conclusive and accurate results readings below the threshold value 0.5μg/litre will need to be obtained.

Table 4.7 Mercury levels (μg /lire) and size of Carp and Catfish (length in cm) caught in the Umgeni River (Study Area) at sample sites D, E and H.

Sample no	Size cm	mercury μg /lire
D (a) carp	16.	**<0.5**
D (b) carp	18.	**<0.5**
D (c) catfish	16.	**<0.5**
E (a) carp	17.	**<0.5**
E (b) carp	18.	**<0.5**
H (a) catfish	17.	**<0.5**
H (b) catfish	18.	**<0.5**

As indicated in the literature pH of the water also appears to influence the concentration of mercury found in fish species. For example Andesson *et al.* (1995) found that the highest level of mercury in fish was found where the water was a pH of 5 and that mercury accumulation thereafter decreased with increasing pH of the water. These findings were also confirmed by Povari *et al.* (1998) and others. It appears that the pH of the water in this study has had little effect on the accumulation of mercury in the fish.

4.1.5 Overview

Finally, it is important to consider that when analysing mercury there are inherent limitations. As already stated, in Chapter 2 section 2.12, Wagermann *et al.* (1997) have pointed out there are limitations in terms of accuracy due to the possible contamination of the sample and differing methods of analysing and calculating mercury. Although a crytical analysis of the types of analysis and laboratory procedures used in the Umgeni Water's Analytical Laboratory are beyond the realms of this study, the findings of Wagemann *et al.* (1997) reemphasise the need to apply the strictest criteria when analysing mercury, particularly at low levels. This applies most when the mercury is likely to be in the form of methylmercury. The US EPA (1999)has stated that all mercury in fish should be considered to be methylmercury. Therefore, the detection of very low readings is essential. For example when comparing consumption levels of mercury in fish as demonstrated in Table 2.9 and 4.8. Despite Umgeni Water Analytical Services Department being accredited in terms of the South African National Accreditation System and that they execute stringent controls in their laboratory, the possibility of contamination effecting mercury measurement at very low levels cannot be excluded because of errors such as contaminated glass ware, water vapour or other laboratory procedures (Annexure C section 5).

Despite these limitations and uncertainties the results do indicate that the concentration of mercury directly below Thor Chemicals (Site A) has remained high over the eight year period since 1990. This is possibly due to the elevated pH levels recorded in the river water. Further, although statistically there is no significant difference between mercury levels in fish obtained from Inanda and Nagle Dams, the available data portends to the possibility of a degree of bio-accumulation of mercury taking place in the fish. These findings may be useful in an environmental impact assessment of mercury in the region.

4.2 ENVIRONMENTAL IMPACT ASSESSMENT OF MERCURY POLLUTION.

Although the mercury levels in fish complying with the various regulatory standards as shown in Table **2.8** there is a need to quantify the risk of the fish-eating population residing in the study area. Of particular concern are the larger fish and in particular the consumption of Catfish. There appears to be little risk of consuming the smaller fish caught in Umgeni in the region of sample sites D, E and H. However, to be assured of any risk to the population it appears necessary to measure mercury levels sufficiently low enough in order to conduct meaningful risk assessment investigations in terms of all fish consumed. Of particular concern are the effects of mercury consumption on high risk groups such as pregnant women and children[3]. Infants are considered to be at a greater risk then adults (Rice, 1995 and Harada, 1995). In order to protect the South African population from mercury exposure through fish consumption, particularly those persons who regularly consume fish and high risk groups, it may be necessary to reevaluate the requirements of methylmercury in fish as laid down in the Foodstuffs, Cosmetics and Disinfectants Regulations, Metals in Foodstuffs R 1518 of 1994 (FCD Reg, 1994) and is briefly discussed below.

Once the concentrations measured in μg/litre (as given by the atomic absorption spectrometer) were converted to μg/gram, the values could be compared to guidelines levels as quoted in the literature. All the fish samples in both the study and control areas revealed mercury concentrations which were less than the maximun level (0.5 μg/gram) of mercury permitted in fish allowed by the the South African Foodstuffs, Cosmetics and Disinfectants Regulations Relating to Metals in Foodstuffs (FCD Reg, 1994). This is clearly shown in figure 4.2. In addition the measured mercury concentrations fall well below the US FDA action level of 1ppm (given as μg/gram) of methylmercury in fish (US EPA, 1997). However, the latest mercury update from the US EPA in 1999, suggests a levels considerably lower than the FDA action level (US EPA, 1997) and the South African Foods, Cosmetics Regulations (FDC Reg,1994) requirements for mercury in fish[3]. The US EPA mercury levels are based on fish meals consumed in a month for an average adult[3]. Table 2.9, in Chapter Two, provides the recommended monthly consumption levels for fish contaminated with methylmercury[3]. The scenario emerges to be considerably

different when comparing consumption levels to action or singular levels such as stated above in the South African Foods, Cosmetics Regulations for metals in foodstuffs (FCD Reg,1994). Table 4.8 shows and compares the mercury levels found in the fish from Inanda Dam (as shown in Table 4.6 above) to the recommended levels for consumption of fish as stated in Table 2.9 and are discussed below.

Table 4.8 Relationship between mercury levels in Catfish and Carp from Inanda Dam to recommended fish meals for an average adult based on US EPA levels*[3]

mercury concentration in fish from Inanda. (μg/gram: wet mass)	**Number of Samples with related mercury Levels**	**Number of recommended fish meals per month**
0.05	1	16
0.07 to 0.08	2	12
0.12	1	8
0.19 to .21	5	4
0.25	1	3

* Average adult based on weight of 72 kg consuming 227 grams of fish calculated over 30.44 days (1 month)

From this table it can be seen that 60% of the fish sampled contained sufficiently elevated mercury levels to restrict a diet of fish from Inanda Dam to three to four fish meals in a month. If the assumption were made that fish were consumed on a daily basis then restrictions should be placed on the community to restrict fish consumption by half. In order to determine the possible risk to those residing in the study area it would be necessary to carry out a risk assessment in the area. The aim being to establish the risk of exposure by investigating the general population and in particular the sensitive population groups being pregnant women, nursing mothers and young children[3]. This would include data concerning the body weight of the average adult, and the number of fish meals consumed by the community in a month. Further, it would be necessary to determine to what extent fish consumption from Inanda Dam should be restricted in terms of fish meals in a month. This study does indicate the number of fish meals

recommended in terms of Table 2.9 should be restricted. but that further data needs to be obtained to quantify the risk to the exposed population in general and as suggested above.

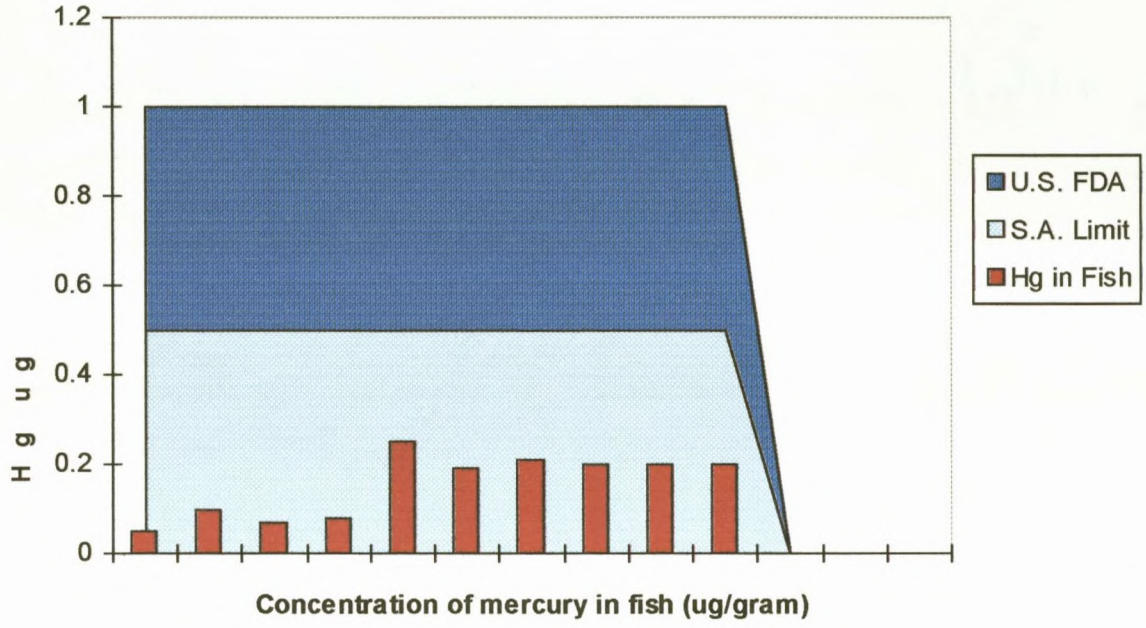

Figure 4.2 A comparison of mercury concentrations (μg/gram) found in fish obtained from Inanda Dam to the statutory limits of mercury in fish (0.05 μg/gram) as laid down by the South African Cosmetics and Disinfectants Regulations for metals in foodstuffs Regulation 1518 of 1994 and the recommended action level for mercury in fish as given by the United States Food and Safety Administration.

Some of the mercury concentrations measured in fish from the control area (Nagle Dam) are also cause for concern (Table 4.6). Two of the levels recorded (0.1μg/gram) would restrict the eating of fish from this dam to only eight meals of 227 grams of fish per meal in a month. The higher levels of mercury of 0.2μg/g and 0.24μg/g will restrict fish meals to four meals and three meals per month respectively. These levels are a cause for concern, despite that 60% of the remaining levels were below detectable limits. In consideration that Nagle Dam is only 16 kilometres linear

distant from Thor Chemicals, air pollution from the factory cannot be excluded as a factor effecting mercury levels in the entire region. Therefore, these levels suggest the need to carry out a further more comprehensive environmental study to determine the effects of air emissions on the region from Thor Chemicals.

A further area of concern, regarding environmental impact, is the region directly below Thor Chemicals. The possibility that the leaching of mercury could occur, from the sediment bed in the Mngceweni River, directly below Thor Chemicals at Sample A, cannot be disregarded. Fortunately it appears that the mercury is presently being bound to the sediment by a high pH (7) of the water. However, should the pH level be reduced for any reason, the mercury could then become available to be taken up by fish in the Umgeni River. The probability that the mercury has methylated to become methylmercury, due to the high temperatures recorded at the site, also has to be considered (Park and Curtis, 1997). Fish within the Umgeni River could be contaminated by directly taking up the more highly toxic methymercury, which can be retained within the fish for longer periods then the less toxic inorganic mercury (Smith *et al.*, 1996). A further factor that could be retaining the mercury at this site below Thor Chemicals, is that the area is densely overgrown with vegetation. The streambed of the Mngceweni River at this point is over abundant with grass and reeds. Plate 4.3 below indicates the dense vegetation of this particular part of the river. It appears unlikely that heavy rains will wash much of the contaminated sediment downstream, as the sediment could be bound by the root systems of the plants. Should it ever be contemplated to have the contaminated sediment removed, the probability of creating a greater problem further downstream may have to be assessed. The removal of the vegetation, to extract the sediment, could result in the contaminated sediment being washed down further into the Mngceweni and Umgeni River. However, should conditions remain as they are the mercury may not become mobilized.

Plate 4.3 Sample Site A on the Mngceweni River approximately 500 metres down stream from the boundary of Thor Chemicals taken in December 1998.

Umgeni Water is the present water provider for the region, which includes the study and control areas. The company routinely samples and analyses for mercury in the water along various points of the Umgeni River and Inanda Dam [2]. These tests are conducted in compliance with the General Standards for waste waters as laid down in the previous Water Act; No 54 of 1956, which stipulates that a maximum of 0.02milligrams per litre of mercury in waste waters cannot be exceeded. At this time, the General Standards are the only statutory requirement available to control mercury pollution of rivers in South Africa (Dept. Water Affairs, 1996). Provisions have been made in this new National Water Act; No 36 of 1998 Act to allow for the revision of the present criteria and standards for the control of pollution of rivers, but this has still to be enacted (Water Act, 1998). The reviewed literature and the results of this study indicate the need to evaluate mercury in the sediments and biota beyond the confines of river water. In addition, the analysis of mercury needs to be revised to ensure that low levels of mercury can be detected. This may result in the detection of levels that are sufficiently low to allow convincing conclusions to be reached with regard to the mobilization, accumulation and biomagnification of mercury in

aquatic systems. There appears to be little evidence to support mercury concentrations in river water as being the only means to assess the impact mercury may have on the environment. As expressed by Kannan *et al.* (1998) and others, mercury rapidly binds to sediment and thereafter is transferred into the ecosystem through various trophic levels, and that this is dependent on such factors as pH and temperature. All of these factors should be taken into account by the Catchment Management Agencies who will be appointed through the National Water Act (Water Act, 1998) or where investigations are conducted in terms of the National Environmental Management Act (NEMA, 1998). Both of these Acts confer considerable power, responsibilities and obligations on management agencies, offenders or owners of land to attend to and address the impact of pollution. These two Acts have only been recently promulgated and therefore are still in their infancy in terms of specific action plans. Nevertheless, the legal ammunition to deal with environmental impacts and injustices has been made available through the above legislation. The issues pertaining to Thor Chemicals remain unsolved and in consideration of the outcome of these results many issues need to be addressed. The legal means, as stated, are available and should be implemented so as too finally assess the environmental impact Thor Chemicals may have had on the region.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION.

For many years the "Thor Chemicals" issue has evoked numerous heated debates, accusations and arguments. The fact that gross negligence and subsequent occupational and environmental pollution occurred cannot be ignored, however, the environmental debate thus far, has been based on assumptions and emotionally charged outrage rather than fact. Environmental health issues in particular were poorly understood and investigated. This study was designed to shed some light on the main issues of concern, namely the extent of environmental pollution and the possible health risk that the surrounding community may be exposed.

It is evident that extensive mercury pollution occurred a number of years ago. High levels of mercury in sediment, has been found in the direct vicinity of the Thor Chemicals plant (Johnston *et al.*, 1991). It appears that the area directly below Thor Chemicals is still contaminated and could remain a source of potential bio-accumulation and mobilization of mercury into the ecosystem for many years to come. The degree to which mobilization is taking place could not be conclusively established. Although statistically inconclusive there is also a possibility that bio-accumulation of mercury may be taking place within the larger fish and in particular Catfish from Inanda Dam. It must however be emphasised that the bulk of the mercury pollution appears to be contained in the immediate vicinity of Thor Chemicals and for as long as this scenario continues it is unlikely to be of any danger to those residing in the study area. A risk assessment needs to be conducted on the fish-eating population. Although such a risk assessment should not be delayed in consideration of the potential threat of mercury affecting those that consume fish from the area.

It is probable that the containment of the pollution can be attributed to the unique topography of the area, owing to the density of the vegetation and that the pH of the river water which is relatively high, thereby preventing leaching of mercury from the sediment bed. The stream is relatively small and slow flowing, (even during the rainy season), and the area, including the streambed, is covered by extremely dense vegetation. This thick vegetation serves to minimise access to the stream by animals and humans, and likely binds the sediment, even during periods of "high flow". In addition the area is not inhabited and there is no evidence of livestock having access to the stream. The stream does not support fish.

The area further downstream from Thor Chemicals, (2km and beyond), which is inhabited, appears to be free from major mercury pollution in that the majority of the levels of mercury in algae, fish and cattle were found to be low and fall well within national and international standards, although this has still to be quantified in terms of fish meals consumed by local people. However, the reviewed literature and the results of this study clearly demonstrate the difficulty in assessing mercury in that it can be affected by a multitude of variables that have to be considered and carefully assessed in order to quantify the effects of mercury pollution on the environment.

5.2 RECOMMENDATIONS.

The recommendations from this study include the following:

i) Although there is some evidence of mercury contamination near the Thor Chemicals plant, it is not suggested that this should be removed physically. The mercury is currently well contained. Disturbing the vegetation in the stream bed could pose a threat of generating pollution further downstream where there are settled human populations where fishing activities are currently practised.

ii) The contaminated zone around Thor Chemicals should be clearly identified and fenced off, in order to restrict access.

iii) Some form of environmental remediation, other than physical removal, should be implemented in the contaminated area, since this could remain a possible source of future pollution for many years to come. Studies by Reuther (1996), Lee *et al.* (1998) and Scholes *et al.* (1998) clearly indicated that reeds and other aquatic plants are effective in removing heavy metals from the substrate and that the metal uptake is greatest in the roots. These studies further suggested that suitably constructed wetlands could be considered as a viable alternative to the treatment of metal contaminants as apposed to conventional re mediation methods. In the case of the contaminated area this may be considered as a viable alternative.

iv) The community, government agencies, such as the Department of Water Affairs and Forestry and the Department of Health, Thor Chemicals, The Valley Trust and other interested parties will be informed of the outcome of this research and for the need of a risk assessment study to be conducted on the fish eating population residing in the area. This will be achieved by advising these organisations in writing and by submitting a synopsis of the thesis to them.

v) Umgeni Water or the appointed Catchment Management Agency should be encouraged to monitor fish mercury levels in the Inanda Dam in the future as a routine precaution. In the event of the contaminated sediment being mobilised, the logical endpoint of sediment transportation would be the Inanda Dam. In addition regular monitoring of the sediment along the length of the Mngcewewni River needs to be carried out to rule out increases in mercury levels or confirm that there is a pollution problem.

vi). A suitable method for the disposal of remaining stockpiles of mercury waste by Thor Chemicals must be sought. Keeping mercury waste on the premises for extended periods of time is deemed to be more hazardous than the controlled recycling thereof.

vii) Should development take place within the vicinity of Thor, in particular Fredville Township, special regard should be taken of the utilisation of ground water in the area and a hydrological survey should be conducted to assess ground water impact from Thor Chemicals.

5.3 AREAS FOR FURTHER RESEARCH

In terms of the findings obtained from the results and conclusions reached, the following possible areas for research are recommended:

i) The contaminated area around Thor Chemicals provides an ideal opportunity for research to be conducted on the use of local plants or bacteria for bio-remediation purposes.

ii) Research could be conducted to determine other factors which could contribute to mercury pollution of the area. To ascertain if mercury contamination has been contained in a small area and to determine what factors lead to the mobilisation thereof.

iii) There is an urgent need to conduct a risk assessment of the fish-eating population within the region. Particularly high risk groups, such as pregnant women and children.

iv) Ascertain the possible effects that gaseous emissions of mercury emanating from Thor Chemicals may have had on the region.

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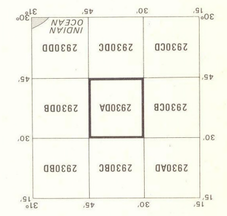
2930DA CATO RIDGE



INDEX TO SHEETS INDEKS VAN VELLE

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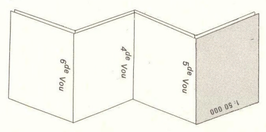
HOE OM TE VOU

HOW TO FOLD

HORIZONTAL FOLD



VERTIKALE VOULYNE

1st FOLD

2nd FOLD

6de VOU 6th FOLD

4de VOU 4th FOLD

5de VOU 5th FOLD

2930DA CATO RIDGE

1:50 000 SOUTH AFRICA SUID-AFRIKA

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Gepubliseer deur die Hoofdirektoraat: Opmetings en Grondinligting, Privaatsak X10, Mowbray.

REFERENCE	VERKLARING
National Freeway; National Route	Nasionale Deurpad; Nasionale Roete
Arterial Route	Hoofverkeersroete
Main Road	Hoofpad
Secondary Road; Bench Mark	Sekondêre Pad; Hoogtemerk
Other Road; Bridge	Ander Pad; Brug
Track and Hiking Trail	Dowwe Pad en Voetslaanpad
Railway; Station or Siding	Spoorweg; Stasie of Sylyn
Other Railway; Tunnel	Ander Spoorweg; Tonnel
Embankment; Cutting	Opvulling; Deurgrawing
Power Line	Kraglyn
Built-up Area	Beboude Gebied
Buildings; Ruin	Geboue; Murasie
Post Office; Police Station; Store	Poskantoor; Polisiestasie; Winkel
Place of Worship; School; Hotel	Plek van Aanbidding; Skool; Hotel
Fence; Wall	Draadheining; Muur
Windpump; Monument	Windpomp; Monument
Communication Tower	Kommunikasietoring
Mine Dump; Excavation	Mynhoop; Uitgrawing
Trigonometrical Station; Marine Beacon	Peilbaken; Seevaartbaken
Lighthouse and Marine Light	Vuurtoring en Seevaartlig
Cemetery; Grave	Begraafplaas; Graf

Cadastral information supplied by the Surveyor-General, Natal
Original Farms

Metres 1000 0 1 2 3 4 5 6 7 8 9 10 Kilometres

Mag. N. True N. Ware N.

Mean magnetic declination 20°18′ West of True North (Jan.1981). Mean annual change 2′ Eastwards (1975–1980)

Gemiddelde magnetiese deklinasie 20°18′ Wes van Ware Noord (Jan.1981). Gemiddelde jaarlikse verandering 2′ Ooswaarts (1975–1980)

Heights are in metres above mean sea level
Hoogtes is in meter bo gemiddelde seespieël

CONTOUR INTERVAL 20 METRES KONTOERTUSSENRUIMTE 20 METER

Gauss Conform Projection. Central Meridian 31° East. Clarke 1880 Spheroid
Gauss se Konforme Projeksie. Middelmeridiaan 31° Oos. Clarke 1880 Sferoïed

The grid lines of the South African Co-ordinate System are indicated in the margin by short black ticks at 10 000 metre intervals, with co-ordinate values in units of 10 000 metres in blue.

Die ruitlyne van die Suid-Afrikaanse Koördinaatstelsel word in die kantruimte aangetoon deur kort swart strepies 10 000 meter van mekaar, met koördinaatswaardes in eenhede van 10 000 meter in blou.

INDEX TO SHEETS INDEKS VAN VELLE

2930AD	2930BC	2930BD
2930CB	2930DA	2930DB
2930CD	2930DC	2930DD INDIAN OCEAN

Printed by the Government Printer, Private Bag X85, Pretoria
Gedruk deur die Staatsdrukker, Privaatsak X85, Pretoria

REFERENCE	VERKLARING
International Boundary and Beacon	Internasionale Grens en Baken
Provincial Boundary	Provinsiale Grens
Game, Nature Reserve & State Forest Boundary	Wild- en Natuurreservaat en Staatsbosgrens
Perennial River	Standhoudende Rivier
Perennial Water	Standhoudende Water
Non-perennial River	Nie-standhoudende Rivier
Non-perennial Water	Nie-standhoudende Water
Dry Water Course	Droëloop
Dry Pan	Droë Pan
Marsh and Vlei	Moeras en Vlei
Pipeline (above ground)	Pyplyn (bo die grond)
Water Tower; Reservoir; Water Point	Watertoring; Reservoir; Waterpunt
Coastal Rocks	Kuslynrotse
Prominent Rock Outcrop	Prominente Klipbank
Erosion; Sand	Erosie; Sand
Woodland	Beboste Gebied
Cultivated Land	Bewerkte Land
Orchard or Vineyard	Boord of Wingerd
Recreation Ground	Ontspanningsterrein
Row of Trees	Rye Bome

Kadastrale inligting verstrek deur die Landmeter-generaal, Natal
Oorspronklike Plase

2930DA CATO RIDGE THIRD EDITION DERDE UITGAWE 1989

Annexure A

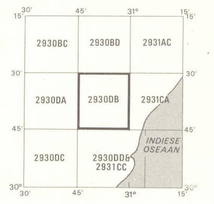
1:50 000 Topographical maps. 2930DA Cato Ridge 3rd Edition;

2930D Inanda 4th Edition. Surveyor Generals Office, Pietermaritzburg.

1:50 000

2930DB INANDA

INDEKS VAN VELLE INDEX TO SHEETS



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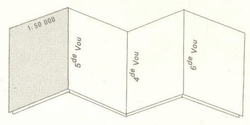
HOE OM TE VOU

VERTIKALE VOULYNE



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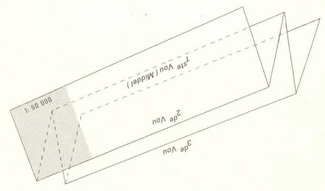

HOW TO FOLD

5de VOU 5th FOLD

4de VOU 4th FOLD

6de VOU 6th FOLD

2de VOU 2nd FOLD

1ste VOU 1st FOLD

3de VOU 3rd FOLD

2930DB INANDA

1:50 000 SUID-AFRIKA SOUTH AFRICA

Gepubliseer deur die Hoofdirektoraat: Opmetings en Grondinligting, Privaatsak X10, Mowbray.
Published by the Chief Directorate: Surveys and Land Information, Private Bag X10, Mowbray.

Meter 1000 0 1 2 3 4 5 6 7 8 9 10 Kilometer

Gedruk deur die Staatsdrukker, Privaatsak X85, Pretoria
Printed by the Government Printer, Private Bag X85, Pretoria

VERKLARING — REFERENCE

- Nasionale Deurpad; Nasionale Roete — National Freeway; National Route
- Hoofverkeersroete — Arterial Route
- Hoofpad — Main Road
- Sekondêre Pad; Hoogtemerk — Secondary Road; Bench Mark
- Ander Pad; Brug — Other Road; Bridge
- Dowwe Pad en Voetslaanpad — Track and Hiking Trail
- Spoorweg; Stasie of Sylyn — Railway; Station or Siding
- Ander Spoorweg; Tonnel — Other Railway; Tunnel
- Opvulling; Deurgrawing — Embankment; Cutting
- Kraglyn — Power Line
- Beboude Gebied — Built-Up Area
- Geboue; Murasie — Buildings; Ruin
- Poskantoor; Polisiestasie; Winkel — Post Office; Police Station; Store
- Plek van Aanbidding; Skool; Hotel — Place of Worship; School; Hotel
- Draadheining; Muur — Fence; Wall
- Windpomp;Monument — Windpump; Monument
- Kommunikasietoring — Communication Tower
- Mynhoop; Uitgrawing — Mine Dump; Excavation
- Peilbaken; Seevaartbaken — Trigonometrical Station; Marine Beacon
- Vuurtoring en Seevaartlig — Lighthouse and Marine Light
- Begraafplaas; Graf — Cemetery; Grave

Kadastrale inligting verstrek deur die Landmeter-generaal, Natal
Oorspronklike Plase

Gemiddelde magnetiese deklinasie 21°41′ Wes van Ware Noord (Jan. 1994).
Gemiddelde jaarlikse verandering 8′Weswaarts (1987-1990).
"Voorsien deur Hermanus Magnetiese Observatorium"

Mean magnetic declination 21°41′West of True North (Jan. 1994).
Mean annual change 8′Westwards (1987-1990).
"Supplied by Hermanus Magnetic Observatory"

Hoogtes is in meter bo gemiddelde seespieël
Heights are in metres above mean sea level

KONTOERTUSSENRUIMTE 20 METER CONTOUR INTERVAL 20 METRES

Gauss se Konforme Projeksie. Middelmeridiaan 31° Oos. Clarke 1880 Sferoied
Gauss Conform Projection. Central Meridian 31° East. Clarke 1880 Spheroid

Die ruitlyne van die Suid-Afrikaanse Koördinaatstelsel word in die kantruimte aangetoon deur kort swart strepies 10 000 meter van mekaar, met koördinaatwaardes in eenhede van 10 000 meter in blou.

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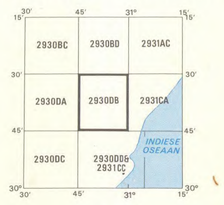
INDEKS VAN VELLE — INDEX TO SHEETS



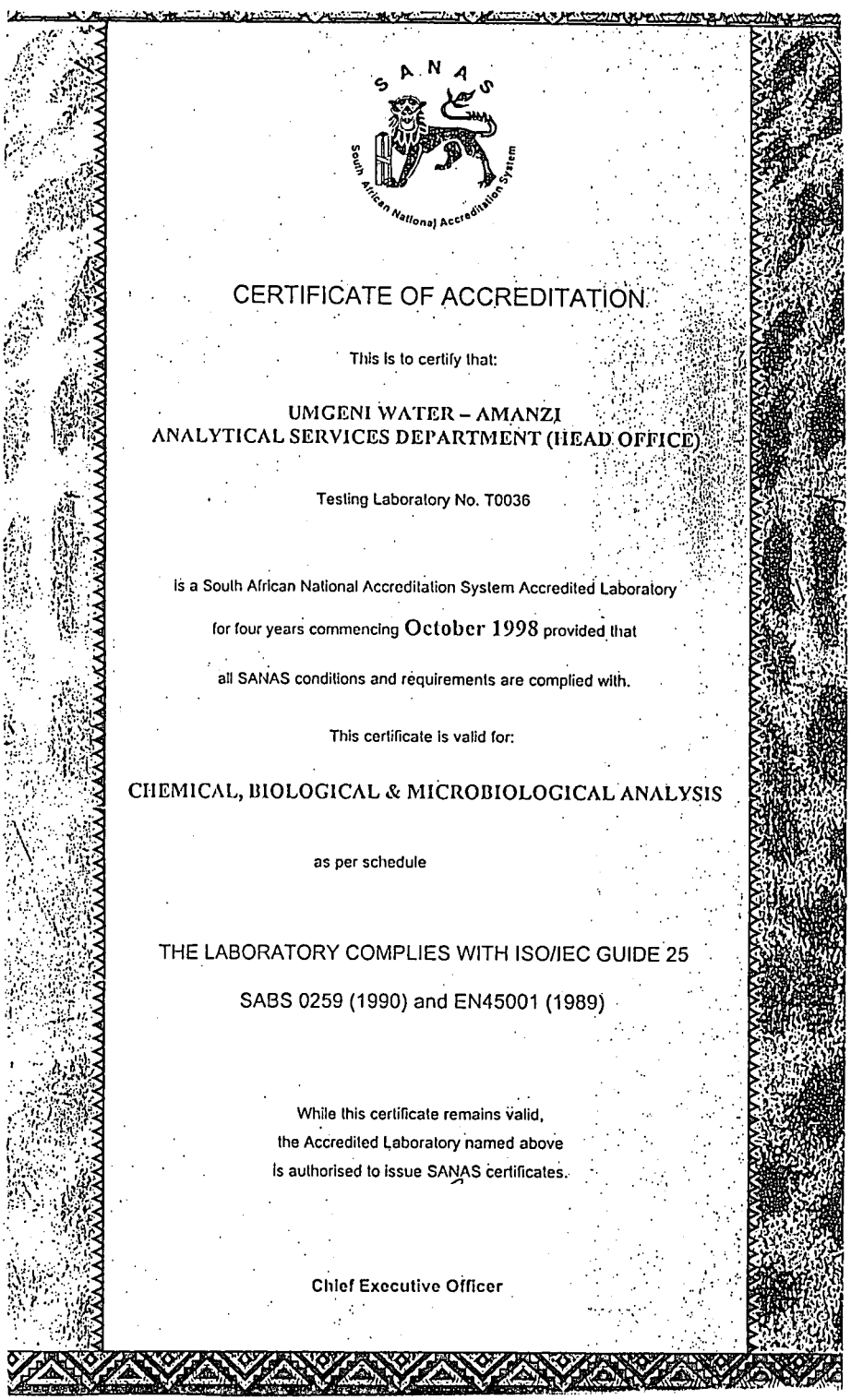
VERKLARING — REFERENCE

- Internasionale Grens en Baken — International Boundary and Beacon
- Provinsiale Grens — Provincial Boundary
- Wild- en Natuurreservaat en Staatsbosgrens — Game, Nature Reserve & State Forest Boundary
- Standhoudende Rivier — Perennial River
- Standhoudende Water — Perennial Water
- Nie-standhoudende Rivier — Non-perennial River
- Nie-standhoudende Water — Non-perennial Water
- Droëloop — Dry Water Course
- Droë Pan — Dry Pan
- Moeras en Vlei — Marsh and Vlei
- Pyplyn (bo die grond) — Pipeline (above ground)
- Watertoring; Reservoir; Waterpunt — Water Tower; Reservoir: Water Point
- Kuslynrotse — Coastal Rocks
- Prominente Klipbank — Prominent Rock Outcrop
- Erosie; Sand — Erosion; Sand
- Beboste Gebied — Woodland
- Bewerkte Land — Cultivated Land
- Boord of Wingerd — Orchard or Vineyard
- Ontspanningsterrein — Recreation Ground
- Rye Bome — Row of Trees

Cadastral information supplied by the Surveyor-General, Natal
Original Farms

2930DB INANDA VIERDE UITGAWE FOURTH EDITION 1989

Annexure B Certificate of Accreditation: Umgeni Water Analytical Services Department (Testing Laboratory No T0037).



SANAS

South African National Accreditation System

CERTIFICATE OF ACCREDITATION

This is to certify that:

UMGENI WATER – AMANZI
ANALYTICAL SERVICES DEPARTMENT (HEAD OFFICE)

Testing Laboratory No. T0036

is a South African National Accreditation System Accredited Laboratory

for four years commencing October 1998 provided that

all SANAS conditions and requirements are complied with.

This certificate is valid for:

CHEMICAL, BIOLOGICAL & MICROBIOLOGICAL ANALYSIS

as per schedule

THE LABORATORY COMPLIES WITH ISO/IEC GUIDE 25

SABS 0259 (1990) and EN45001 (1989)

While this certificate remains valid,
the Accredited Laboratory named above
is authorised to issue SANAS certificates.

Chief Executive Officer

ANNEXURE C

Method 34

1 Introduction

All forms of mercury, including organic derivatives, were oxidized to ionic mercury by acidic potassium permanganate. Inorganic mercury was rapidly reduced by sodium borohydride in an acidic solution to form mercury vapour The vapour was purged continuously with argon into an unheated quartz tube in the light path of an atomic spectrometer where absorbance is determined at 253 7 nm

2. Equipment and Apparatus.

The following equipment was used:

- Atomic absorption spectrometer; Varian Spectra AA 220.
- Hydride generator; Vapour generation accessory with pump system.
- Glassware; certified measuring cylinders as required.
- Pump tube sizes:

Sample line :	purple white (three pump tubes)
Acid line:	orange-orange
Borohydride line:	orange - orange

2.1 Reagents.

Sodium borohydride solution was made up by dissolving 3.0 grams of sodium borohydride and 2.5 grams of sodium hydroxide in a 500 millilitre volumetric flask using ultra pure water. This solution was made up on a daily basis.

Bleach solution was prepared by dissolving 60 grams sodium chloride and 60 grams of hydroxyl ammonium chloride in a 500 millilitre volumetric flask using ultra pure water. This solution was prepared on a daily basis.

Potassium permanganate solution (5%mass to volume) was made up by dissolving 100grams of mercury free potassium permanganate in a 2000 millilitre volumetric flask using ultra pure water ultra pure water. Solutions 3 month or older were discarded and a new solution was prepared before being used for analysis purposes.

Nitric acid stock solution (50% volume to volume) was diluted 1:1 in ultra pure water.

Hydrochloric Acid stock solution (50% volume to volume) was made up in the same way as nitric acid above.

Dichromate stock solution (5% mass to volume) was made up by diluting 50 grams of potassium dichromate in a 1000 millilitre volumetric flask, using ultra pure water.

Sulphuric acid solution (50% volume to volume) was prepared as for the nitric acid stock solution above.

Dichromate/ nitric acid bath for soaking glassware and bottles was prepared as follows. 101 reverse osmotic water was poured into a 251 bath. 1000 millilitre of nitric acid and 10grams of potassium dichromate was added and mixed well until dissolved. Further 101 reverse osmosis water was added to the bath and mixed throughly. All glass ware used in the analysis of the mercury samples was soaked in this solution over night and then throughly rinsed with ultra pure water before being used.

2.2 Preparation of standards.

The mercury standard stock as provided by the supplier of which 0.5 millilitre was pipetted into a 500 millilitre volumetric flask along with 5 millilitre of dichromate solution and 5 millilitre of nitric acid. Ultra pure water was added to make up the total volume. Any solution older then three months was discarded and not used in the analysis procedure.

In terms of mercury working standards the following quantities of mercury stock were used:

Standard 1	2μg/litre:	0.4 millilitres of intermediate stock.
Standard 2	5μg/litre:	1.0 millilitres of intermediate stock.
Standard 3	10μg/litre:	2.0 millilitres of intermediate stock

For all of the intermediate stock solutions 200 millilitres of ultra pure water was added to each volumetric flask. Thereafter 2 millilitre dichromate solution and 2 millilitres nitric acid was also added into each of the volumetric flasks.

2.2.1 Preparation for analytical quality control (AQC)

The mercury AQC intermediate stock was made up by pipetting 0.5milliliters of stock as provided by the supplier into a 500 millilitre volumetric flask. 5mlliliters of dichromate solution was added with 5 millilitres of nitric acid and the remaining 500 millilitre was made up using ultra pure water. Any solution older then three months was discarded and not used in the analysis of the mercury.

2.2.2 Mercury working solution

With reference to standard 2 (5μg/l), 1.0 millilitres of AQC stock made up to 200 millilitres using ultra pure water was prepared, followed by the adding of 2 milliliters of dichromate solution and 2millilitres nitric acid. This solution was prepared fresh for every run.

3 Analytical procedure.

3.1 Sample pre-treatment.

100 millilitres of the sample was transferred into a beaker using a certified measuring cylinder containing 5 millilitres of sulphuric acid and 5milliliters potassium permanganate. If the sample had high turbidity or a high organic content more potassium permanganate was added. In order to ensure that the correct levels of potassium permanganate were being maintained it was imperative to ensure that a purple colour was maintained throughout the digestion process. The beaker was then covered with a petri dish and the sample digested in a preheated water bath set at 80°C +- 5°C for 8 hours. The sample was then removed from the water bath and allowed to cool at room temperature. 2.5 millilitres of bleach was added and mixed well in order to remove excess potassium permanganate. In cases where excess potassium permanganate had been used sufficient bleach was added to bleach to decolourise the potassium permanganate. Thereafter the sample was made up to 150 millilitres using ultra pure water using a certified measuring cylinder.

3.2 Standards and AQC pre- treatment.

200 millilitres of each standard and AQC solution was transferred into separate beakers. Into each beaker 10 millilitres of sulphuric acid and 10 millilitres of potassium permanganate was added. The beakers were covered with petri dishes and the solutions digested at 80°C +- 5°C for 8 hours. These solutions were allowed to cool at room temperature. Thereafter 5 millilitres of potassium permanganate was added in order to remove excess potassium permanganate. The solution was made up to 300 millilitres using ultra pure water using a measuring cylinder.

3.3 Blank preparations.

10 millilitres of nitric acid and 10 millilitres of dichromate solution was added to 1000 millilitres of ultra pure water. The solution was transferred to a glass bottle. 50 millilitres of sulphuric acid and 50 milters of potassium permanganate was then added.

The bottle was covered with a petri dish and digested at in a preheated water bath set at 80° C +- 5°C for 8 hours. This solution was allowed to cool to room temperature. Thereafter 25 millilitres of bleach was added and mixed well to remove any excess potassium permanganate. The blank was made up to 1500 millilitres with ultra pure water using a measuring cylinder.

3.4 Atomic absorption spectrometer; Varian Spectra AA 220: Set up and calculation of results.

The atomic absorption spectrometer was switched on and the mercury lamp was allowed to warm up for 10 minuets before analysis was started. The atomic absorption spectrometer was calibrated in terms of the standards from which the calibration graph was established. Sample concentrations were read from the calibration graph. As the atomic absorption spectrometer could not perform automatic dilutions all calculations or manual dilutions were recorded on the run sheet. All readings were given as μg/litre. In order to convert from μg/ litre to μg/ gram the mercury μg/litre reading was multiplied by 0.1 and divided by the weight of the sample.

4 Specific laboratory methodology

4.1 Sediment, algae and hair

In the case of sediment samples a duplicate mass of each sample was weighed out and then 40 millilitres of potassium permanganate and 10 millilitres of sulphuric acid was added to each sample. The sample was made up to 100 millilitres before digestion in the water bath. Due to the extra potassium permanganate that had to be added 20 millilitres of bleach was added before analysis was carried out. The reported results reflected the average of the duplicate results obtained . Due to the difficulty in obtaining a completely homogeneous sediment sample, this procedure was performed for all samples.

In the case of hair and algae samples the same procedure as above was carried out except that no duplicate analysis was performed due to the quantity of the samples obtained. Algae and cattle hair samples were measured in μg/litre in that there was insufficient sample mass to convert the value to μg/ gram.

4.2 Analysis of mercury in Fish

The following reagents were used:

5% Potassium persulphate
Sulphuric acid
5% potassium permanganate
Nitric acid

The preparation of the standards and AQC was conducted in terms of method 34 as described in Section 3 above.

1 gram of the muscle of the fish from the area adjacent to the dorsal fin was removed and weighed and placed into a beaker. 10 millilitres of potassium persulphate and 10 millilitre of sulphuric acid were added. The beaker was covered with a petri dish and digested in a pre-heated water bath set at 60°C for 5 hours. The sample was left overnight and the following morning 40 millilitre of potassium permanganate was added. The sample was again left overnight. 1 millilitre of sulphuric acid was added. The sample was bleached as described in

terms of method 34 section 3.above. The fish sample was then analysed by cold vapour generation.

4.3 Cone and quartering methos applied to sediment and algae samples.

All the sub-sample were combined, homogenised and mixed well to form one sample. From this sample a cone was formed and separated into quarters. The bottom left and top right was discarded. The remaining quarters were mixed well and a cone was formed. This cone was also separated into quarters. The bottom right and top left was discarded. The remaining sample was again mixed well and a cone formed . The procedure of discarding the top right and bottom left in the first instance and in the second instance of discarding top left and bottom right was repeated twice again. The remaining portion of the sample was then analysed.

5 Sources of error.

In any analytical laboratory procedure there are potential areas of sources of error. In the case of the analysis of mercury using Method 34 the following where considered: Contaminated glass ware, water vapour and the use of incorrect pump tubes.