

**AN APPLICATION OF THE MASS BALANCE TECHNIQUE TO  
STUDY THE IMPACTS OF MINING OPERATIONS ON THE  
HYDROGEOCHEMISTRY OF THE KAFUE RIVER AS IT CROSSES  
THE COPPERBELT OF ZAMBIA**

**BY**

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I declare that this dissertation was written in accordance with the rules and regulations governing the award of Master of Mineral Sciences of the University of Zambia. I further declare that the dissertation has neither in part nor in whole been presented as substance for award of any degree, either to this university or any other university.

Where other people's work has been drawn upon, acknowledgement has been made.

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## PREFACE

This report is a result of a joint project carried out by the University of Zambia and Lulea University of Technology. The project was funded by the Swedish International Development Cooperation Agency. Sample collection was carried out by the author and Mr Ulf. T. Pettersson, a PhD candidate, with the occasional help of Masters degree students in Environmental Planning and Design from Lulea University of Technology, Sweden, who were coming to Zambia on a regular basis for their field work. During sample collection, the project team was based at the Mines Safety Department in Kitwe. This report has also been compiled at the same institution.

The samples were collected during the period of March 1995 to April 1996

This report is only one of a number of reports which will be published as a result of this project.

So far three reports have already come out. These are:

- 1 'A study of the suspended solids in the Mwambashi river - *A tributary of the Kafue river, Zambia*'  
by: Annelie Hedström and Lisa Osterman.
- 2 'Environmental effects from the mining industry on the sediment quality in the Kafue river, Zambia - *A geochemical investigation of a tropical river.*'  
by: Sanna Isaksson and Anna Säfvestad

3 A sediment study in the Kafue river, Zambia

by: Magnus Bäckström and Benny Jonsson

Quote: Science is made up of facts just like a house is made up of bricks. However an accumulation of facts does not make science any more than a pile of bricks makes a house

**- Henri Poincaré**

Christopher Nkandu

*Mines Safety Department*

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## Abstract

A mass balance technique was used to investigate the hydrogeochemistry of the Kafue river as it crosses the Copperbelt mining area between Raglans farm and Machiya ferry. The study is done by examining the mass flow-rates of ten chemical parameters, namely: total dissolved solids, total suspended solids, elemental cadmium, cobalt, copper, iron, manganese, lead, barium and sulphur. In this study, the aqueous concentrations in the rivers were obtained from samples collected at four sampling stations along the Kafue river and one station on the Mwambashi river. The volume discharge rates were obtained from the Department of Water affairs. Further data was obtained from Zambia Consolidated Copper Mines Limited.

The mass flows for the parameters are computed on a monthly basis as the average of the product of the concentrations of the parameters and discharge rates for the particular month.

Results obtained indicate that the mass flows of these chemical constituents increase after the river enters the mining areas and decrease after exiting the areas. The relative impact of the mining operations on the river basin varies from place to place and chemical to chemical. In the Mwambashi river on one hand, practically all the total dissolved solids flowing in the river during the dry season seem to emanate from mining operations. On the other hand, dissolved iron flow rates at certain times of the year actually drop as the river enters the area of the mining operations.

Redox conditions also seem to have an effect on the speciation of metals like iron, lead and



manganese. Photosynthesis by aquatic plants has been found to determine the level of dissolved oxygen and the redox potential level.

Copper flows from Fishers farm to Machiya appear to be affected by iron speciation as a result of the ability of iron oxyhydroxides in adsorbing various heavy metals. The same seems to apply to lead.

For cadmium, mining activities may not be major factor in the mobilisation of the metal since the biggest input of the metal appears to come between Fishers farm and Machiya ferry sampling point. Most of the mining activities discharge their effluent into the Kafue at points upstream of Fishers farm.

This study has thrown some light on the hydrogeochemical processes taking place in the Kafue river. It has shown how mine effluent is effecting the water quality in the Kafue river and how the river itself effects the effluent.

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## 1.0.0 Introduction

The copper and cobalt deposits in the Copperbelt province of Zambia together with those in the adjacent Copperbelt in neighbouring Zaire are among the world's great mineral provinces. Mining for copper has been carried out in this area since historic times. In the last sixty years though, mining has been carried out on a large scale with variety of attendant problems which such mining operations bring with them.

Present day mining in the Zambian Copperbelt is carried out through both underground and open pit mines. Active underground mines are at Konkola (Chililabombwe), Nchanga (Chingola), Mufulira (Mufulira), Chibuluma (Kalulushi), Nkana (Kitwe) and Luanshya (Luanshya). [NB: The names of the towns in which the mine is located are given in brackets.] The Konkola underground mine in Chililabombwe, with 270,000 - 350,00M<sup>3</sup>/ day of water pumped out of the mine, is one of the wettest mine in the world. As can be seen in appendix 1, the magnitude of this water is such that the Konkola mine is a major source of both suspended and dissolved solids discharged into the Kafue river even though the mine does not host major metallurgical plants. The Mufulira underground mine was at one time the second biggest underground mine in Africa.

Active and closed open pit mines are found at Chingola, Chambeshi, Bwana Mkubwa and Nkana. The Nchanga open pit in Chingola is the second biggest open pit in the world. The open pit mine at Chambeshi is now closed. After the closure of open pit mining operations at Chambeshi, the mining operations first went underground before they too ceased in 1986. Recently, efforts are being made to re-start operations. The open pit mine at Bwana Mkubwa also closed down in 1982. Operations were however re-started in early 1998 through the re-treatment of stockpiled

tailings from earlier operations. This though was after the sampling work for this project had been concluded.

In both underground and open pit mines, mining cannot take place in the presence of a water table. To get rid of the water table, water has to be pumped out of the mine. This water is discharged into the rivers and streams and can contain high levels of dissolved and suspended elements which contributes to the pollution carried by these rivers. Such de-watering operations, therefore, do have an impact on hydrogeochemical processes in the river systems which would not be present in the absence of such operations.

Both sulphide and oxide ores are mined and both pyro- and hydro-metallurgical operations are employed in recovering finished copper and cobalt from the ores. Due to the ease with which sulphide ores can be concentrated by flotation and then smelted, mining during the early years tended to concentrate on recovering sulphide ores. Smelters were built at Nkana, Mufulira and Luanshya to produce anode copper which was refined at refineries in Kitwe, Mufulira and Ndola. Since concentrators were designed to produce a copper concentrate for treatment in the smelter, the aim was to maximise the copper grade in the concentrate. This in turn normally entailed the suppression of the pyrite co-existing with the copper sulphides. This pyrite was eventually dumped at the tailings dams and may have resulted in acid mine drainage. Sulphur dioxide and particulate emissions from the smelters which contribute to acid rain and atmospheric transportation of heavy metals respectively would be some of the other environmental issues associated with such plants.

The earliest metallurgical operations used pyrometallurgy. The pyrometallurgical route, however,

could not recover the cobalt fraction of the ore and so this element ended up on the slag dumps. To recover the cobalt, a new metallurgical process route had to be implemented. This is the roast, leach and electrowin (RLE) route. In this process, the cobalt concentrate, which may contain both sulphide and oxide minerals, is first heated to a temperature of about 700°C at which the sulphides are oxidised to sulphates and oxides. This roast product is then leached in an acidic solution to dissolve the copper and cobalt oxides and sulphates. After solution purification, the solution is sent to tank-houses where first, the copper and then the cobalt are recovered through electrolysis. There are two of these plants in operation at the moment. One plant is in Kitwe whilst the other one is in Chambishi. Sulphur dioxide and particulate emissions as well as waste water effluent would be some of the environmental issues associated with these plants.

The biggest hydrometallurgical plant in the Copperbelt was built at Nchanga in Chingola. This plant, called the Tailings Leach Plant (TLP) started off as a cement copper producing plant. The cement copper was produced by the precipitation of copper, leached from oxide ores, with scrap iron. The cement copper was then dispatched to a smelter for further processing. In 1974, cementation was done away with and the plant switched to the production of copper cathodes through electrowinning from an advance electrolyte solution purified in a solvent extraction plant. The TLP solvent extraction circuit was at one time twice as big the next biggest similar plant in the world with a design capacity of 60,000 tonnes of copper per year. Due to its size, any poor operations in this plant have a considerable capacity to impact heavily on the local rivers and streams.

When the TLP started operating the solvent extraction process, it used the first generation of solvent extractants which limited the tenor of the leach solution which could be treated to about

3.5 grams per litre of copper. The extractants were changed to the second generation of extractants in 1985, and this change could theoretically double the capacity of the plant as the extractant could handle leach solutions with tenors of up to 7 grams/ litre. Any escape of spillage from the plant of the new higher tenor process liquors would be expected to have a greater pollution impact than before.

The Zambia Consolidated Copper Mines and its successor companies after the on-going privatisation have been trying to implement an environmental programme to monitor metal losses to the environment from their mines and metallurgical plants. Previously, this used to be from the economic point of view. More recently however, this has been due to environmental concerns as well. This internal company data has been used to supplement the data collected in this study so that, as far as possible, the effects on the hydrogeochemistry of the Kafue river basin can be traced to particular mines and metallurgical plants.

Other work has been done on the various industrial impacts on the hydrogeochemistry of the Kafue river by people such as Pettersson, Nkandu and Gilman and organisations like JICA. The work by Pettersson, in particular, served as a preliminary survey for this study.

## **2.0.0 Objectives**

The mining operations on the Copperbelt and the secondary industrialisation which they have spawned may have resulted in a number of environmental impacts. The Kafue river flows almost through the centre of the mining area of the Copperbelt and so is the final recipient of many effluent discharges from these mining operations. The objective of this project was to use the mass

balance technique to investigate the hydrogeochemistry of the Kafue river as it crosses the mining area of the Copperbelt and to determine the part which mine effluent play in modifying this.

### **3.0.0 Literature review**

#### **3.1.0 *The mass balance***

The mass balance is a technique which can be used to study the transport of chemical species by rivers. Basically this involves working out the rate of a particular chemical species flowing past a particular point. This species flow rate determination can be calculated for any particular species so long as the species can be differentiated from the other chemical species through the use of analytical techniques. A simple example is the case of an element, say dissolved copper, which is evenly distributed throughout the river water flowing past a particular point. A sample of this water is taken and analysed for its copper concentration. When this value is multiplied by the value of the river discharge rate at that point, the result is the mass flow rate of copper at that point. Since matter can neither be created nor destroyed, comparisons of the mass flow rate of particular species at different points along the river make it possible for definite statements to be made about the hydrogeochemical processes taking place in the river.

As an example, if this determination is made on the dissolved state of element A only and it is noticed that the downstream location has a lower flow rate for the dissolved state of A than the upstream location, then this can only mean that some of the element A has been transferred from the dissolved state to the suspended state. This suspended state may eventually be deposited on the river bed as sediment or it can be carried along by the river all the way to the sea. If a total



transportation analysis is done of the element A above by including the transportation of suspended solids as well and the total transportation at the downstream location is still lower than the upstream location, then there must be a sink for element A somewhere along the route. Most likely element A has been deposited at the river bed. If the total transportation at the two location is equal but with a higher proportion now in the suspended state then it will mean that although element A has been transferred from the dissolved state to the suspended state, it is being carried along by the river with no deposition taking place. It might also be possible that the transportation at the downstream location is higher than the upstream location. This would mean that there is another source of the particular chemical entering the river at a point between the two sampling locations. This could be from the entry of a natural stream or industrial effluent or it could be from the re-mobilisation of sediment from the river bed. Therefore by using the mass balance technique one can follow the chemical route taken by a particular chemical and the eventual fate of that chemical. These principles are shown in fig. 1.

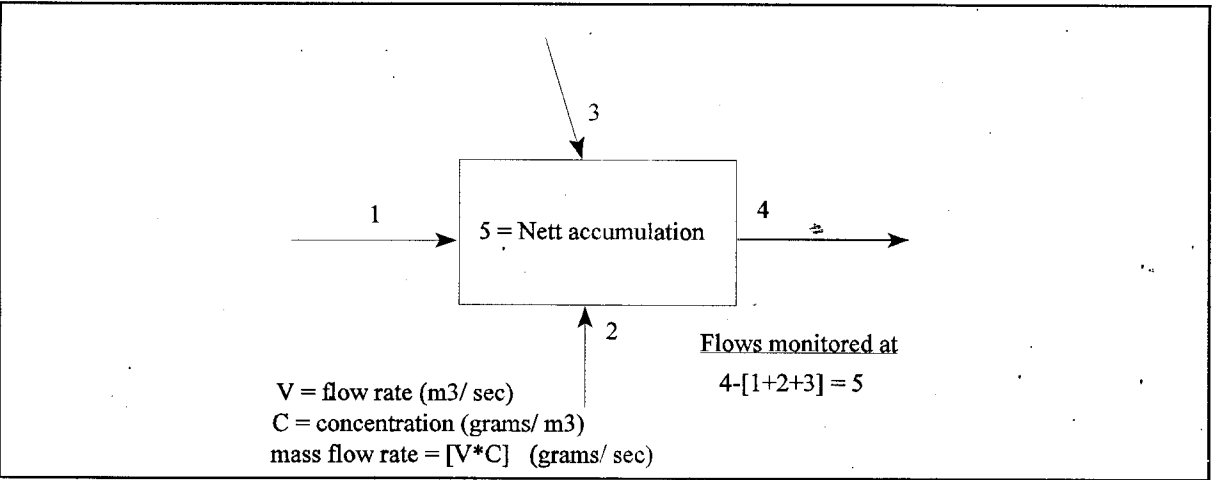


Fig. 1 - Principles of the mass balance in river transport of chemical species

This comparison of the state of a particular chemical species at two different points assumes that the residence time taken by the water to flow between the two sampling points makes no difference to the results. Strictly speaking, if a sample is taken of water at point A, one has to wait

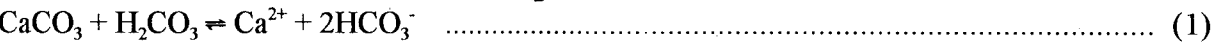
until that water has reached point B before one can take another sample of that water to make the deductions referred to above. In practice this is not always possible as the residence time is not always known. One may also be looking at different sources for the chemical species in question and these may have different lag times before the water whose samples were taken at the two upstream sampling stations arrive at the common downstream sampling point. If the variations in the concentrations of the chemical species are of a random nature, this problem can be reduced to a certain extent by taking a lot of samples and then averaging the results. Such an approach does not always lead to interesting answers though as, by averaging everything, one eliminates the individual variations whose impacts one is studying in the first place.

Internationally, the mass balance technique has been used study environmental processes such as the movements of various elements between different reservoirs. These studies range from the transfer of carbon in fossil fuels to atmospheric carbon dioxide and the transfer by rivers and streams of weathering products from land to sea. This method has been able to clarify some issues, such as whether the sea is an infinite sink or not for the weathered products or whether carbon accumulations into the atmosphere represent a long term problem. The total transfer of elements to the sea by rivers and streams when computed over geological times is far greater than the total amount of the elements in the seas [Stumm, 1981]. This can only be because a process exists for removing the accumulations of these elements from the sea. Thus the sea is cannot be considered as an infinite sink for the elements deposited into it. The increase of atmospheric carbon dioxide concentration, which causes the green house effect, also means this compound is not being removed from the atmosphere as fast as it is being released into it. This increase is therefore a long term phenomenon.

In Zambia the mass balance technique has traditionally been performed in metallurgical calculations to monitor process plant behaviour and to determine losses of economically important metals from such plants to tailings dams [ZCCM, 1996]. With the increasing awareness of environmental issues by the companies and the community at large, such studies have recently been extended to the study of estimating the discharge of pollutants into the environment. Studies, for internal company consumption or regulatory reporting, for most effluent discharges are now also being monitored on a contained metal tonnage basis as opposed to a concentration basis alone. However the studies are still localised to the areas around the mines and no attempt to determine how the effluent affect the hydrogeochemistry of the whole river basin has been carried out until now.

3.1.1 *Elemental transport in rivers*

The transport of metals by rivers is part of the geological cycle undergone by all elements. When rain falls, it may dissolve atmospheric gases which may make it acidic. The usual gas in this respect is carbon dioxide which is dissolved by rainwater to form carbonic acid. Sometimes other gases such as the oxides of sulphur and nitrogen, which can be of natural or anthropogenic origin, can be dissolved by rainwater to form sulphuric and nitric acids. This acid rain then reacts with basic soil and rock components in the earths lithosphere such as the reaction with limestone:



The dissolved ions become part of the dissolved solids load and are then transported to the sea together with the river water. Along the way to the sea or even in the sea itself, the conditions

might cause the precipitation of the dissolved elements which are later deposited on the river or sea bed. As an example, the calcium in reaction (1) can be absorbed by sea creatures which use the element to build up their shells. When these creatures die their remain are buried in the sea sediments to form new lime deposits. After millions of years, earth movements can serve to raise these deposits to the surface or near surface where they can be reached by new rain water. This will re-dissolve the deposit to be transported to new seas to start the process all over again.

Rivers do not only carry dissolved solids. Solids can also be carried in the suspended phase. These suspended solids may have been produced by soil erosion from the river's basin or from the sediment on river bed. The sediment itself may have been deposited at an earlier time from material which was either originally suspended or dissolved but was then subsequently precipitated [Salomons et al, 1987].

To study the transport of elements from land to sea it is thus necessary to study the water cycle. This encompasses the manner in which water is evaporated, falls as rain and then flows back to the sea. On its way back to the sea, the water may flow over land as surface run off. In so doing it may cause soil erosion. Water may also first enter the ground before re-emerging as stream water. As the water passes through permeable rocks and soils, it can dissolve various elements which are then carried off in the stream water [Bluth et al, 1994; Meybeck, 1980]. These principles are shown in fig. 2.

Hydrology studies the manner in which the suspended and dissolved load is carried and what factors determine where and when it is dropped [Kattan et al, 1987; Walling et al, 1989; Horowitz et al, 1990]. This includes studying whether the various suspended and dissolved loads are carried

out uniformly across the river cross-section and depths or whether stratification does occur.

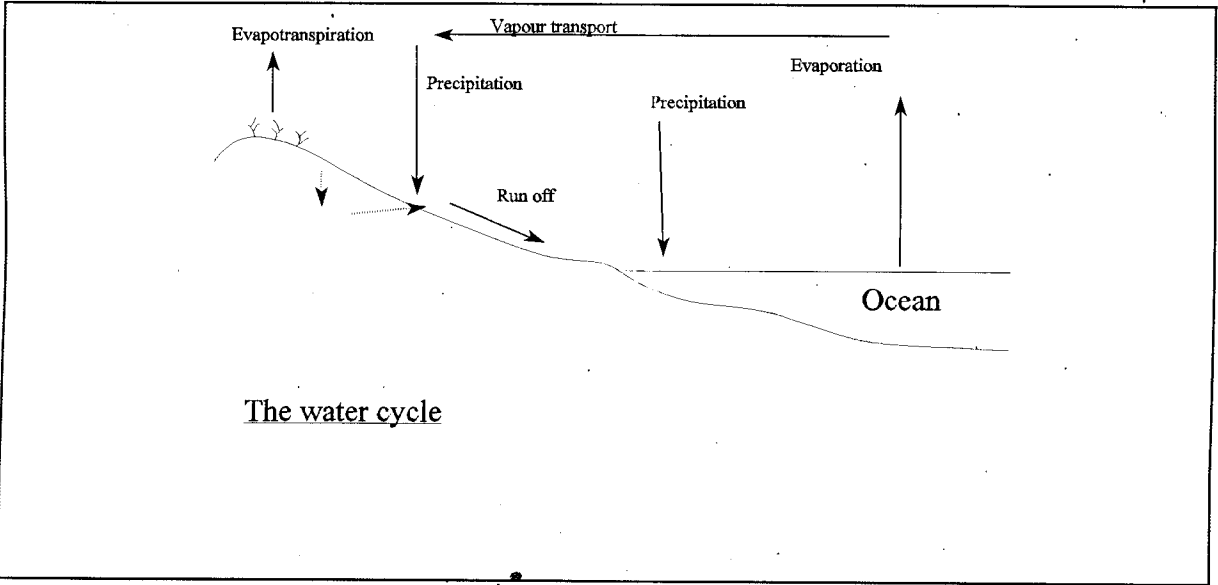


Fig. 2 - The water cycle in hydrogeochemistry

Since the river can transport solids in both the dissolved as well as the suspended form, it is necessary to know what determines the speciation of the load carried by the river. A lot of factors do play a role in this. Rain water can dissolve elements from the lithosphere. It can also scour the soil as soil erosion. Some of the river inputs may be effluent discharges of anthropogenic origin. However once all of this load gets into the river, it is subjected to all sorts of physical, chemical and biological environments which tend to affect the speciation.

Physical parameters such as temperature can affect the kinetics and/ or thermodynamics of certain reactions. For example, the increase in the dissolution of carbon dioxide to form carbonic acid at the lower temperatures found temperate countries can increase the dissolution rates of the bedrock compared to tropical countries [Bluth et al, 1994].

The presence of certain organic and inorganic chemical species, e.g. ammonia and the chloride ion, which can act as ligands can also affect the speciation of elements by increasing the tendency

of the element to stay in solution. Other chemical species such as sulphides and carbonates will however cause a precipitation of insoluble compounds [Latimer, 1939; Matsunaga et al, 1980; Schinitzer 1983].

Yet another effect is the presence of certain solids in the water with good adsorption sites such as iron and manganese oxyhydroxides. Metals can attach themselves to these solids and so stay in a suspended phase when they would otherwise be in solution [Tessier et al, 1984; Hem, 1977].

Redox conditions in the river can also affect the speciation of redox elements such as iron and manganese. When conditions are oxidising, these elements are normally in a solid state. However if conditions are allowed to become reducing, these elements can revert to lower oxidation states which are more soluble even at neutral pH.

Since, as explained above, iron and manganese oxyhydroxides can adsorb other elements, their dissolution, when conditions become reducing, can also result in the transfer to the aqueous phase of metals like copper and lead which may not have been affected directly by the change in oxidising state. It has also been shown [Nkandu et al (5), 1997] that the manganese speciation can also be affected by other conditions like hydro-carbonate concentration.

In surface water, the redox potential level is mainly controlled by the pH and the dissolved oxygen level. This latter parameter is controlled by the physical ability of the river to absorb oxygen from the atmosphere or the occurrence of chemical and/ or biological reactions which tend to consume or produce oxygen. Slow moving rivers may experience difficulties in absorbing sufficient oxygen especially if oxygen depleting reactions are taking place in the river. An example is when eutrophication occurs through the excessive input of untreated sewage which is subsequently

utilised by river borne aerobic bacteria for food. On the other hand the presence of aquatic plants and algae can cause an increase in the dissolved oxygen level of the water through the release of oxygen in photosynthesis reactions [Hettler et al, 1995, Nkandu et al(2), 1996].

In situations where dissolved oxygen is lacking, the redox potentials level can also be effected by other chemical species such as the nitrate/ ammonia, sulphate/ sulphide couples. Although the nitrate/ ammonia couple can take place almost at the same level as the oxygen/ water couple, the sulphate/ sulphide couple does not normally come into action until the dissolved oxygen has been exhausted. However a redox couple involving sulphate was found to be active in the Mwambashi at certain times of the year even though the river was not completely de-oxygenated [Nkandu et al(5), 1997].

The change of redox couple is only one way by which biological systems can affect the hydrogeochemistry of a river. The interactions of biota with the river can affect the transport of the elements in other ways. It has already be said that eutrophication can cause a depletion in the dissolved oxygen level leading to the change in speciation of not only the redox elements such as iron and manganese but also of those elements which may be adsorbed on the surfaces of such solids. There are also other effects. The elements can either voluntarily or involuntarily be adsorbed onto or be absorbed by the biota and end up playing a beneficial or adverse role in the biota's own metabolic needs. A case in point is the geochemical cycle of calcium already given. Other examples involve microorganisms such as iron and manganese bacteria [Ingri et al, 1986, Ghiorse, 1984]. Bacteria perform enzyme mediated reactions which tend to recycle elements and are in fact postulated to have caused the reactions which have brought about the present geological state of the earth from its primeval distant past. One reported case [Fenchel, et al 1979]

is a study on anaerobic bacteria in gypsum springs in the red sea, where the bacteria were observed to be using the calcium sulphate as an oxidant with an accompanying precipitation of calcium carbonate and elemental sulphur. It is highly probable that the observations cited above on the sulphur redox couple in the Mwambashi had a similar cause.

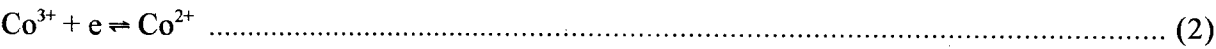
### *3.1.2 Speciation and the thermodynamic considerations involved*

As already said in 3.1.1, elements being transported by a river can exist in a number of forms and it is not always that an element adopts only one form from the start until it reaches the sea. The physical and chemical conditions existing in the river can cause the element to undergo various chemical transitions. A complete study of how any element is being transported thus calls for a determinations of the various forms in which the element exists at different stages.

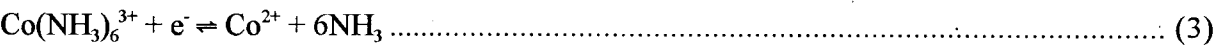
Within the dissolved and suspended forms are also several sub-forms. These sub-forms can cause significant differences in the way the particular element is transported and how it reacts with its environment. Sometimes analytical methods are available to distinguish between the different chemical forms of an element. For example there are methods to distinguish between dissolved iron in the plus II and III valence states:

As stated in section 3.1.1, the dissolved form can occur as the free ion or it can form a chelate with other organic or inorganic ligands. This chelation can considerably affect the stability of the element under particular conditions. As an example [ Latimer, 1939] the reported standard electromotive force (emf) of the transitions from cobalt II to cobalt III state in the absence of ammonia is 1.842 volts:





In the presence of ammonia, this value is reduced to 0.1 volts.



The presence of ammonia thus makes it much easier for cobalt to attain the trivalent state. Further, in the absence of ammonia, the pH region in which cobalt III can remain in the dissolved state is in the very acid region close to a pH of zero. In the presence of ammonia, a region of stability for  $\text{Co}(\text{NH}_3)_6^{3+}$  is opened up at pH values ranging from 7 to 11. Values of pH close to zero are not encountered in normal rivers whilst it is possible to have a normal river with a pH value of 7 to 9. The presence of ammonia in reducing environments, such as water coming from swamps or in deeply buried sediments, can therefore act to dissolve cobalt which would otherwise remain in the suspended form or locked up in the sediment.

In the suspended solids phase, the elements can occur in various forms which are mainly distinguished by the ease with which they can be transferred to the dissolved phase [Hakansson et al, 1989; Tessier et al 1984]]. This is done by leaching a known amount the solid under varying conditions. The resulting solution is then analysed for its concentration. The concentration of the metal in the solution can then be used to back calculate the concentration in the original solids. Solids can be leached under conditions varying from a magnesium chloride or acetic acid-leach at pH of 5 through various mineral acids at ever lower pH and greater oxidising potentials to the lithium meta-borate method. This latter method involves reacting the solids with lithium meta-borate at a temperature of 1000°C. The bead which is formed is then dissolved in hydrochloric

acid. In this latter method *all* elements are converted to the dissolved form and so the concentration obtained is the total concentration [Pettersson et al., 1993].

The proportion of a particular element in the suspended state which is easily available to biota is that which is easiest to dissolve from the solids. This form is termed the non-detrital or non rock form and is usually the adsorbed fraction.

Calculation of precipitation indexes show that, normally, most metals do not transfer to the suspended state through the precipitation of an insoluble phase. Adsorption to existing surfaces is a more probable route [Chapman et al, 1983]. Changes in the thermodynamic conditions such as pH and redox potential which tend to affect the speciation of the substrate can therefore affect the speciation of the adsorbed metals. When manganese or iron, whose speciations are redox dependent go into solution, they do so together with all the adsorbed metals which they may be carrying. Therefore even elements like copper and cobalt which are not affected directly by changes in the redox potential of the water could be affected by these changes if they have been scavenged on the manganese substrate. The number of ions of any metal which can be adsorbed onto the manganese or iron particles depends on the number of available adsorption sites. Therefore the greater the amount of manganese or iron particles being carried by the river, the more the metals they can adsorb. The carrying capacity is also controlled by the tenacity with which a particular ion can adsorb onto the manganese oxides at the prevailing conditions in the water. These conditions relate mainly to the competition from other positively charged ions for the binding sites on the manganese oxides. The hydrogen ion has the biggest influence in this regard.

### 3.1.3 *Practical definitions of speciation*

In the study of river transport of elements, the difference between dissolved and suspended solids is normally defined by filtration. The water is filtered and those solids which pass through the filter are called dissolved solids and those that are retained on the filter are called suspended solids. The pore size of the filter is normally chosen arbitrarily. A value of  $0.45\mu\text{m}$  is the usual value. This means suspended colloidal particles smaller than this figure are treated as dissolved. It is possible to have a smaller filter pore size than  $0.45\mu\text{m}$  but it is very difficult to pump any appreciable quantities of water through such filters. The value of  $0.45\mu\text{m}$  is therefore chosen as a compromise figure because of the practical difficulties encountered with finer pore sizes.

Filtration is ideally done in situ. This reduces the chance that reactions between the suspended and dissolved phases will continue as the samples are being taken to the laboratory from the sampling site. Once delivered at the laboratory itself, the samples are normally stored below  $4^{\circ}\text{C}$  to further slow down any reactions which may occur.

Dissolved heavy metals can adsorb themselves to sample containers and this might affect the eventual accuracy of the results. The filtered samples are therefore acidified to reduce the pH to about 2. This tends to keep the metals in solution. Using precautions such as this, one can make sure that the chemical analyses will be done on samples which are in a state which is reasonably close to what they were in at the time they were sampled.

### 3.1.4 *Hydrology of the transport of different chemical species*

In any sampling processes, due cognisance should be paid to the fact that the particular chemical species of interest may not be evenly distributed across all river sections. In the dissolved state this lack of uniformity may be particularly experienced for what can be termed as redox elements. These are metals like iron and manganese which can change their oxidation state fairly easily depending on the oxidation potential of the water. In deep, slow moving rivers, there can be quite a big difference between the dissolved oxygen levels at different depths. Under such conditions, there could be a significant difference in the concentrations of a particular oxidation state at different levels. To have a good value of the average concentration, it is necessary to collect and combine samples from all depths. For the purpose of making mass balance calculations, one can even go further by taking account of the different discharge rates at different depths for the different chemical species occurring at those depths. However, owing to the turbulent flow regime which exists in most rivers, this is normally unnecessary. It suffices to just get an average concentration and an average discharge rate.

Whatever the problems there might be in the accurate determination of dissolved solids transportation, these problems are minor compared to those involving suspended solids. The magnitude of spatial and temporal differentiation in the concentration of suspended solids load can be very significant, particularly if erosion and deposition is taken place at the same time. This happens when a river has reached what is termed old age and it is moving in a slow meandering fashion. At the bend, erosion could be taking place on the inside curve whilst deposition could be taking place on the outside curve. Thus sampling from one spot can give very wrong values of

the average concentration of suspended solids. This was noticed at Machiya as can be seen in table 1 in section 4.2.3.

Proposals have been made that to determine the geochemical flow of solids, one needs only to analyse the  $-63\mu\text{m}$  fraction [Horowitz et al, 1990]. This fraction is also assumed to be evenly distributed within the body of the water. Therefore by designing a sampling programme which ensures that this fraction is obtained from a near surface point, correct inferences can be made on the flow suspended solids. This idea was disproved in tests at several river locations in the United States. It was shown that the  $+63\mu\text{m}$  could not be disregarded for the purpose of determining the transport of elements.

Turbidity checks across the river cross section and depth can, to a certain extent, be used to tell whether there is significant difference in the total suspended solids concentration at the different positions. If the turbidity values at different points are similar, then no great sacrifice in accuracy can be expected if samples are taken at one spot.

The best way of ensuring a homogeneous sample is, if possible, to take the sample just downstream of rapids. The turbulent flow experienced by the water at a rapids serves to mix the different chemical components and this ensures homogeneity so long as the sample is not taken so far downstream of the rapids that re-stratification starts to take place. Stratification is also minimised in narrow rivers and streams.

To determine the transportation rate of a particular species in the suspended form, one first needs to determine the total solids transportation rate. This is done by multiplying the river discharge

rate and the total suspended solids concentration. This rate is then multiplied by the concentration of the desired chemical species in the sampled solids to get the flow rate of the particular chemical species in the suspended state.

All these principles were put into consideration in the design of the sampling programme to ensure the reliability of the data.

#### **4.0.0 Methodology**

The experimental procedure adopted involved taking samples at selected sites on the Kafue and Mwambashi rivers over a period of 14 months from March 1995 to April 1996. Since the wet season lasts from October to April, the time of maximum water discharge is around March of every year. Therefore the sampling period covered two such maxima.

##### ***4.1.0 Sampling points and intensities***

The sampling points used in this project are shown in fig. 3. The samples for the pre-mine area state of the Kafue river were collected at Raglans Farm on a weekly basis. This schedule was reduced to once a fortnight during the dry season. The wet season intensity was higher because of the need to pick up sporadic pulses which occur during this season.

At Machiya ferry, which is the exit of the Kafue river from the Copperbelt, the original intention was for a similar sampling intensity as at Raglans Farm. However the distance of the site from

Kitwe and the poor state of the road made this an impossible target. The sampling intensity was therefore reduced to once every three to four weeks for both the dry and wet seasons.

At the sampling sites within the Copperbelt, the Kafironda and Garneton sites were sampled once a month in the dry season and once a fortnight during the wet season. The Fishers farm site was sampled more intensively because the river will have received most of the mining effluents by this time. Therefore, this point was considered as being almost an exit point from the Copperbelt and as such was sampled at the same rate as Raglans Farm. This helped to compensate for the reduced sampling rate at Machiya ferry.

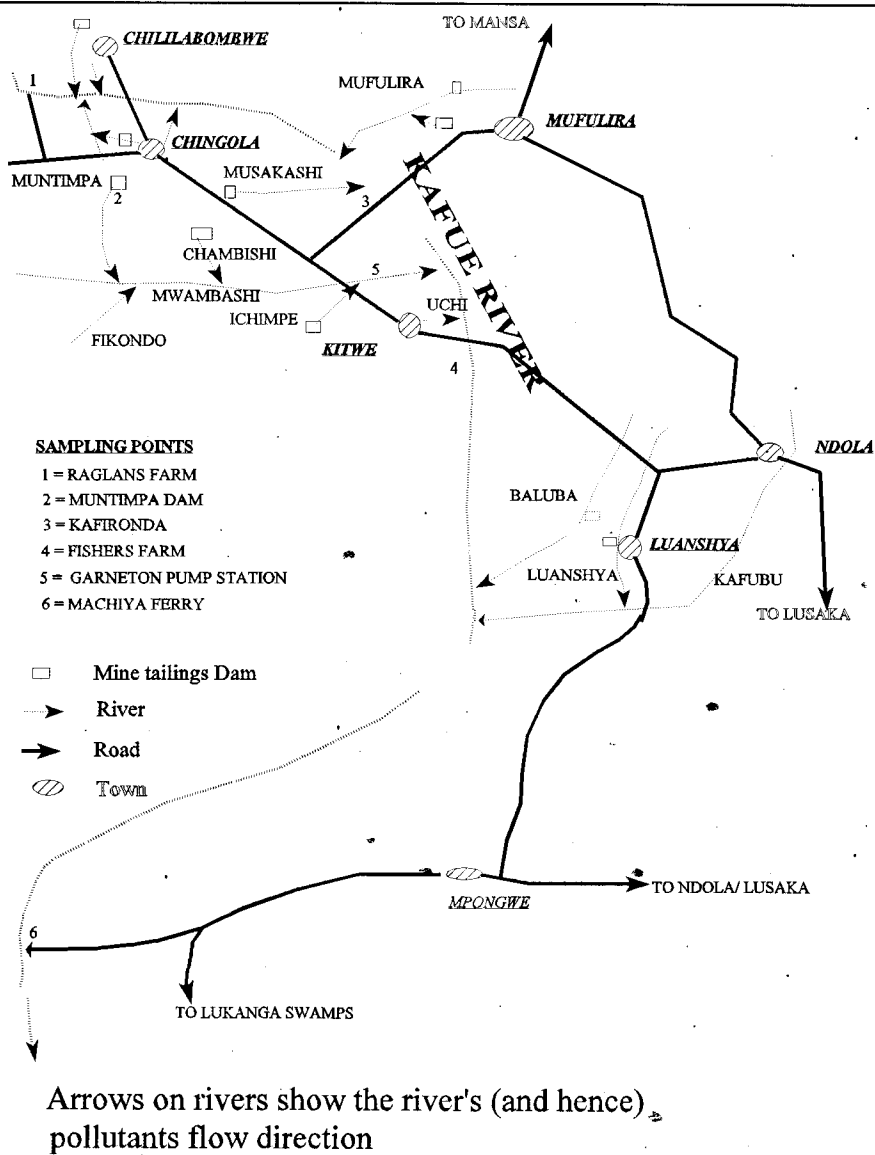


Fig. 3 - Schematic map of the sampling points used in this study



#### *4.2.0 Data sources and water sampling and analysis procedures*

The data used in this report comes from two different sources, that which was collected in this project and the other which was obtained from other parties. This latter data is on the water discharge rate in the Kafue and Mwambashi rivers and the amount of effluent discharged from mining operations. The data on the water discharge rate is from the Water Affairs Department in the Ministry of Energy and Water Development. The data on effluent discharged from mining operations was obtained from company reports in the Environmental Services Department of ZCCM.

#### *4.2.1 Data obtained during study [March 1995 - April 1996]*

##### *(a) Suspended solids*

At Kafironda and Fishers farm, the water was sampled just downstream of some rapids. Therefore, water at this point was thought to be well mixed. At the Raglans farm and Machiya ferry sampling points, there were no rapids close by. These points had been selected for other reasons such as the presence of water discharge rate gauging stations close by.

The water at Machiya ferry was sampled while standing on the ferry. The width of the river at Machiya ferry meant that there was a real possibility of stratification in the load carried by the river. It was thus essential that samples should be taken from all parts of the river. Therefore samples were taken whilst the manually towed ferry was in motion. This allowed for the sampling of water from positions across the river width. The overall sample taken was thus a mixture of

individual samples taken from these different positions. The river at Raglan's farm was thought to be narrow enough to ensure good mixing.

The determination of total suspended solids was done as follows: A depth water sampler capable of being closed under water was used to take a sample from the required depth. This sample was then used to fill a Millipore filtration set. The filtration set consisted of a sample cup which was screwed on top of a filtrate receiver. In between the sample cup and filtrate receiver was placed a pre-weighed  $0.45\mu\text{m}$  pore size filter paper. The filter paper had first been oven dried at a temperature of  $105^{\circ}\text{C}$  after which it had been cooled in a desiccator before being pre-weighed. The pre-weighing was done on a balance capable of weighing up to an accuracy of  $0.00015\text{ g}$ .

The filtrate receiver was connected to a hand held vacuum pump and filtration was initiated by inducing a vacuum in the filtrate receiver until all the sample had been filtered. More sample water was collected and put into the sample cup and this procedure was repeated until sufficient solids had accumulated on the filter paper. The indication for this was the time needed to filter a sample. When the time needed to filter a sample started becoming very long, it was considered that the filter pores were almost clogged because sufficient solids had accumulated on the filter paper. The total volume of water filtered was then recorded.

During the filtration the sample cup was covered on top to ensure that no dust was blown into the sample. At the laboratory, the filter paper was put into a clean petri dish and stored at  $4^{\circ}\text{C}$  until the time came for the actual analysis. Analysis involved removing the filter paper and drying in an oven set at  $105^{\circ}\text{C}$  for 24 hours. Thereafter the filter paper was removed and cooled in a desiccator. The dried filter paper was later weighed to the same accuracy as before. The

calculation of the concentration of total suspended solids was then made on the figures of dry solids collected and sampled volume filtered. Handling of the filter paper at all times was done with clean stainless steel tongs.

For the purpose of analysing the chemical composition of suspended solids, filter cake samples from river water filtered in the field were collected. The water was pumped out of the river through silicone tubing with the help of a battery powered Geotech peristaltic pump. This water was then passed through  $0.45\mu\text{m}$  pore size Millipore cellulose filters mounted on a 14 cm diameter Geotech polycarbonate holder. A sample of the filtered water was collected in 500 ml sample bottles acid washed for one week each in 50% hydrochloric acid and 10% nitric acid before being rinsed with deionized distilled water. The possibility of picking up contamination when the water was being drawn through the long silicone tubing meant that this was not the preferred sample and it was only used as a back-up sample in case some other contamination was suspected in the sample obtained by the preferred method. This method is described in the section on dissolved solids.

The filtration with the 14 cm diameter Geotech polycarbonate filter holders was carried on until no more water could be passed through the filter. The signal for this was when the filter holder started indicating that the water would soon start emerging from between the faces of the two halves of the holder between which the filter was placed. This procedure was repeated with four different filters on each sampling occasion. The first two filters were to be used for major element determination and the other two for minor element determination. The volume of the total filtrate from the four filters was recorded.

At the end of the sampling, the still un-opened filters holders were put into plastic bags to reduce the chance of contamination from road dust when being transported to the laboratory. At the laboratory, the filters holders were opened. Using clean *acid washed plastic* forceps, the filters from two of the four filter holders were removed and placed into a clean petri dish and given a label which showed the sampling location and date of collection. In a similar manner, the filters from the other two filter holders were put into another clean petri dish and labelled accordingly. The water and cake samples were stored in a refrigerator at 4°C until they were dispatched to the laboratories of SGAB in Lulea, Sweden where they were analysed for the elemental concentrations.

As a further measure to check for the possibility of sample contamination in the whole process of sample collection, transportation and storage, travelling filter blanks were taken on a number of occasions. These blanks were loaded into filter holders in the same way as the filters to be used for sample collection. They were then carried to the sampling sites together with the normal filters but were not used for sample collection. Back at the laboratory, they were prepared in the same way as the other filters although they were labelled as blanks. They were then analysed the same way as the other filters to derive the total amount of individual elements in the blank. This amount was then compared to the corresponding amount in the actual samples. The amount of an element found in the blank was considered to be the amount of that element in the actual samples which was of spurious origin. This gave an indication of the contribution of particular elements in the analysed sample that were either due to the filter material itself or from any contamination picked up along the way. *Very little contamination of the samples was detected in this way. Potassium showed the highest level of contamination at about 3% of the total weight analysed in the sample.* The contribution to the analysed sample that came from either contamination or the filter

material for the rest of the elements was lower than 0.1% of the weight for the total amount found in the samples.

The analytical procedure used in analysing both the aqueous and solid samples has been described elsewhere [Pettersson, 1993].

*(b) Dissolved solids*

Two methods were used for collecting aqueous samples. In the preferred method, a plastic syringe dedicated to the site was first rinsed out with the river water several times. Afterwards some of the river water was drawn into the syringe. A filter assembly, consisting of a 0.45  $\mu\text{m}$  Millipore cellulose filter placed inside a 3 cm diameter polycarbonate filter holder, supplied by Sartorius GmbH of Gottigen, Federal Republic of Germany, was then attached to the end of the syringe. The water in the syringe was then forced through the filter and into a 60 ml capacity sample bottle which had previously been acid washed the same way as the 500 ml bottles described above.

The back-up method has already been described above.

For total dissolved solids in mine effluent affected waters such as the Kafue river, ZCCM uses a factor of 0.74 to convert a conductivity expressed in  $\mu\text{S}/\text{cm}$  to a concentration expressed in ppm. This factor, which compares with the 0.65 normally used for natural waters, has been used to calculate the total dissolved solids concentrations in this report.

(c) *Turbidity*

Turbidity was measured with the help of the he Hydrolab H2O Multiprobe manufactured by the Hydrolab Corporation of Austin, Texas, USA. Calibration for turbidity was done approximately once very ten days. Turbidity was calibrated using Formazin from Hach company. The standard Formazin has a turbidity of 4000 NTU. A 1 ml sample of the standard was taken out and diluted to 250 ml with distilled water to make a suspension with a turbidity 16 NTU. This suspension was then used for the actual calibration.

At all sampling locations turbidity profiles were obtained and the values of turbidity quoted in this report are the averages of the values in the profile. In the first four weeks of the project, problems were encountered with the turbidity readings. Values of zero were being recorded even when the water was visibly turbid. This problem arose from the calibration procedure which was being attempted in direct sunlight [ Hydrolab Corp, H2O Multiprobe user's manual, 1993]. Once this problem was realised, the calibration procedure was only done out of direct sunlight. This change in procedure produced better results. As a result of this, the turbidity results for the first four weeks of sampling have not been used. On some occasions, it was not possible to obtain turbidity values. This normally depended on the brightness of the day and the depth of the river. If the day was very bright, turbidity values could not be obtained at any depth. On less bright days, it was only for the water near the surface that turbidity values could not be obtained. If turbidity values could be obtained at any depth, the average of these values have been used in the analyses.

4.2.2 Discharge rate data

The data on the water discharge rates in the Kafue and Mwambashi rivers was obtained from the Water Affairs Department. The department maintains gauging stations at Raglans farm, Smith Bridge and Machiya ferry in the Kafue river as well as at Chingola road bridge on the Mwambashi river. There are no gauging stations at Garneton, Kafironda and Fishers farm. The data from the first four stations in conjunction with effluent data from ZCCM has been used to estimate the approximate discharge rates at the Kafironda, Fishers farm and Garneton sampling sites.

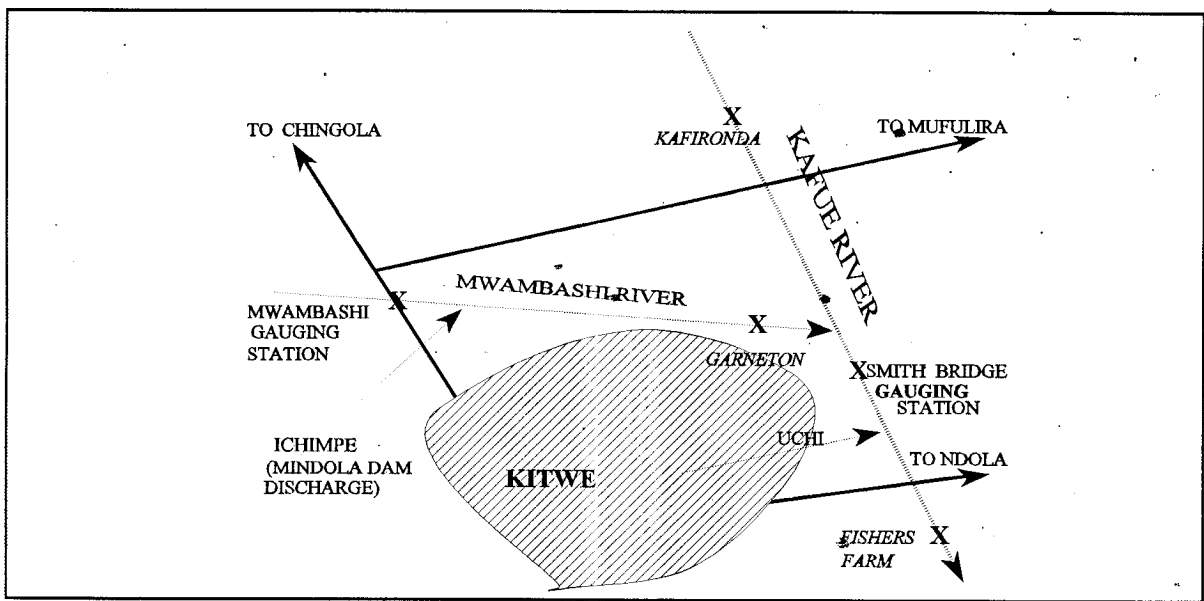


Fig. 4 - Relative positions of the Garneton, Kafironda and Fishers farm sampling locations to the gauging stations on the Mwambashi and Kafue rivers

As can be seen from fig. 4, the Mindola dam effluent joins the Mwambashi after the gauging station but before the Garneton sampling site. Therefore the discharge rate at this site has been estimated as the Mwambashi discharge rate plus the Mindola dam discharge rate. The Kafironda discharge rate has been estimated as the Smith bridge discharge rate minus the Garneton discharge

rate as calculated above. The Fishers farm discharge rate has been estimated as the Smith Bridge discharge rate plus the Uchi stream discharge rate.

There are other streams in the area apart from those considered. It is however thought inclusion of these would only marginally affect the general value of the discharge rate at any time of the year. This can be appreciated by comparing the sizes of the Mwambashi and the Kafue rivers. Although there are other small streams, the Mwambashi is the major tributary of the Kafue in the area. The Kafue in its turn is about 10 times bigger than the Mwambashi. Thus any value calculated as the discharge rate in the Kafue river using the above method is unlikely to change by more than 10% even if all the other tributaries were considered.

4.2.3 *Effluent discharge data from ZCCM*

The main discharge streams for effluent arising from ZCCM operations which eventually find their way into the Kafue river are monitored by the environmental officers of ZCCM. Weekly and monthly data is kept on the water quality of these effluent streams. This data has been obtained and is summarised in appendix 1. Table 1 gives the list of effluent streams used in this study. A more detailed map of the discharge routes from the individual mines to the Kafue river is also given in appendix 2. Agreement or otherwise between these reported discharges and the loads carried in the river, as calculated from the product of sample concentrations of samples collected during the sampling discussed in section 4.2.1 and the corresponding discharge rates from the Water Affairs Department, would indicate the comparability or otherwise of the two sets of data



**Table 1      Monitored effluent streams from ZCCM divisions**

<b>MINE/ DIVISION</b>	<b>FINAL EFFLUENT STREAMS DISCHARGING INTO PUBLIC WATER</b>
Konkola	(1) No. 2 channel into Kafue, (2) Combined drain
Nchanga	(3) Pollution control dam overflow, (4) concentrator effluent to Nchanga stream, (5) Muntimpa dam overflow
Chambeshi	(6) New dam overflow, (7) Musakashi dam overflow
Mufulira	(8) Mufulira combined discharges = Main mine effluent, TD 11 overflow, TD 10 overflow and seepage
Nkana	(9) Mindola dam overflow, (10) Uchi streams, (11) Wusakili storm drain, (12) Frikkers lake,
Luanshya	(13) Luanshya combined discharges = Musi dam into Baluba river and Chonga dam, Nos. 18 and 14 shafts underground water and Tailings pump house discharges into Luanshya river

## **5.0.0 Results and discussion**

### **5.1.0 Effluent from mining operations**

Mine discharges are often sporadic events. As can be seen in fig. 5 the suspended solids discharged at the Pollution Control Dam and in the Concentrator effluent of Nchanga division show no seasonal pattern in the distribution. This is probably because the data is based on daily grab samples which can vary significantly. As a result it was decided that the total suspended solids discharged into the Kafue from mining operations in any month would be more accurately represented by the value obtained by averaging the reported discharges during the whole sampling

period than by the average obtained from the, up to five, samples collected during that particular month. Additionally, the data from ZCCM was not complete in the sense that in some months samples were not collected. The average values have thus been assigned for those months where the data is missing.

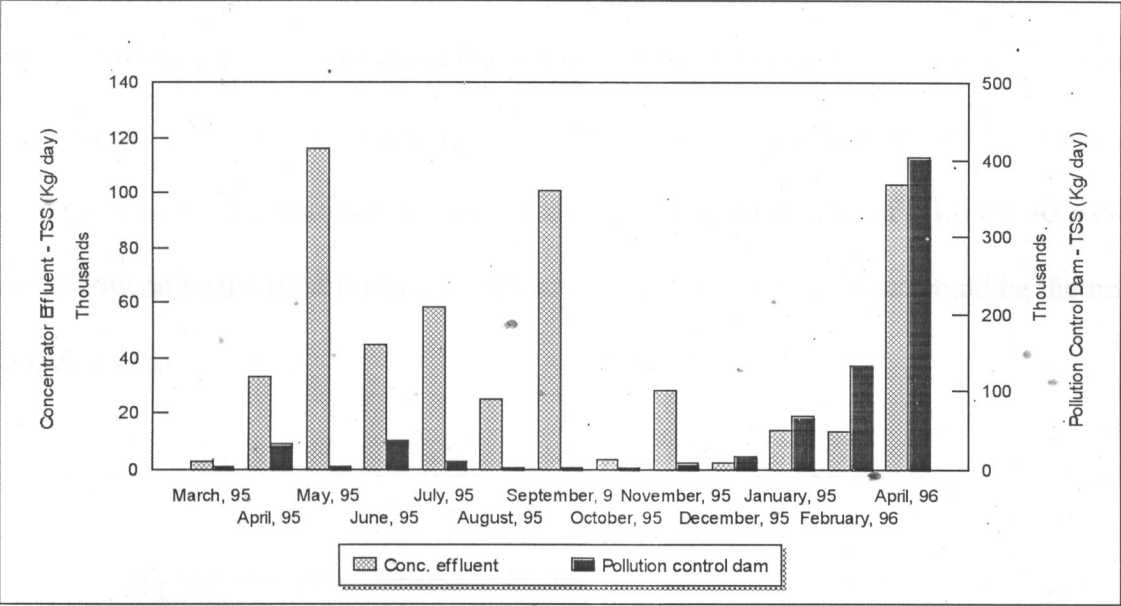


Fig. 5 - Pattern of suspended solids discharged from Nchanga Division

Some parameters, particularly those representing dissolved solids, do show a clear seasonal pattern though as can be seen in fig. 6 of the Chambishi cobalt plant effluent streams.

The problem which arises here is what the most appropriate value to be used for all the months would be. If a single value is used as the quality of effluent discharged into that stream like in the case of suspended solids, this would understate the amount discharged during the peak months and vice versa during the low months. Additionally, since the Kafue river discharge data is being presented on a basis of the average values of a particular parameter in the samples taken for each particular month, the ideal situation would be to find monthly averages for the ZCCM effluent streams and use these in conjunction with the Kafue river data.

The compromise which has been arrived at is to use the actual monthly average where the data is available. Where it is not, the average value for that parameter obtained over the whole 14 month sampling period is used as a default value for that particular month. Where this has been done the default value as shown in the tables in the appendix is written in italics.

Lastly, the concentrations of some of the species in the ZCCM samples were, in some cases, given as indefinite values such as 'less than 0.1 ppm'. Such a value could not be used in a mass balance. In such cases, the concentration has been taken as the maximum value of 0.1 ppm. As a result the mass flow rate calculated for that particular species on such occasions would be the maximum possible value.

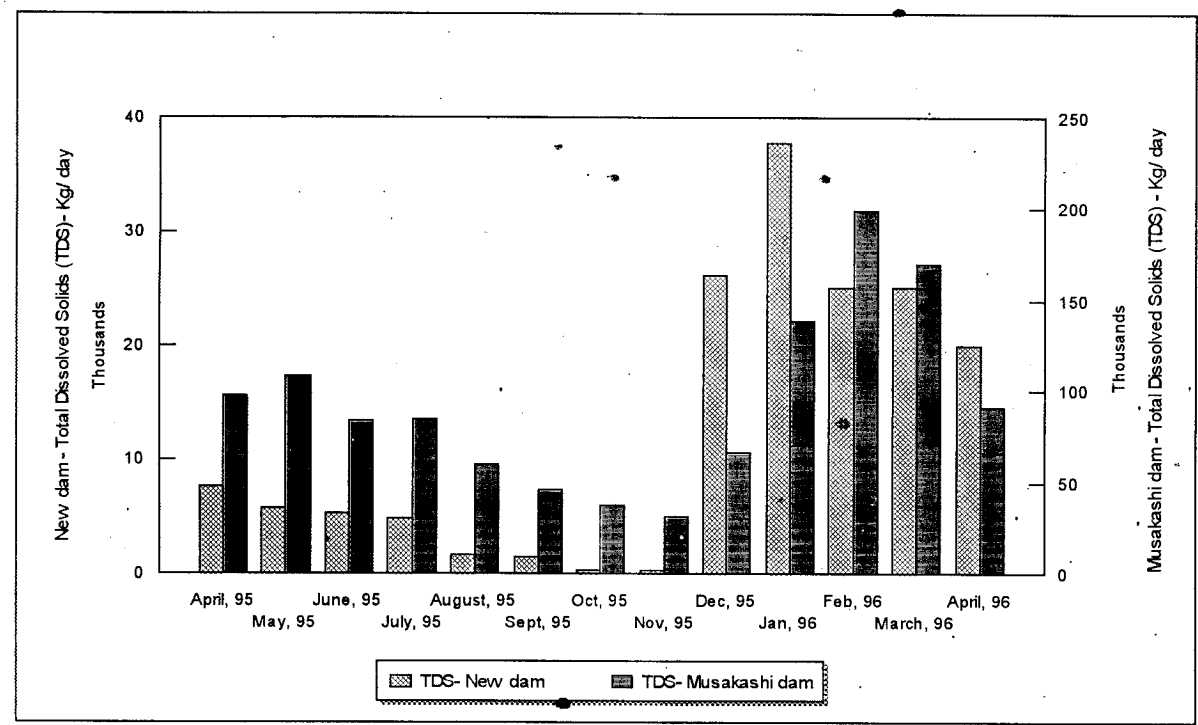


Fig. 6 - Pattern of dissolved solids discharged from Chambishi cobalt and acid plant

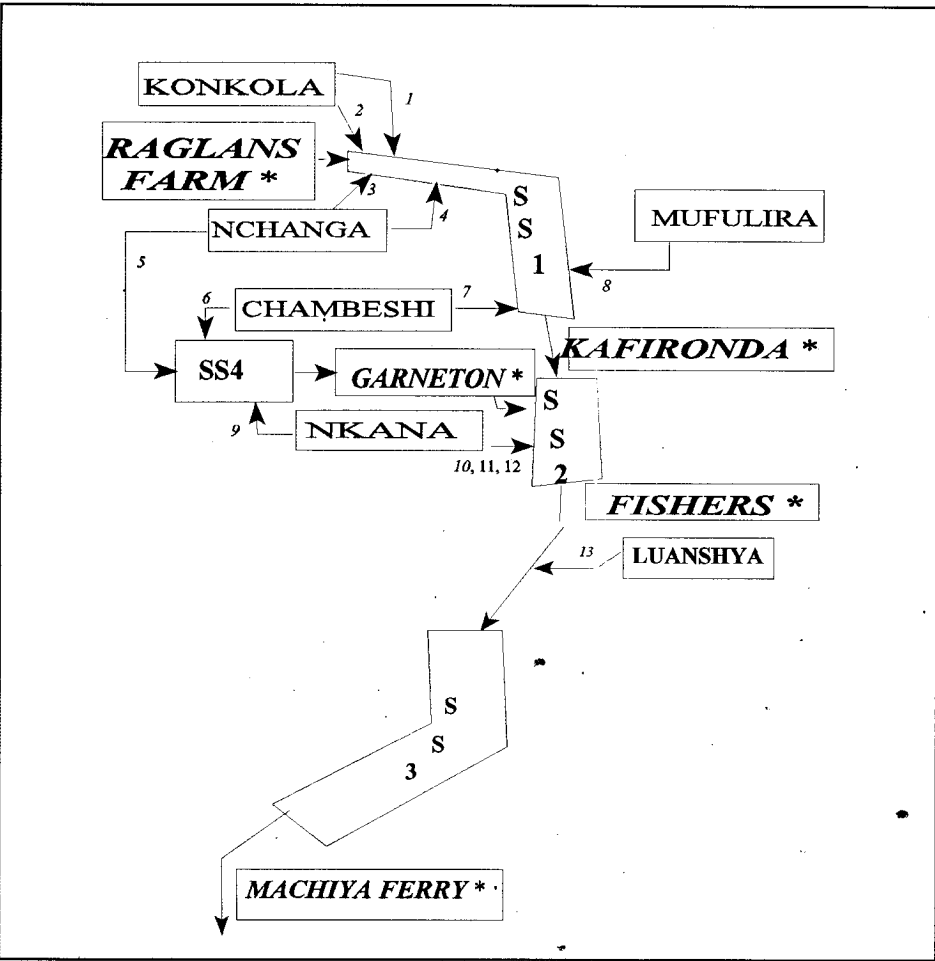


Fig. 7 - Mass balance calculation blocks in relation to the sampling sites and the confluence of the effluent streams with the Kafue river.

Block SS1 receives the mine effluent from Nchanga, Konkola and Mufulira divisions as well as the Chambeshi cobalt plant of Nkana division. As said above analysis of Hydrogeochemical activity in this block will be restricted to the dissolved state as chemical analyses could not be performed on the suspended state for samples collected at Kafironda.

Block SS2 receives the output from blocks SS1 and SS4. Effluent discharges also reach it mainly via the Uchi stream which carries water from Nkana mine operations.

Block SS4 covers the Mwambashi river which is a tributary of the Kafue river. This block mainly

receives effluent discharges from the Muntimpa dam of Nchanga division. It however also receives effluent from Chambeshi cobalt plant, Mindola dam and underground water from Chibuluma mine.

Block SS3 receives the combined effluent discharges from Luanshya mine. However there are also small emerald mining operations being carried out on the west bank of the Kafue river and these would also join the Kafue river in this block. The impact from the emerald mining operations is only likely to be in form of suspended solids inputs.

#### 5.2.1 Sources and sinks

The analyses are based on the average monthly inputs and outputs of total suspended solids, total dissolved solids, dissolved sulphur, dissolved and suspended copper, cobalt, iron, manganese, barium, cadmium and lead into and out of the four boxes. The effluent discharges for total suspended and total dissolved solids, dissolved sulphates, total and dissolved copper and total and dissolved cobalt from ZCCM operations used in these calculations are also given in the appendix 1.

Fig. 8-14 give the annual average of the effluent discharged via these routes. This gives an idea of the relative importance of each particular discharge route. The figures indicate that, with the exception of Muntimpa dam, the most important discharge routes are those lying furthest upstream of the Kafue river like the combined drain at Konkola and the pollution control dam and Nchanga concentrator discharge at Nchanga.

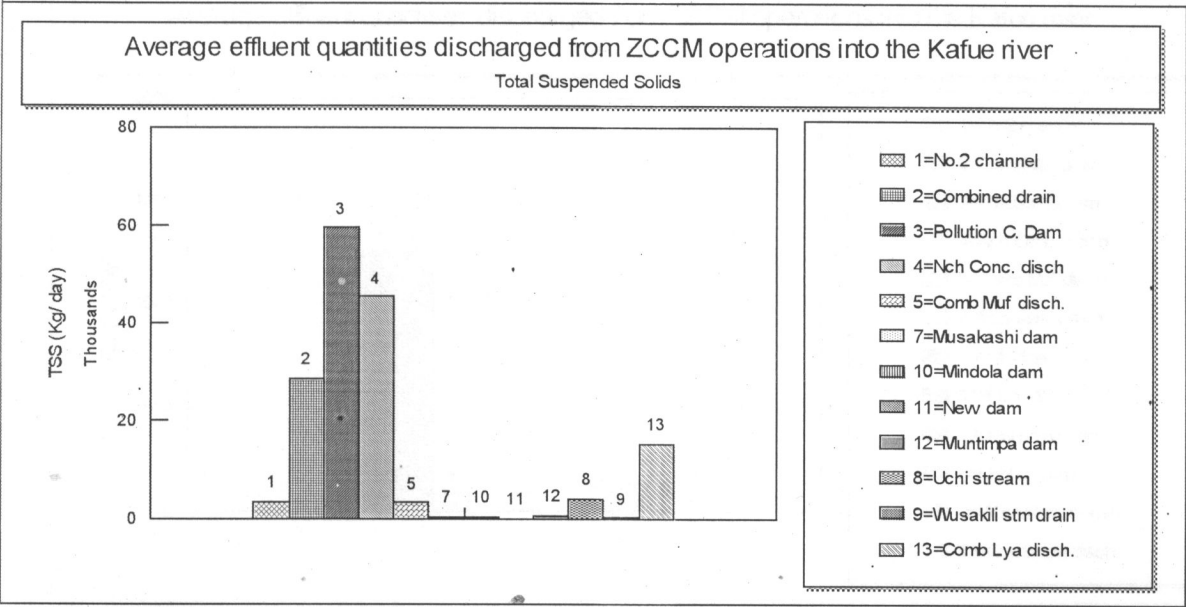


Fig. 8 - Total suspended solids discharged via monitored mine effluent points

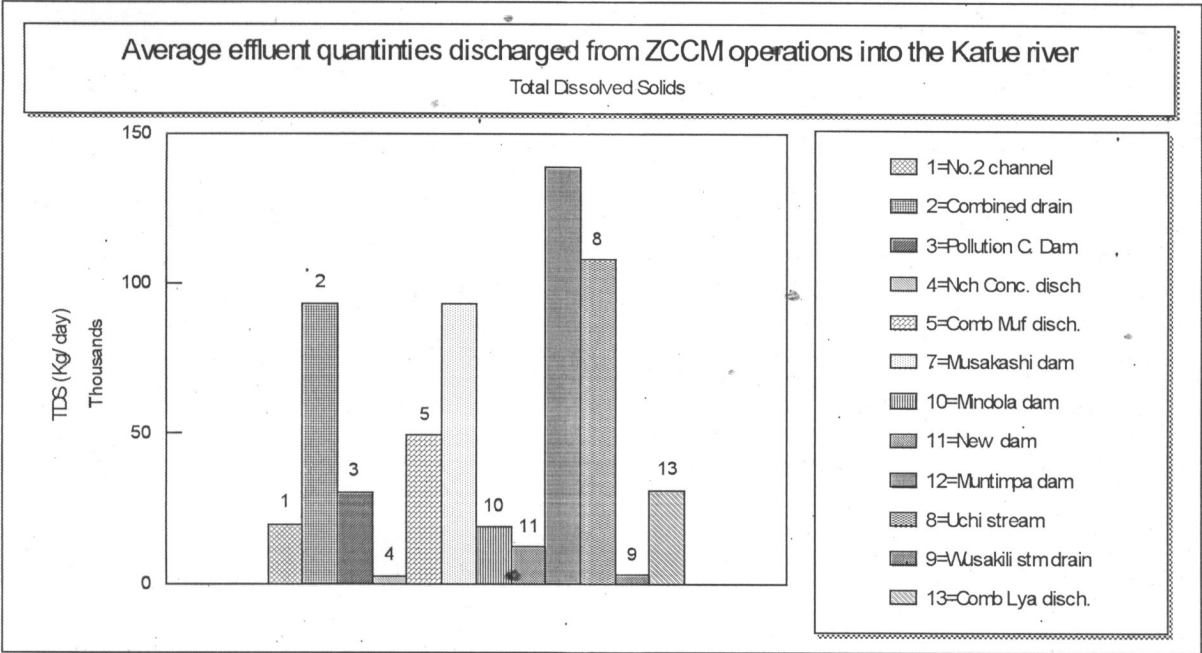


Fig. 9 - Total dissolved solids discharged from monitored mine effluent points

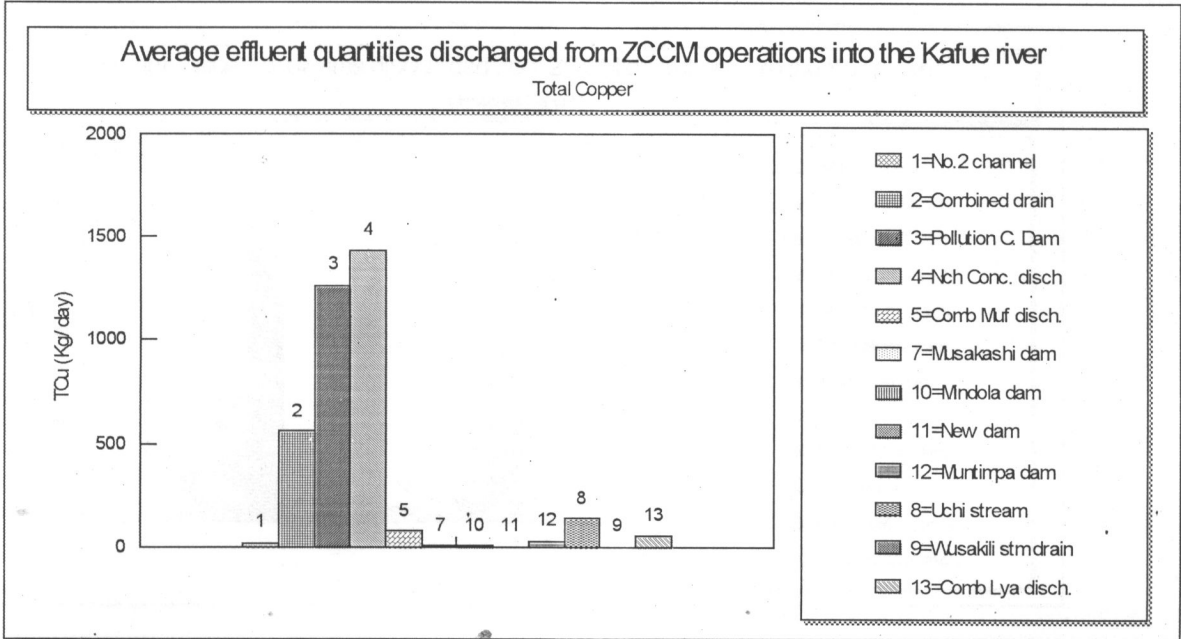


Fig. 10 - Total copper discharged via monitored mine effluent points

### Average effluent quantities discharged from ZCCM operations into the Kafue river

Dissolved Copper

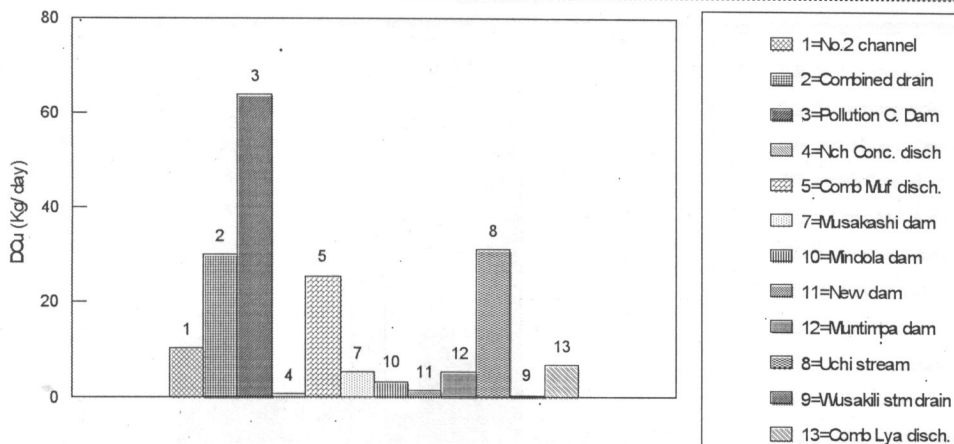


Fig. 11 - Dissolved copper discharged via monitored mine effluent points

### Average effluent quantities discharged from ZCCM operations into the Kafue river

Total Cobalt

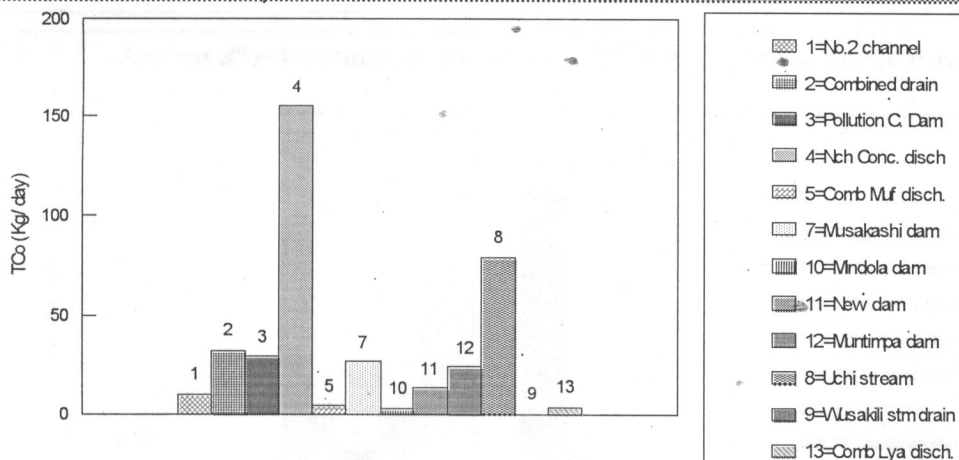


Fig. 12 - Total cobalt discharged via monitored mine effluent points



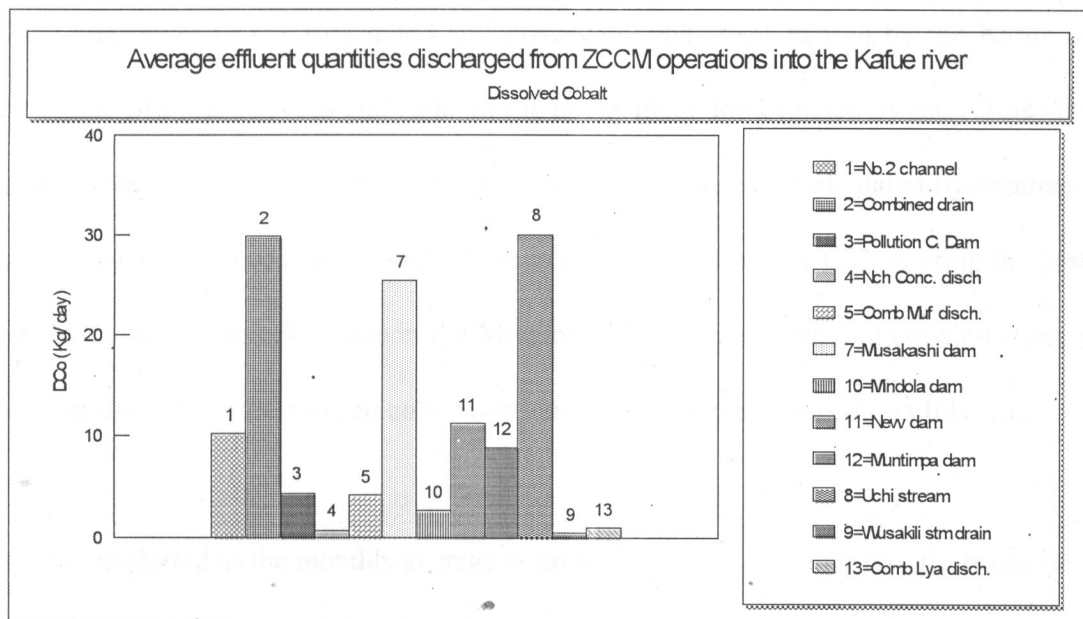


Fig. 13 - Dissolved cobalt discharged via monitored mine effluent points

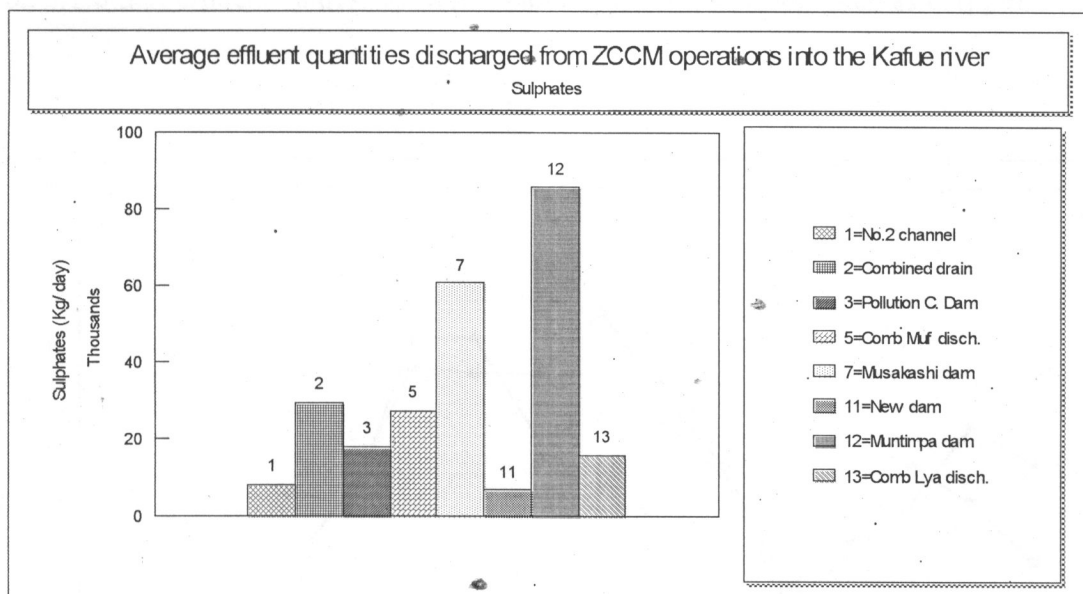


Fig. 14 - Dissolved sulphates discharged via monitored mine effluent points

Apart from the monitored effluent discharges, it is possible that other sources and sinks exist which contribute to the suspended and dissolved solids load carried by the Kafue river. The magnitude of other sources and sinks to the heavy metal load carried by the Kafue river and its tributaries can be quite considerable as fig. 15 shows. The ratio is calculated by dividing the mass flow rate of the dissolved copper and cobalt in the effluent from ZCCM entering the Mwambashi river by the total mass flow rate in the Mwambashi river of copper and cobalt as determined by the river discharge rate and the concentrations in the samples collected in this study.

The data is plotted as the monthly average against the 15 th day of that month. It can be seen that with the exception of the rain season, most of the copper and cobalt discharged into the Mwambashi never gets to the Garneton sampling site. Another possible reason however could be that the amount of these metals in the effluent has been grossly over-estimated. It was said in section 5.1.0 that effluent values reported as less than 0.1ppm were taken as 0.1ppm.

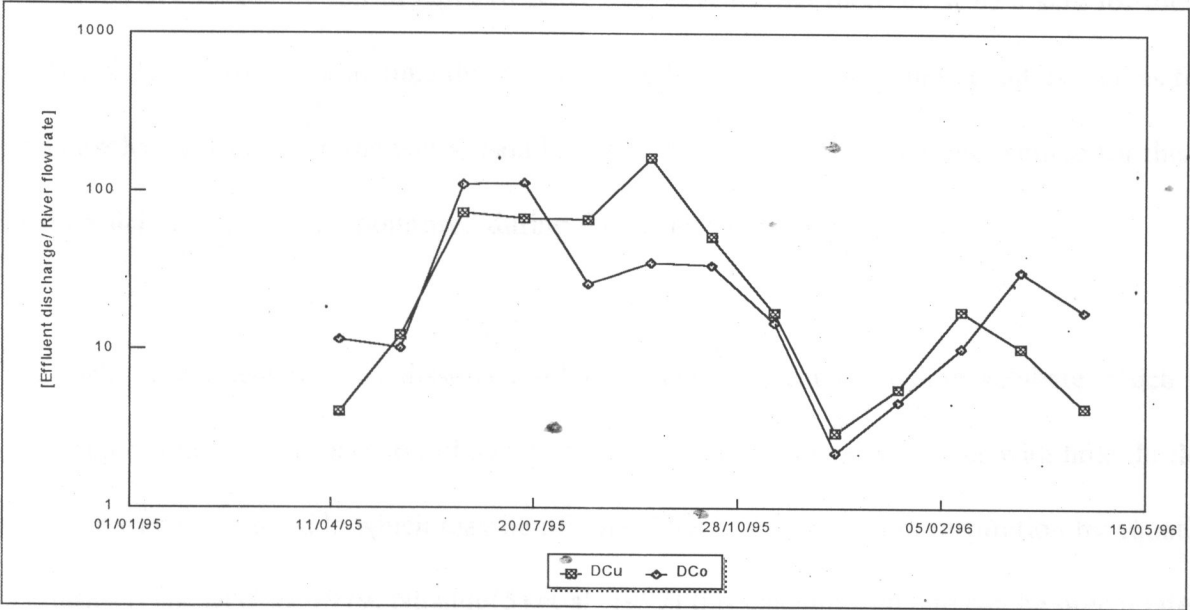


Fig. 15 - Ratio of amount of copper and cobalt in effluent to amount monitored in the Mwambashi

On the other hand, the figures for dissolved sulphur shows a much greater impact on the Mwambashi river from the mining operations as fig. 16 and fig. 17 show. Whilst 16 is plotted on a percentage basis fig. 17 shows this data in terms of mass flow rates.

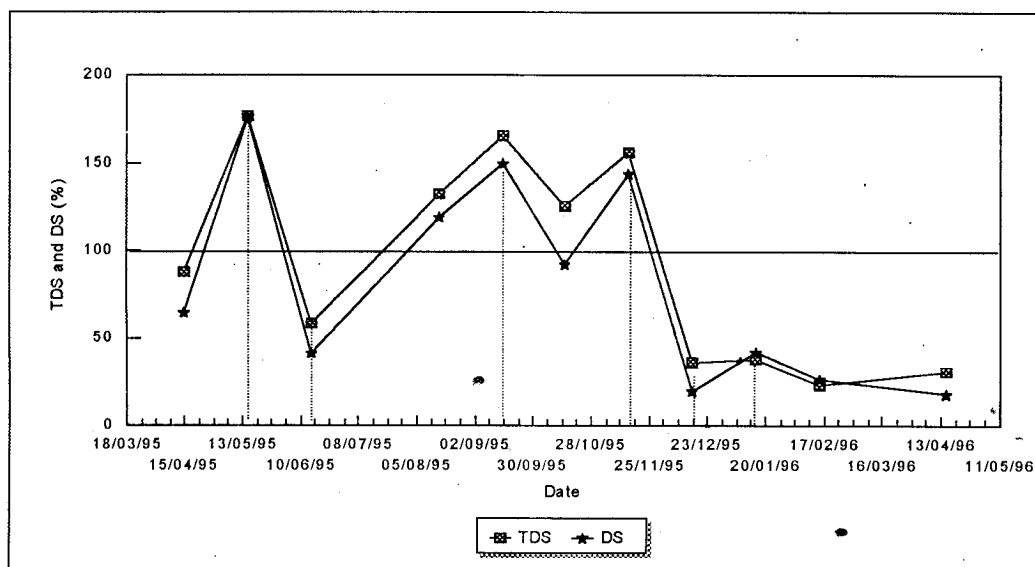


Fig. 16 - Total dissolved solids and dissolved sulphur in mine effluent discharged into the Mwambashi river as a percentage of the amount monitored in the river

The greater than 100% load in the effluent streams compared to that in the Mwambashi river during the dry season period of April to November reveals that there must be a sink for these solids in the river. At the same time the less than 100% load for copper and cobalt as well as for total dissolved solids during the wet season indicates that there must be another source for these solids which was not being monitored during the project sampling.

The main constituent of total dissolved solids in mine effluent is calcium sulphate which is produced during the precipitation of sulphuric acid and heavy metal sulphates with lime. In the presence of carbon dioxide which may be of atmospheric origin or from respiration by aquatic organisms [Fenchel et al, 1979; Nkandu(5) et al, 1997] this calcium sulphate can be precipitated out of solution to produce calcium carbonate and sulphuric acid.

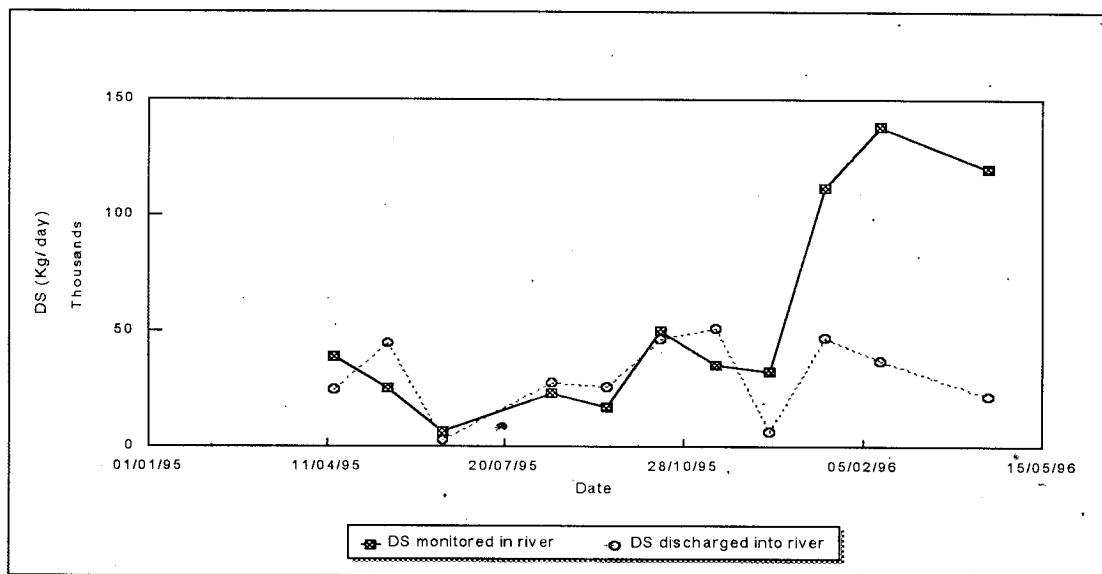
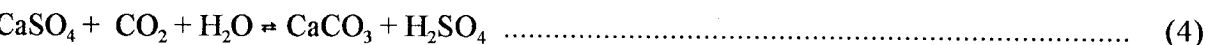


Fig. 17 - Mass flows of dissolved sulphur monitored in the Mwambashi river and that discharged to the river as mine effluent.

Fig. 18 suggests that reaction (4) was occurring in the Mwambashi river. It can be seen that every time there was an increase in the conductivity of the water, there was a corresponding drop in the alkalinity. If one bears in mind that the data in fig. 18 is for the weekly or fortnightly samples whilst the data in fig. 16 is for monthly averages, one can notice that the peaks and valleys in fig. 18 are matched by peaks and valleys in fig. 16. Therefore every time there was a big discharge of effluent from ZCCM as indicated by a peak in fig. 16, there was a corresponding increase in the conductivity of the water in the Mwambashi river which in turn led to a reduction in the alkalinity of the water as indicated in fig. 18. This is exactly what reaction (4) predicts as an addition of calcium sulphate from mine tailings results in the production of sulphuric acid which then causes a drop in the alkalinity of the water.

It should be noted that the drops in alkalinity whenever there was a jump in conductivity only occurred during the dry season. This is in accordance with the idea of precipitation of calcium carbonate whenever its solubility limit was exceeded. During the rainy season when the high discharge rate in the river reduces concentrations, changes in conductivity move in tandem with changes in alkalinity indicating that dilution rather than chemical precipitation is the major cause for these changes.

Although reaction (4) may be responsible for the removal of some of the dissolved solids, it cannot account for all the solids removed. Reaction (4) is effectively replacing the dissolved calcium sulphate of molecular weight 136 with sulphuric acid whose molecular weight is 98. Therefore even if the reaction was carried to completion, the reduction in dissolved solids would only be  $[(136-98)/136] = 28\%$ . Therefore there has to be another mechanism at work which is responsible for reducing the dissolved solids by the indicated factor of up to about 75%.

In discussing possible redox couples in the Mwambashi [Nkandu et al (5), 1997], it was said the data indicated the existence of a sulphate/ sulphide couple. This couple could be from the assimilation of the sulphur during protein formation by aquatic plants. Thus there might be a biological sulphur sink as well.

Re-suspension, and ultimately re-dissolution of the precipitated calcium carbonate during the rainy season which starts around November may be partly responsible for the mine derived dissolved solids being less than the river borne dissolved solids measured at Garneton in the period from mid November to mid April.

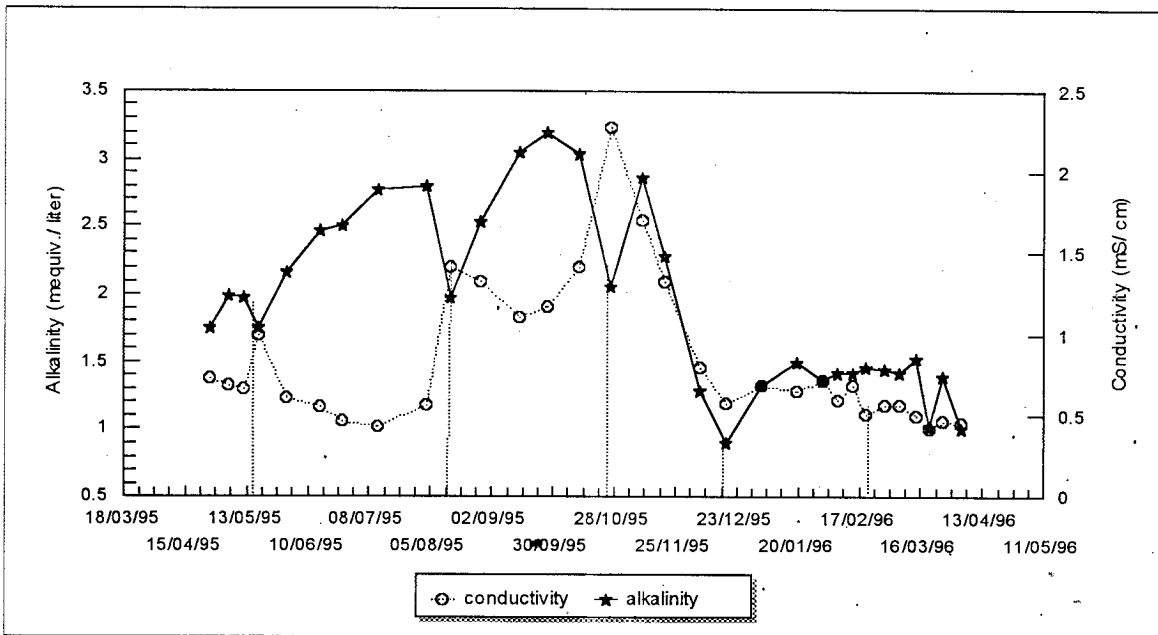


Fig. 18 - Effect of changes in conductivities on changes in alkalinity in the Mwambashi river.

The Luansobe stream in Mufulira is another example of how big these un-monitored sources can be. Mufulira Division normally uses the TD 10 tailings dam as a water storage reservoir and rarely discharges mine effluent in this dam. However there is a provision for sending tailing to this dam should the need arise. During the duration of the sampling no tailings where being discharged into the dam. Seepage from the dam, which is considered essential for dam wall stability, was however being allowed to flow into the Mufulira stream. *No discharge from the dam was flowing into the Luansobe stream.* The water quality in the Luansobe stream was however being monitored as part of the routine monitoring program of the Division. The quantity of total copper flowing in the Luansobe stream is shown in fig. 19 in comparison with the quantity of total copper in the combined regular effluent streams at the division . (NB. At times it was not possible to measure the water discharge rate in the Luansobe stream. It was thus not possible to calculate the amount

of copper flowing in the stream during these months. That is why some months do not show the amount of copper in the Luansobe stream).

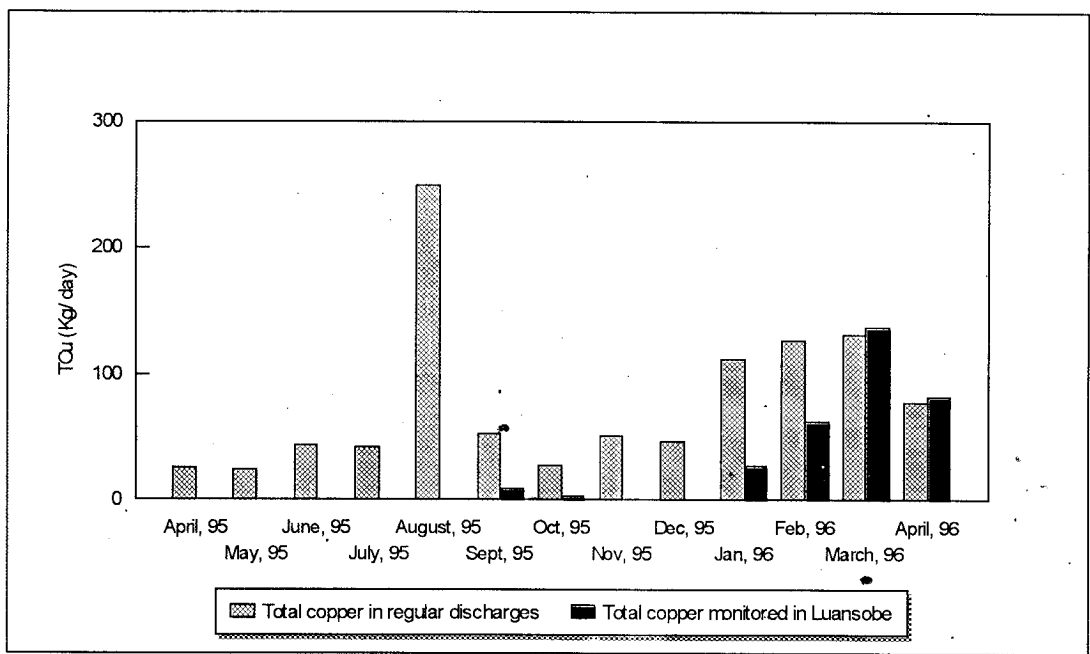


Fig. 19 - Comparison of flows of total copper coming from regular mine effluent to that which comes from indeterminate sources in the Mufulira mine area.

It can be seen that in March and April 1996 the Luansobe stream carried even more copper than the combined regular Mufulira discharge. It is not known where all the copper in the Luansobe was coming from. However it should be appreciated that the Copperbelt is a mineralised area and the water in the river system will always contain copper. This phenomenon could however have been accelerated by recent events such as the generation of acid rain [Nkandu, 1996].

Other reasons for sinks and sources could be the chemical transitions referred to in section 3.1.1 and 3.1.2. This can be seen in fig 20. When the parameter referred to as the reducing potential is negative, it means the conditions are oxidising relative to water. Thus water can be oxidised to

oxygen. When it is positive, the conditions are reducing enough for atmospheric oxygen to be reduced to water by the hydrogen ion [Nkandu et al (1), 1996].

It can be seen that the manganese speciation closely follows the oxidation conditions in the water. When conditions become oxidising, this would have the effect of precipitating the manganese and so the dissolved to suspended manganese ratio drops. The precipitated manganese may subsequently be deposited onto the sediment together with any adsorbed elements. If conditions became reducing this would have the effect of dissolving the manganese together with any adsorbed elements. Thus the sediment can behave as a sink or source.



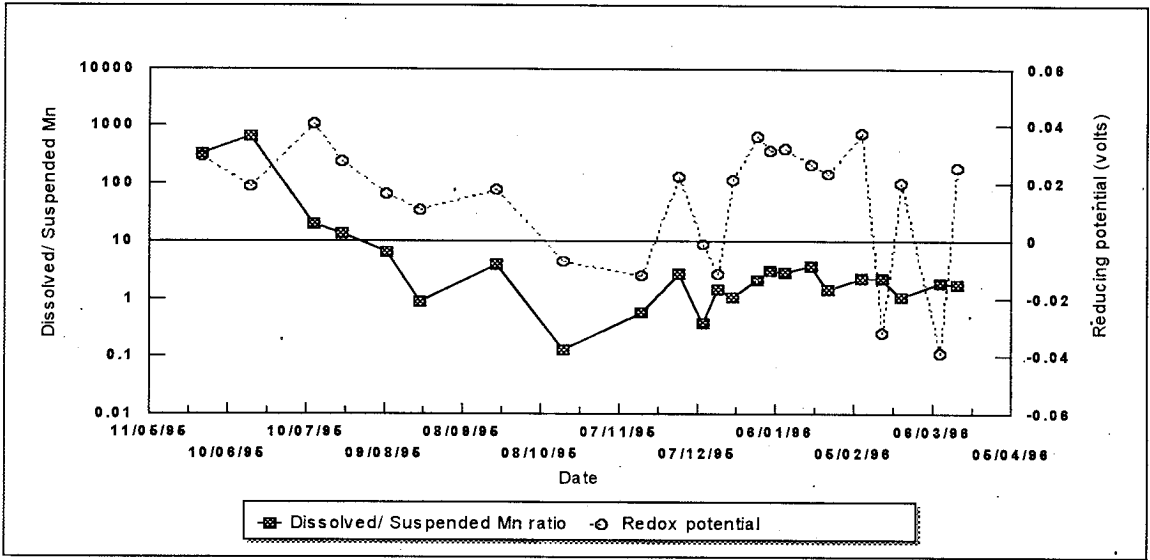


Fig. 20 - Effect of changes in reducing potential on manganese speciation as monitored at Fishers farm

Fig. 21 and 22 give an example of this co-precipitation between manganese and other elements.

It can be seen that changes in manganese speciation move in tandem with changes in copper and cobalt speciation.

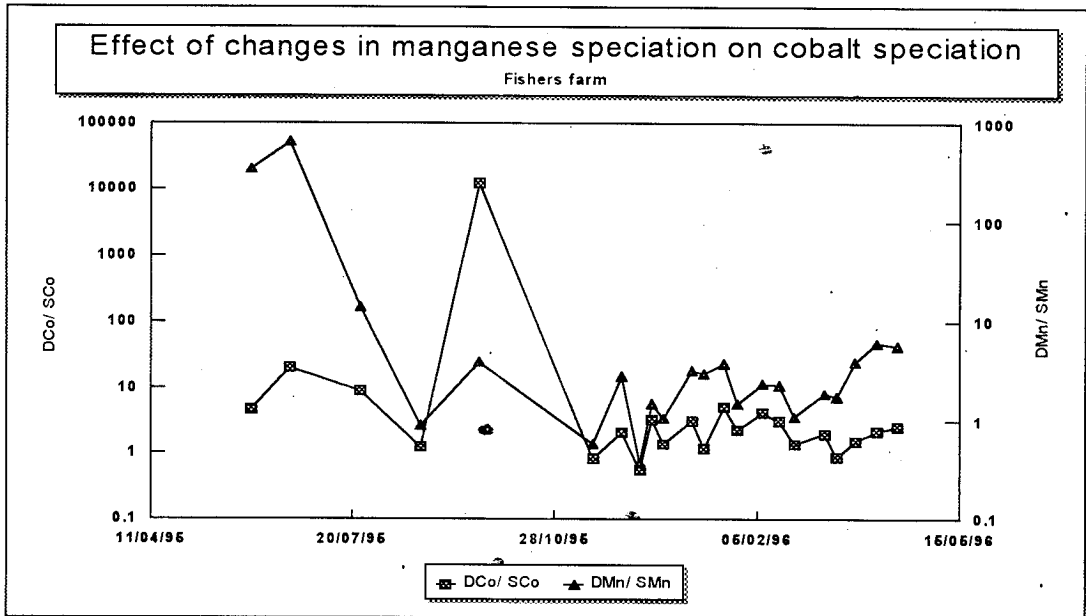


Fig. 21 - Correlation between manganese and cobalt speciation

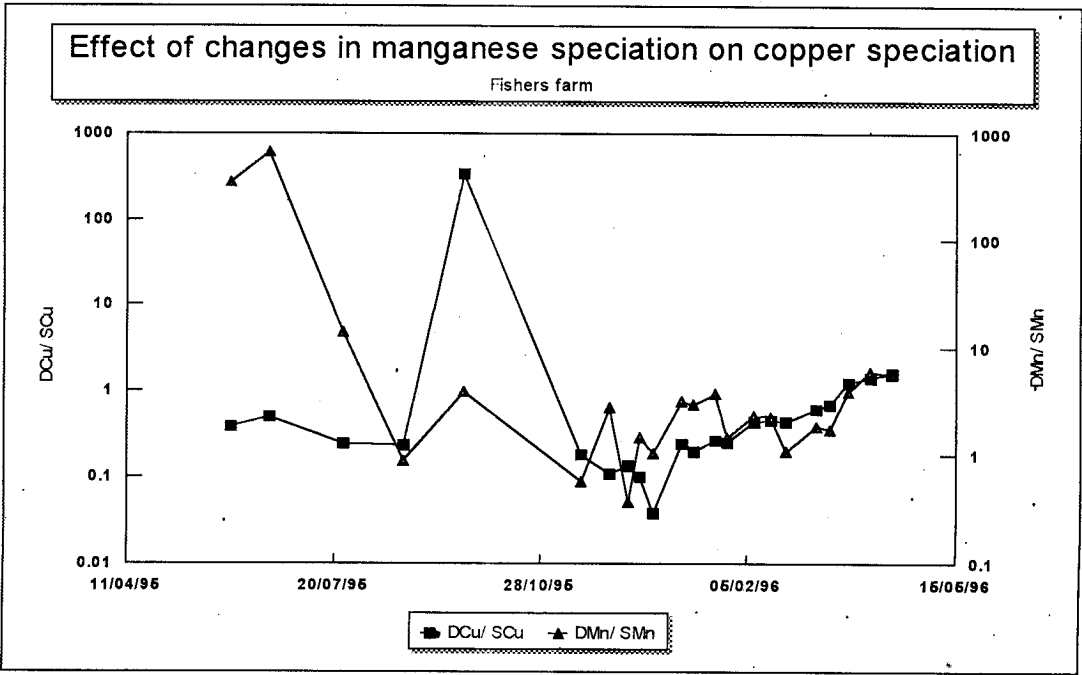


Fig. 22 - Correlation between manganese and copper speciation

The sediment can also become a source or a sink to the water column simply because physical turbulence in the water is either present or absent. This in turn depends on the discharge rate

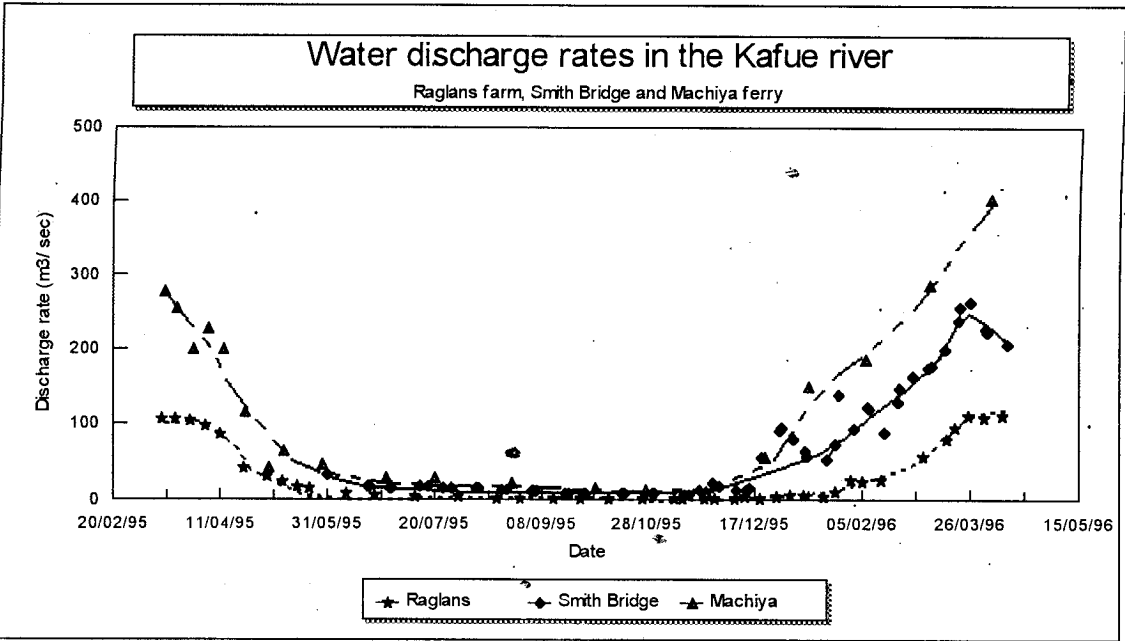


Fig. 23 - Seasonal variations in the discharge rate at three gauging station on the Kafue river

which also depend on the seasons. Fig. 23 gives the discharge rates at the three gauging stations within the sampling area in the Kafue river during the time of the sampling. High suspended solids observed during the rainy season may not only be a result of solids derived from soil erosion which get washed into the river by the rain water but may be due to a re-suspension of previously settled sediment.

### ***5.3.0 Mass balances of individual species***

In this section, unless otherwise stated, the terms flows and flow rates refer to mass flows and mass flow rates respectively.

#### ***5.3.1 Total suspended solids***

As was mentioned in sections 3.1.4 and 4.2.1, the possibility of error when sampling for total suspended solids can be substantial if the river water is not well mixed. Turbidity can, to a certain extent, be used as an indicator of the suspended solids loading at different points in the river. In the case of the non-detrital solids, which comprise most of the suspended solids carried by the river in urban areas, there is a linear relationship between the turbidity and the total suspended solids. The suspended solids accumulated by the river in rural areas such as at Machiya and Raglans, comprise mainly of rotting organic matter. This does not show such a clear-cut relationship. This can be seen from fig 24a and 24b. Despite this, drastic changes in turbidity readings across the river cross section, as table 2 shows for Machiya ferry, can be taken to infer that the suspended solids are not being transported homogeneously. That is why, as was explained in section 4.2.1 (a), the samples for the suspended solids determinations at Machiya ferry were

made up of a composite of samples taken from different positions on the river.

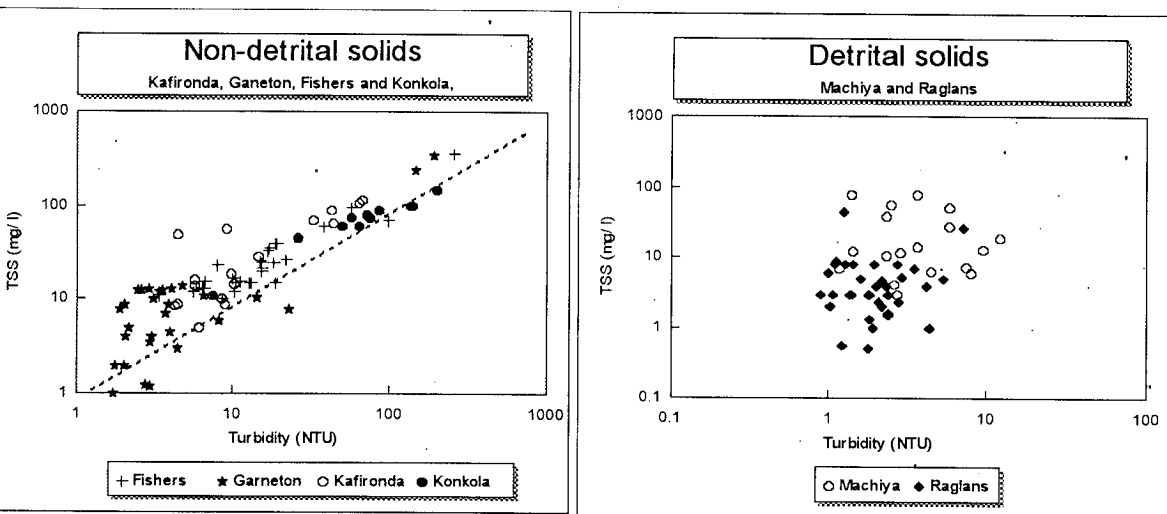


fig. 24a - Linear relationship between turbidity and total suspended solids for non-detrital solids. Correlation  $R^2 = 0.85$ )

fig. 24b - Low co-relationship between turbidity and total suspended solids for detrital solids. Correlation  $R^2 = 0.02$ )

TABLE 2: TURBIDITY VALUES (NTU) AT DIFFERENT RIVER POSITIONS AT THE MACHIYA AND RAGLANS SAMPLING SITES.

Site	Date	Position		
		<i>Eastern bank</i>	<i>Centre</i>	<i>Western bank</i>
<i>Machiya</i>	06/04/95	28	12	12
	11/05/95	27	79	16
<i>Raglans</i>		<i>Northern bank</i>	<i>Centre</i>	<i>Southern bank</i>
	04/04/95	8	8	8
	10/05/95	2	3	2

the much bigger width of the river at Machiya ferry is probably responsible for the definite

ferences in suspended solids loading at the different points of the river cross section. However further reason could be that since the river is meandering in this area, erosion could have been taking place on the outside part of the meandering curve whilst sedimentation could have been taking place on the inside part of the meandering curves. All this means that there was a greater possibility of error in the calculations involving suspended solids at Machiya than at the other sampling locations and the results should be treated with this in mind.

Fig. 25 indicates that there is a seasonal factor in the suspended solids load at both Raglans farm and Kafironda. This is deduced from the similarity of the load distributions throughout the year. However it can also be seen that the load at Kafironda is about 100 times greater than at Raglans farm. The amount of solids carried by the river at Raglans farm ranges from just over 100 Kg/ day to about 10,000 Kg/ day. At Kafironda the range is from about 10,000 Kg/ day to about 500,000 Kg/ day. The seasonal variation in suspended solids discharged into the block from mine operations is less marked and averages about 100,000 Kg/ day.

Since the flow at Kafironda in the dry season months is less than the mine effluent alone, it must be assumed that there is considerable sedimentation occurring within the river basin upstream of Kafironda. During the rain season, the flow at Kafironda is higher than the rate of input from mine effluent and the flow monitored at Raglans farm put together. The addition of the flow at Raglans farm to the mine effluent flow does not significantly affect the position of the latter on the graph because the log nature of the Y axis exaggerates the magnitude of the lower end at the expense of the higher end. In quantitative terms the flow at Raglans is insignificant compared to the mine effluent. The flow at Kafironda is higher than the mine effluent discharge rate in the rainy season. This could be due to a re-suspension of mine effluent deposited during the dry season. This

though, does not exclude the possibility of chemical interactions during the rain season leading to the production of extra solids through a process of precipitation [Nkandu et al (3), 1996].

Fig. 26 for block SS4 shows that during the dry season months, the flow at Garneton closely parallels the mine effluent discharge. At the beginning of the rainy season there is a big leap in the suspended solids carried by the Mwambashi river which subsequently subsides. This increase in suspended solids could be both of chemical or physical origins as is the case in the Kafue river at this time of the year. However the flow of solids in the river is generally higher than the reported mine effluent.

Fig. 27 for block SS2 shows that although the peak which occurred at the beginning of the rainy season in the suspended solids flow for Garneton seems to have been swamped out by the much higher Kafironda flows in the combined Garneton, Kafironda and mine effluent flow, the peak seems to reappear in the Fishers farm flow. This peak is again discernable at Machiya in block SS3. It is possible that the cause for this effect could be traced from events occurring in the Mwambashi river which are then transferred to the Kafue river downstream of the Kafironda sampling station.

The difference between the combined Kafironda, Garneton and mine effluent flows on one hand and the Fishers farm flow are small enough to make one conclude that sedimentation or re-suspension is not a significant occurrence in block SS2. Since the line for the inflows and the outflows cross each other throughout the year, it means that sometimes more solids are flowing into than out of the block with the resulting sedimentation and at others re-suspension is removing the settled solids from the block. The system, as a result, may be in general balance with no net

accumulation of solids over the course of the year.

Significant sedimentation seems to be occurring in block SS3 throughout the year in general and particularly during the rainy season as can be deduced from fig. 28. The river seems to be slightly in balance during the dry season months of July '95 to September '95.

The results are summarised in table 3 and fig 25 to fig. 28.

**Table 3. Average monthly mass flow rates (in Kg/ day) of total suspended solids monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

Month	Rag TSS	Kaf TSS	Gar TSS	Fis TSS	Mac TSS
March, 95	10,686				53,333
April, 95	9,643		2,585		47,103
May, 95	1,995		883	19,571	7,147
June, 95	1,176	5,196	587	6,461	5,873
July, 95	1,348	6,893	1,020	18,655	8,677
August, 95	757	5,561	1,895	9,278	15,003
September, 95	363	5,284	330	3,547	7,429
October, 95	229	4,385	829	7,592	6,701
November, 95	447	8,357	2,547	57,567	7,433
December, 95	494	100,615	59,639	463,328	45,046
January, 96	2,477	186,633	2,354	148,745	155,573
February, 96	6,801	435,200	3,841	188,353	72,132
March, 96	11,437	559,127	3,972	313,531	64,065
April, 96	9,908	270,229	3,263	144,300	49,085



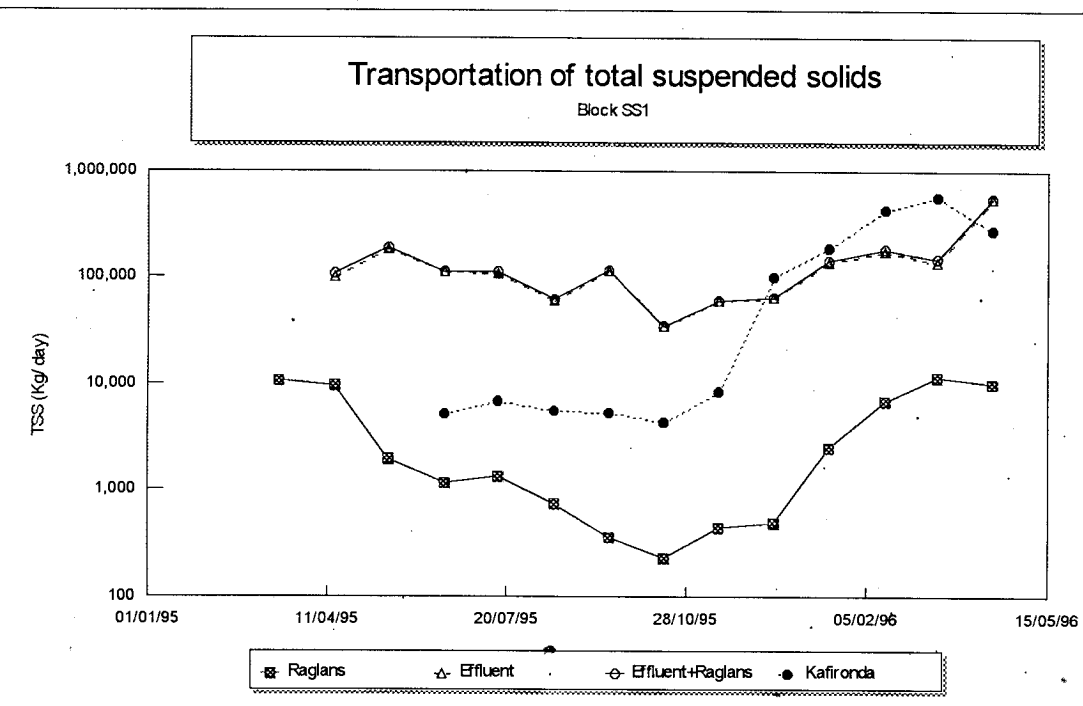
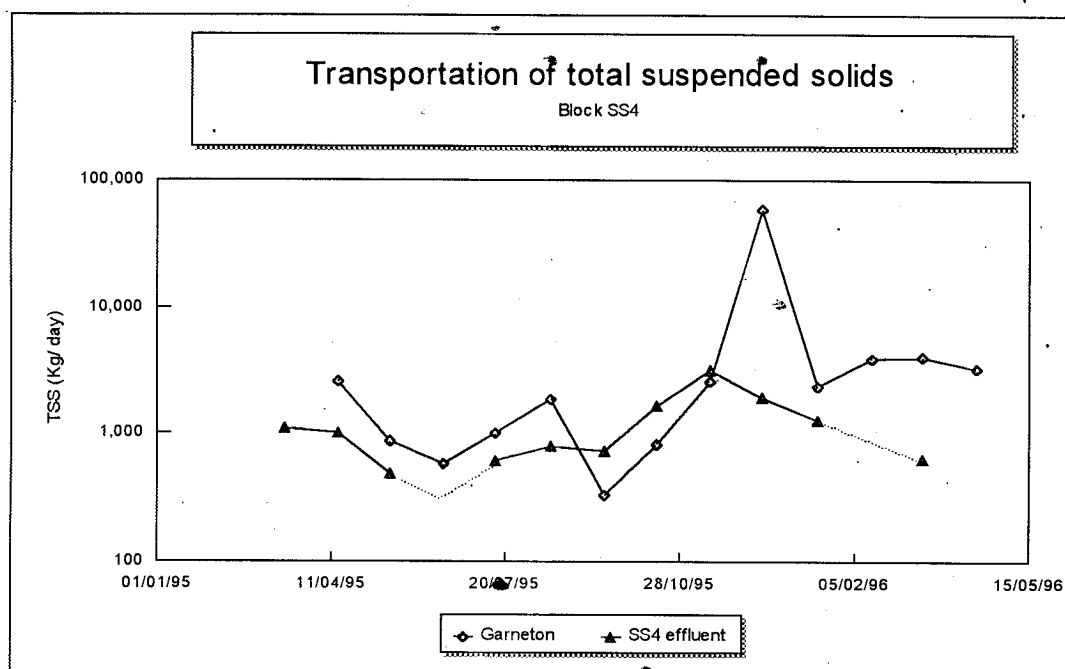


Fig. 25 - Seasonal variation in suspended solids flows at the Raglans and Kafironda sampling points and the magnitude of mine effluent discharges in the sector



Dotted lines are extrapolations because data for July '95 and March '96 for Muntimpa dam was not reported

Fig. 26- Seasonal variation in suspended solids flows in the Mwambashi river and the magnitude of mine effluent discharges in the sector

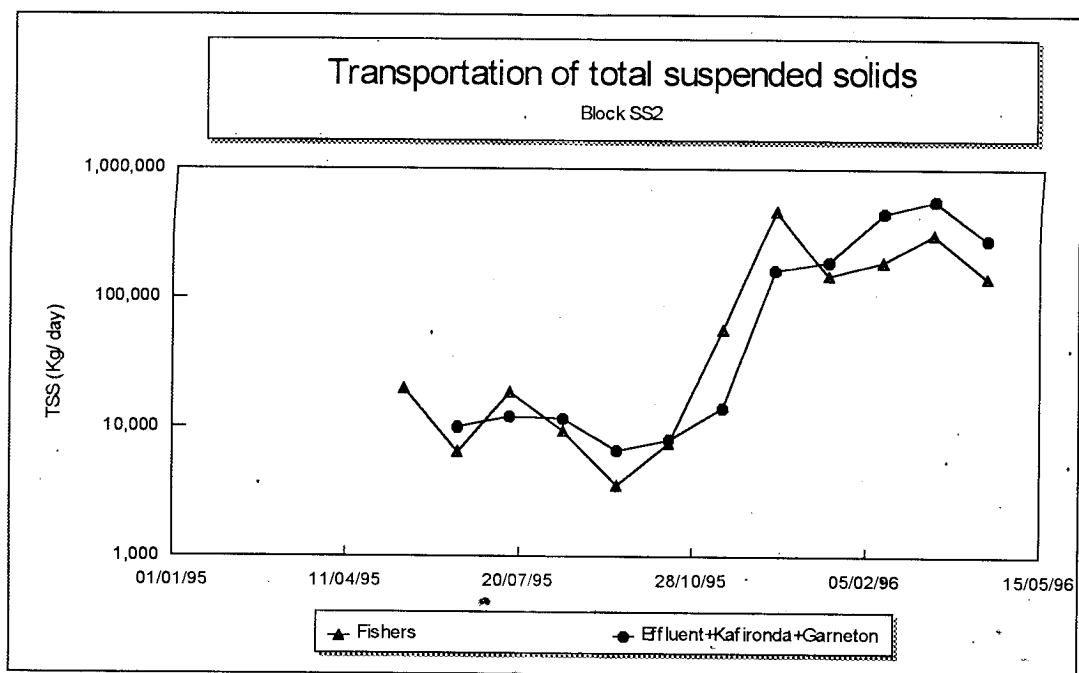


Fig. 27 - Seasonal variation in suspended solids flows at Fishers farm in relation to inputs from the Mwambashi river, Kafue upstream and the mine effluent discharges in the sector

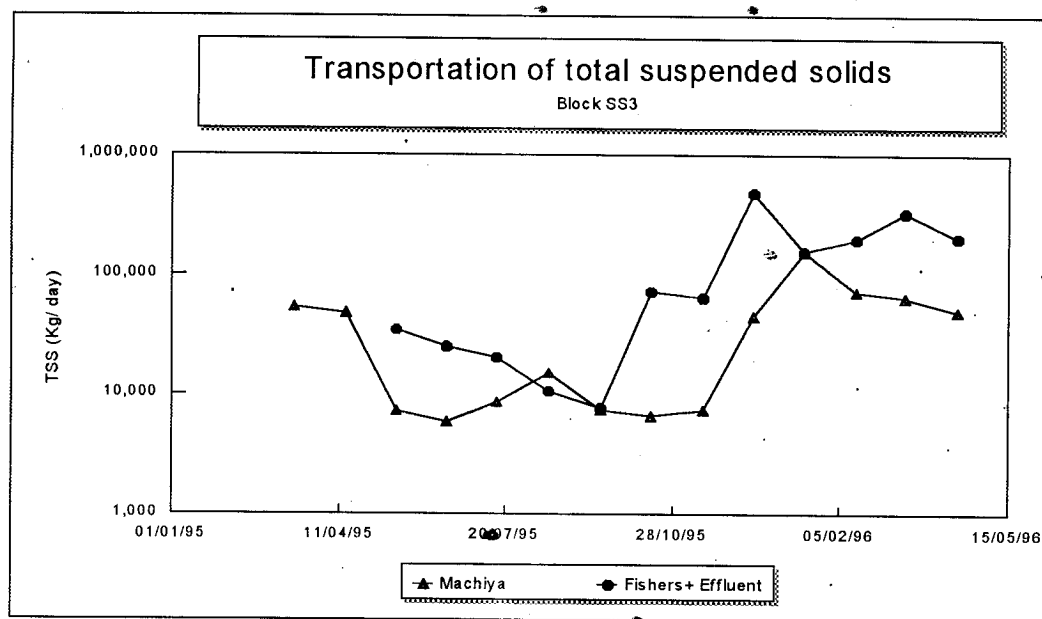


Fig. 28- Seasonal variation in suspended solids flows at the Machiya sampling point in relation to the combined input from mine effluent discharged into the sector and the flow from Kafue upstream

### 5.3.2 *Total dissolved solids*

During the discussion on sources and sinks in section 5.2.1, it was noticed that during the dry season, the discharge from mine operations entering the Mwambashi was over 100% of the flows determined at Garneton. As a result, it was concluded that some precipitation was occurring upstream. During the rain season, the flow at Garneton was more than the mine discharge. It was postulated that this could be due to a re-mobilisation of the solids precipitated during the dry season. However some of the increased flows could also be due to the un-monitored flows such as was shown to be occurring as in the Luansobe stream. The flows for total dissolved solids in blocks SS1, SS2, and SS3 are covered below and in table 4 and fig. 29, 30 and 31.

In the dry season, the total dissolved solids flow at Kafironda is little different from that for the combined flows at Raglans and mine effluent. With the onset of rains in early November 1995, the disparity between these seems to increase probably because un-monitored sources for the dissolved solids, come into play. That dissolved solids from sources other than mine effluent seem to increase with the onset of rains can also be seen from the total dissolved solids distribution at Raglans alone. The flow at this station in some months is seen to be greater than from the mine effluent. If a similar increase is repeated in all or some of the tributaries of the Kafue in this block, then the disparity between the combined mine effluent and Raglans flow on one hand and the Kafironda flow on the other can be explained.

The flows from the combined mine effluent, Kafironda and Garneton inputs seem to be of the same order of magnitude as the flow at Fishers farm although the Fishers flow is slightly higher. This slight rise could be due to the contribution from other inputs which were not being

monitored. In terms of capability to affect the flows of total dissolved solids, such a rise should be taken as being reflective of the behaviour of major rather than minor elements in the dissolved solids.

*Between August and December, the total dissolved solids flow at Machiya is either lower than or equal to the combined Fishers and mine effluent flow. This indicates that some dissolved solids are being transferred to the suspended state. This might be a repetition of the situation which was observed in the Mwambashi river during the dry season. It is also noteworthy that turbidity data was used to infer that during the dry season, chemical reactions were occurring at Machiya which were resulting in the transfer of dissolved solids to suspended solids [Nkandu et al (4), 1996].*

**Table 4. Average monthly mass flow rates (in Kg/ day) of total dissolved solids monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Total dissolved solids (Kg/ day)				
Month	Rag TDS	Kaf TDS	5Gar TDS	Fish TDS	Mac TDS
March, 95	722,477				3,236,063
April, 95	558,214		217,751		2,512,661
May, 95	184,213		141,588	822,062	1,003,811
June, 95	53,688	294,973	58,875	457,788	709,053
July, 95	33,837	331,487	44,120	510,832	666,533
August, 95	22,795	301,955	110,505	620,290	641,875
September, 95	16,581	235,869	88,736	497,163	509,794
October, 95	18,361	205,276	206,649	691,054	532,602
November, 95	21,562	403,544	155,590	972,898	528,900
December, 95	44,063	800,577	177,842	1,688,375	2,138,384
January, 96	100,629	824,205	611,776	2,153,108	3,001,795
February, 96	288,039	1,452,097	713,613	2,357,143	2,945,902
March, 96	510,586	1,752,857	534,621	2,971,329	3,201,736
April, 96	678,390	2,251,163	452,418	2,773,873	4,455,342

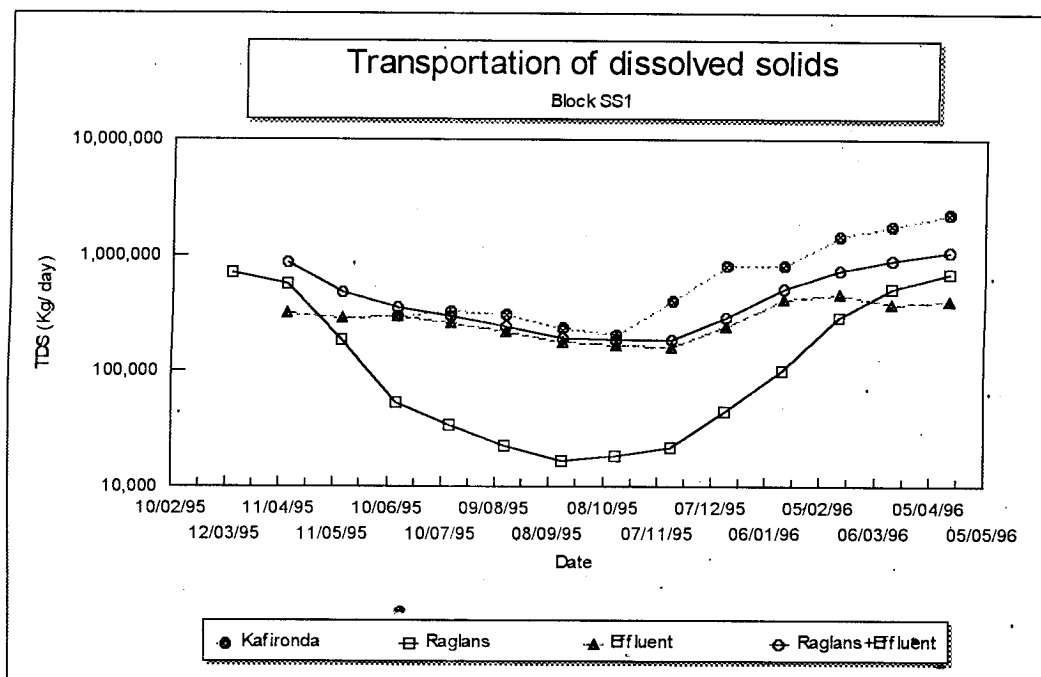


Fig. 29 - Seasonal variation in total dissolved solids flows at the Raglans and Kafironda sampling points and the magnitude of mine effluent discharges in the sector

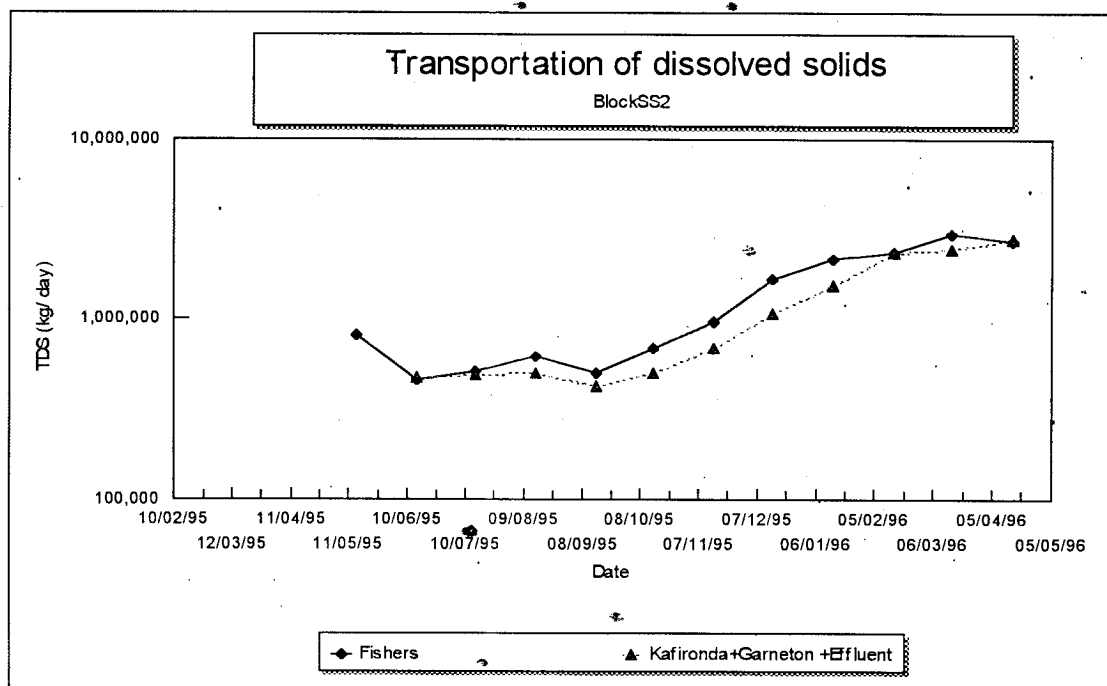


Fig. 30- Seasonal variation in total dissolved solids flows at Fishers farm sampling point relative to the inflow from the Mwambashi, mine effluent discharges in the sector and the Kafue upstream

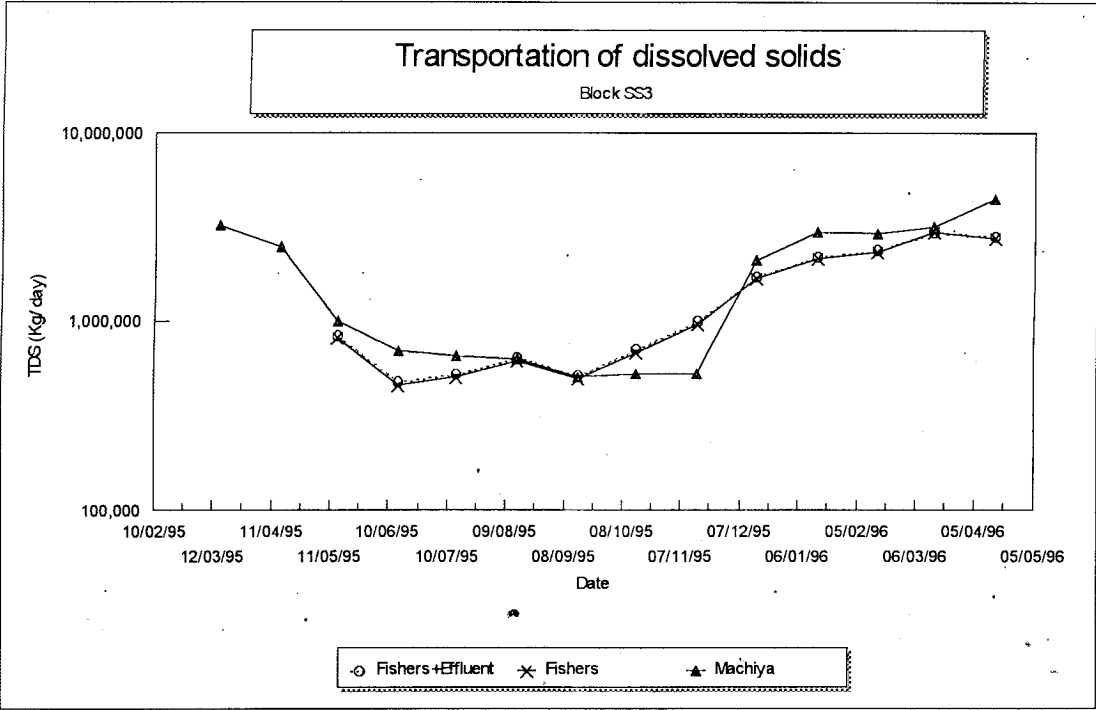


Fig. 31- Seasonal variation in total dissolved solids flows at Machiya relative to combined mine effluent discharges in the sector and the flow from Kafue upstream

5.3.3 Total dissolved sulphur

Nkana Division was reporting total dissolved solids concentrations but was not reporting sulphate concentrations in its effluent. Use was therefore made of the correlation obtained in fig. 32. This shows that for all the mine effluent in the other blocks where sulphate is reported, the sulphate flows are about half of the total dissolved flows. It was assumed that the same situation applies to Nkana division as well.

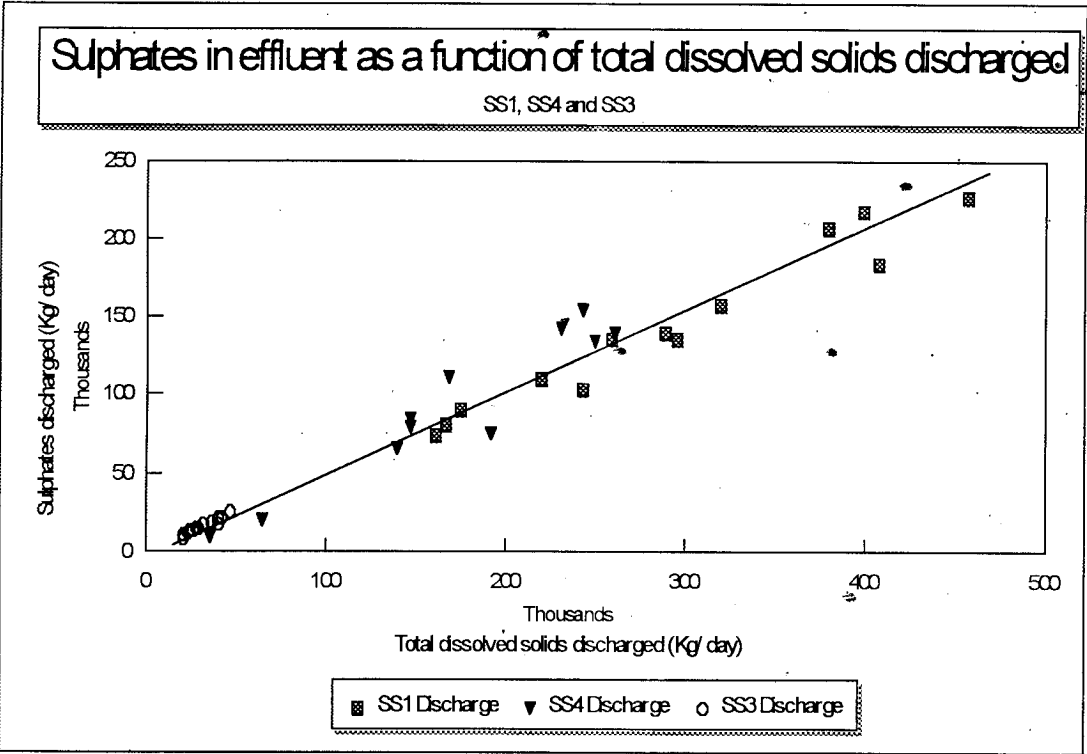


Fig. 32 - Relationship between the mass flows of dissolved sulphates and total dissolved solids discharged in mine effluent.

In many respects, the flows for total dissolved sulphur parallel those for total dissolved solids. This is shown in table 5 and figs. 33- 36. This is not surprising since sulphur is one of the major constituents of the dissolved solids.



In section 5.3.2, it was said the cause of the reduction in total dissolved solids flow between the months of August and December '95 at Machiya could be similar to that observed in the Mwambashi river when the flow total dissolved solids in mine effluent was less than the flow monitored at Garneton. In discussing sources and sinks in section 5.2.1, it was said the case of the Mwambashi could be partly due to the precipitation of calcium carbonate from the calcium sulphate in mine effluent water [Nkandu et al (5), 1997] as well as the possibility of biological. Fig. 37 seems to indicate a similar situation at Fishers farm to that shown in fig. 18 for the Mwambashi, although it is at a more attenuated level in the former. Between the months of July to December 1995 the changes in the conductivity and alkalinity of the water seems to be inversely related just as was observed in the case of the Mwambashi. Although there is only one instance when a sudden increase in conductivity is matched by a sudden decrease in alkalinity and vice versa, the variations seem to show that a maximum in one is paralleled by a minimum in the other. In the case of the Mwambashi such inverse changes were partly attributed to the production of sulphuric acid during the precipitation of calcium carbonate from calcium sulphate. The same is probably true in this case as the phenomenon, just like in the case of the Mwambashi, is being observed at the time of maximum conductivity. The case of the development of a redox couple involving sulphur by aquatic organisms could also be significant here as the presence of sulphide has been invoked before to explain possible sulphate reduction reactions which lead to precipitation of metal sulphides as well as elemental sulphur [Nkandu et al (3), 1996].

**Table 5. Average monthly mass flow rates (in Kg/ day) of dissolved sulphur monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Dissolved sulphur (Kg/ day)				
Month	Rag DS	Kaf DS	5Gar S	Fis DS	Mac DS
March, 95	3,581				227,186
April, 95	1,919		39,042		193,301
May, 95	831		25,419	94,384	97,147
June, 95	379	29,521	7,019	54,920	79,836
July, 95	289	34,106	7,414	65,024	69,996
August, 95	181	33,591	23,360	92,387	56,341
September, 95	130	26,755	17,459	75,505	48,877
October, 95	170	23,745	50,387	132,476	61,011
November, 95	187	56,318	35,598	184,878	63,761
December, 95	1,254	102,222	32,865	275,955	409,548
January, 96	3,279	91,495	111,705	306,527	914,443
February, 96	5,785	135,858	138,283	291,214	403,760
March, 96	3,959	139,474	84,290	279,284	416,914
April, 96	4,255	149,101	120,066	230,558	297,657

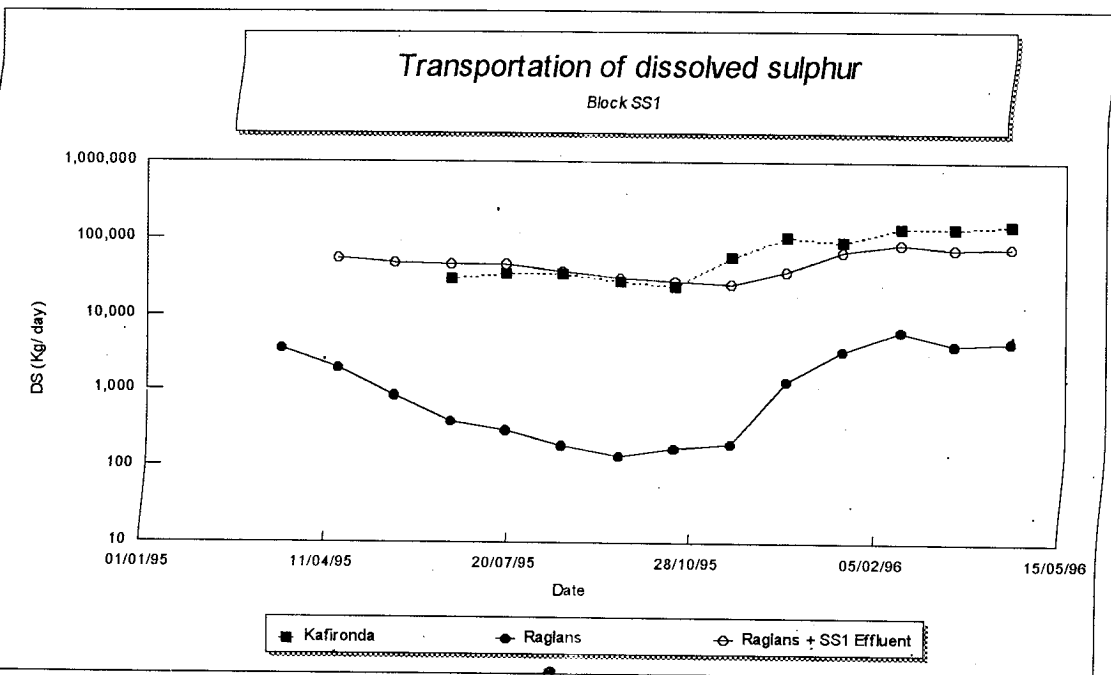


Fig. 33 - Seasonal variation in dissolved sulphur at Raglans and Kafironda and the magnitude of mine effluent in the sector.

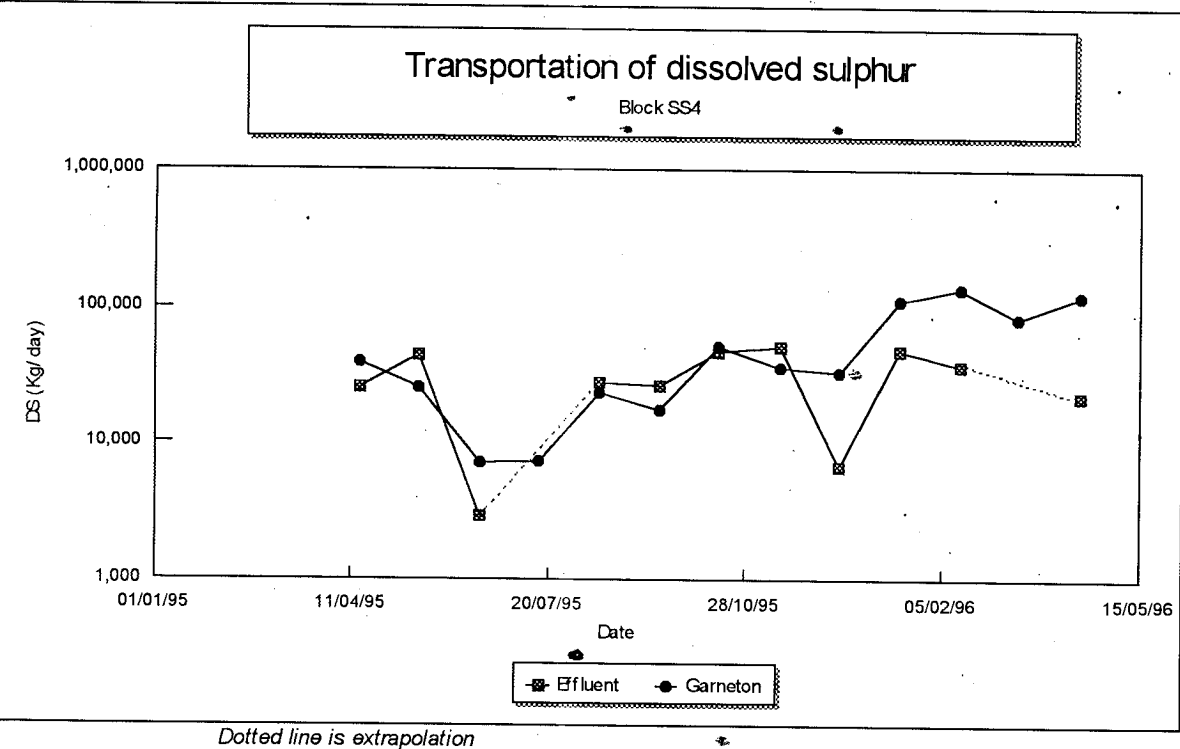
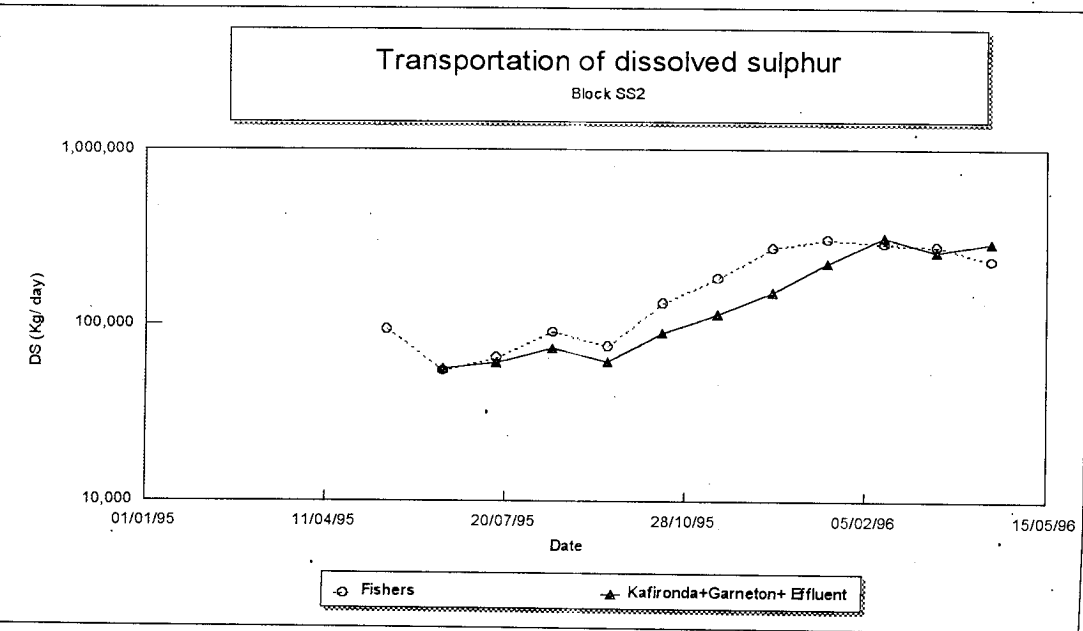
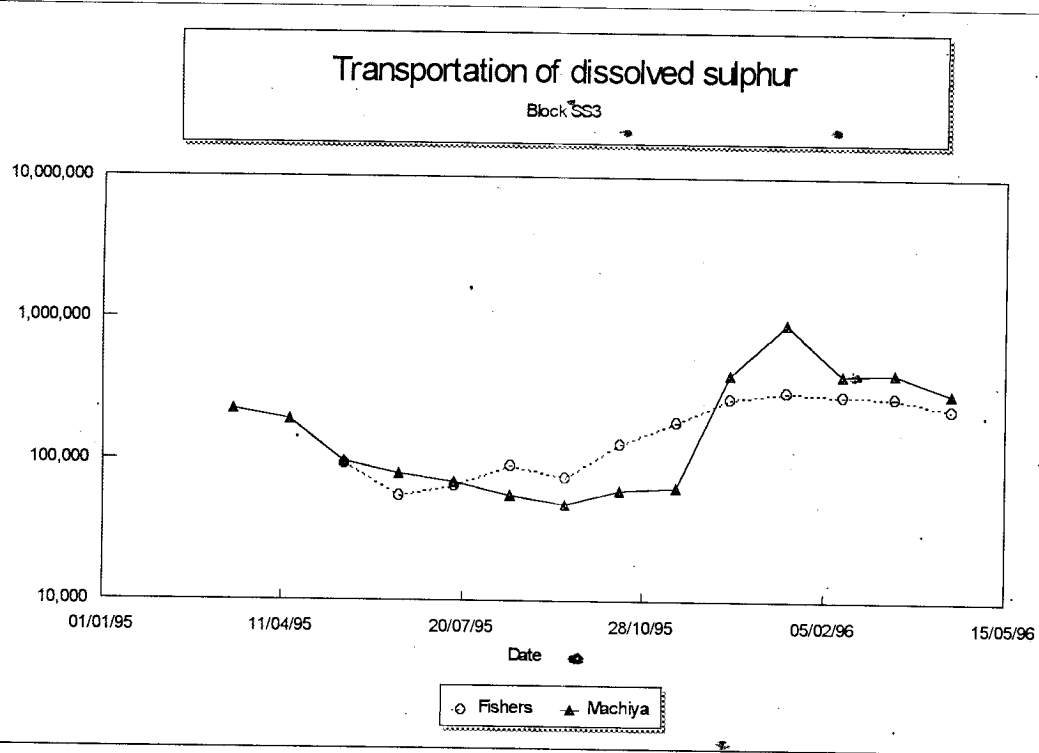


Fig. 34 - Seasonal variation in dissolved sulphur in the Mwambashi and the magnitude of mine effluent into the river.



g. 35 - Seasonal variation in dissolved sulphur at Fishers farm relative to the inflow from the wambashi, the mine effluent discharges in the sector and the Kafue upstream.



. 36 - Seasonal variation in dissolved sulphur at Machiya relative to flow from the Kafue stream.

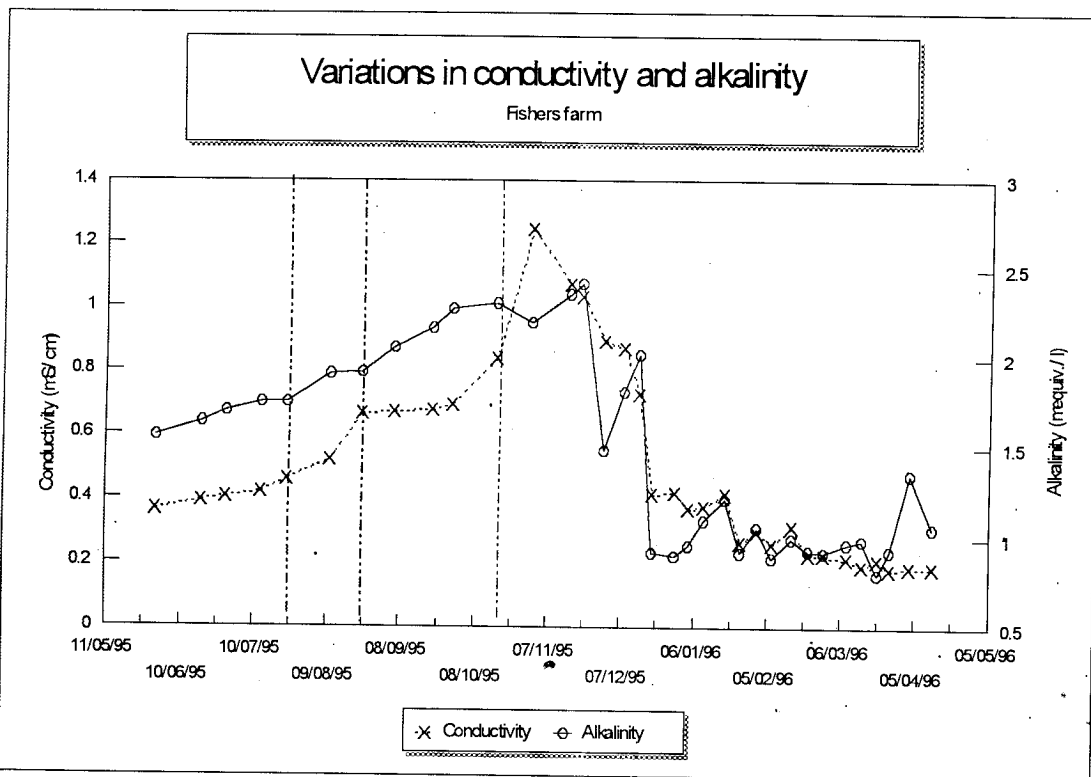


Fig. 37 - Inverse correlation between conductivity and alkalinity during periods of peak conductivity

#### 5.3.4 Barium

The flows for this metal have been investigated because of the possibility that the element might regulate sulphate flows in the Kafue river. Table 6 and fig. 38 seems to cast doubt on this supposition. The quantity of dissolved barium detected in the Kafue and Mwambashi rivers seems to be too small to have an appreciable impact on total sulphur flows detected. Most of the barium seems to originate from block SS1 as can be seen by the difference between the Raglans and Kafironda flows. However the dissolved barium flows increase continuously from Raglans to Machiya.

It would appear from fig. 39 that most of the Barium in the Kafue results from leaching operations in a sulphate media. Thus the barium concentration does not seem to be controlled by the sulphate concentration through the solubility constant for barium sulphate. If this was the case, the relationship between barium concentration and sulphate concentration would be hyperbolic. An increase in barium concentration would result in a reduction in the sulphate concentration and vice versa.

i.e. since  $[Ba][SO_4^{2-}] = K = \text{Const.}$

$$[Ba] = K / [SO_4^{2-}] \dots\dots\dots (5)$$

The linear correlation, even in the Mwambashi river where sulphate concentrations are highest, would suggest that changes in barium concentration are due to dilutions of an initially high barium sulphate concentration with other less concentrated water rather than by changes in sulphate concentration. Whilst the barium sulphate concentration in the effluent could be reasonably constant, and perhaps even in accordance with the solubility constant, dilution of the mine effluent while changing the absolute concentrations would keep the ratios unchanged. That is why the relationship between the two concentrations is linear. The difference in gradient between the Mwambashi and Kafue samples could be due to either a different barium/ sulphate ratio in the initial mine effluent or to a different ratio in the diluting water.

**Table 6. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended barium monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Dissolved Ba (Kg/ day)					Suspended Ba (Kg/ day)	
Month	Rag DBa	5Gar Ba	Kaf DBa	Fis DBa	Mac DBa	Rag SBa	Fis SBa
March, 95	136.8				905.8	3.2	
April, 95	119.9	15.1			748.2	3.5	
May, 95	34.5	9.3		183.0	197.3	0.8	0.5
June, 95	5.7	5.1	66.0	91.0	155.6	0.6	0.1
July, 95	3.6	2.3	72.3	95.9	99.9	0.2	1.6
August, 95	3.5	6.8	62.6	102.1	90.3	0.1	2.0
September, 95	2.8	5.1	50.9	71.1	89.3	0.1	2.5
October, 95	2.9	9.1	40.7	79.4	95.1	0.1	0.0
November, 95	2.6	7.2	85.4	112.2	106.1	0.2	0.0
December, 95	5.3	12.5	189.0	257.4	541.4	0.2	0.0
January, 96	18.7	34.1	244.7	400.3	1,172.6	0.8	0.0
February, 96	44.9	36.5	493.7	522.2	823.3	2.7	0.0
March, 96	95.8	41.0	658.0	930.0	1,136.0	3.0	0.0
April, 96	61.4	16.3	782.0	796.2	1,249.8	2.2	0.0

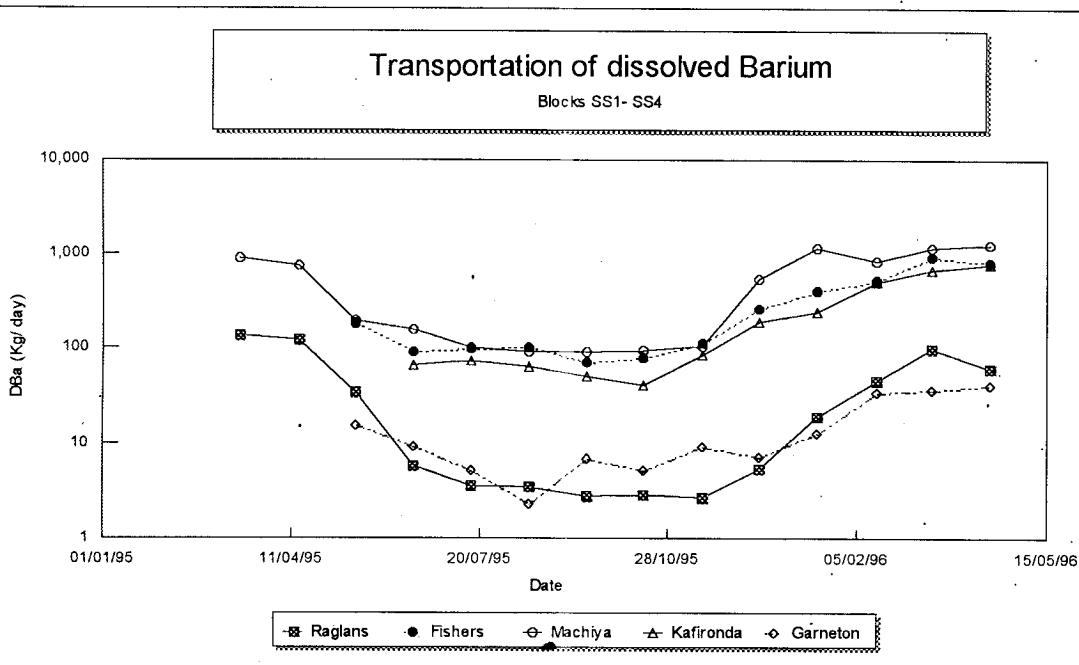


Fig. 38 - Seasonal variation in dissolved Barium at different sampling points in the Kafue and Mwambashi rivers.

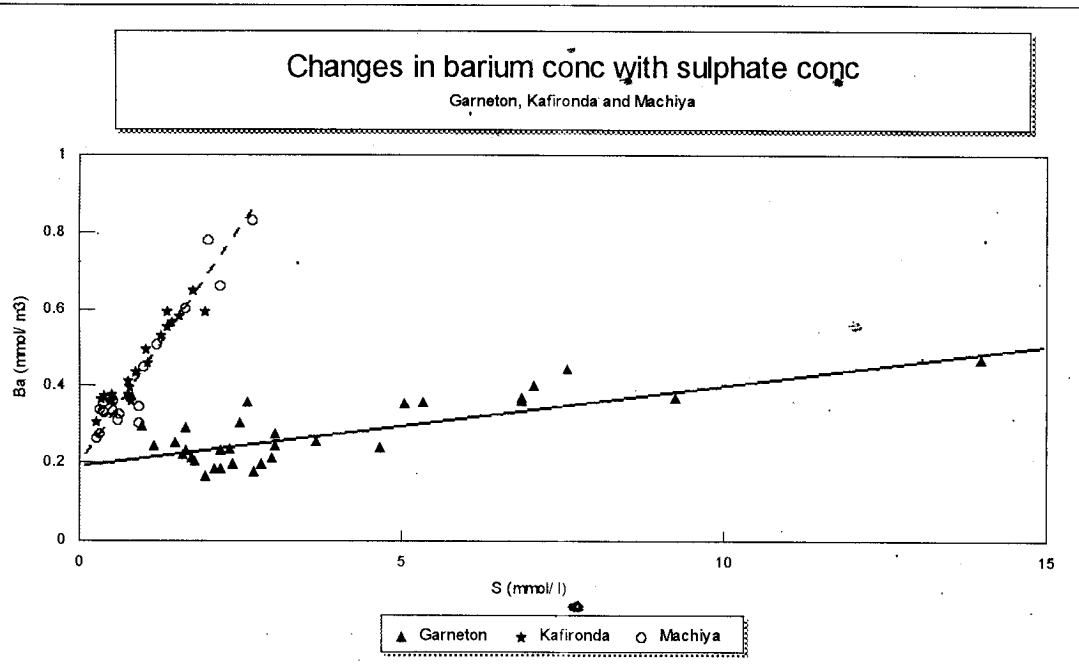


Fig. 39 - Linear correlation between dissolved sulphur and dissolved barium at different sampling points in the Kafue and Mwambashi rivers



5.3.5 Iron

Iron is a multi-valent metal with valencies of plus II and III. At a pH in the region of about 4-7 an intermediate valence oxide Fe<sub>3</sub>O<sub>4</sub> can form at redox potentials less than the water/ oxygen couple [Weast,, 1974; Latimer, 1939 ]. A comparison of the redox couples of iron, and water are given below:

<u>Couple</u>	<u>Nernst equation</u>	<u>E at pH = 7</u>
Fe <sub>3</sub> O <sub>4</sub> + 8H <sup>+</sup> + 2e <sup>-</sup> ⇌ 3Fe <sup>2+</sup> + 4H <sub>2</sub> O	E = 0.97 - 0.09 log [Fe <sup>2+</sup> ] -0.24pH	-0.17
4H <sup>+</sup> + O <sub>2</sub> + 4e <sup>-</sup> ⇌ 2H <sub>2</sub> O	E = 1.23 - 0.06 log Po <sub>2</sub> - 0.06pH	+0.81

The concentration of dissolved iron used in the calculation of E at pH 7 is 10<sup>-6</sup>mol/ l. This was the order of magnitude concentration determined in the samples collected at Kafironda. This means that the transition redox potential for iron exists at a much lower level than for the water/ oxygen couple if the water was at equilibrium with atmospheric oxygen. As such the iron concentration should be reduced even further if it is to come into equilibrium with atmospheric oxygen.

Mine effluent water at Muntimpa dam was shown to be at redox equilibrium [Nkandu et al (1), 1996]. This was attributed to the fact that mine water is heavily agitated in metallurgical plants and this ensures a rapid approach to equilibrium. It should therefore be expected that mine effluent water would contain most of the iron in suspended form.

The results obtained bears this out. Table 7 and fig. 40 shows that the dissolved iron flows at Raglans are almost identical to the Machiya flows for the sampling occasions when the data for

Machiya is available. In fact during the period up to August 1995, the flow at Raglans was **MORE** than the flow at Fishers. This period corresponds to that when the river was determined as being in an oxidising state [Nkandu et al (1), 1996]. The reduction in dissolved iron flows from Raglans to Fishers can therefore be attributed to the precipitation of the iron out of solution after being oxidised to the more insoluble higher valency states. The flows of dissolved iron at Fishers became higher than the flow at Raglans after August '95 when the redox potential in the river became reducing. This is expected because not only would the dissolved iron flowing into the mining area have remained in the dissolved state, the iron in the suspended state from mine effluent and elsewhere would also have been converted to the dissolved state once it got into the Kafue river.

Although it was determined that after December the river became oxidising again, the dissolved iron flows at Fishers remained higher than at Raglans. This might be simply because Copperbelt soils contain a lot of iron which could get leached out by rain water. There might have been insufficient time for this new input of dissolved iron to get precipitated out by the time the river reached Fishers farm. It can however be seen that the flows at Machiya were almost the same as at Raglans which means some of the dissolved iron monitored at Fishers must have precipitated out between Fishers farm and Machiya.

The flows in the Mwambashi can be seen to be very low compared to the Kafue which indicates that very little iron was coming from the Muntimpa dam and the other mine effluent discharging into this river.

The effect of activities in the mining areas on iron flows is more pronounced in the suspended flows. Fig.41 shows the flows at Raglans and Fishers which are the two stations where data is

available. The flows at Fishers were much higher than at Raglans farm. The exact contribution of mine effluent to this increased flow cannot be determined because iron concentrations were not reported for all the mine effluent discharge points. However the difference between the Raglans farm and Machiya ferry flow is an indicator of how much iron was picked up as the river flowed through the Copperbelt.

Table 7. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended iron monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]

Month	Dissolved flow iron (Kg/ day)				Suspended flow iron (Kg/ day)		
	Rag DFe	5Gar DFe	Fis DFe	Mac DFe	Rag SFe	Fis SFe	Mac SFe
March, 95	2,272	.		2,326	924		4,252
April, 95	1,695	15		1,995	939		
May, 95	350	4	237	208	170	1,293	
June, 95	90	5	31	0	52	442	
July, 95	44	5	16	0	26	463	
August, 95	21	1	27	29	10	422	
September, 95	7	2	44		9	229	
October, 95	7	4	15		9	212	142
November, 95	6	5	22		8	3,228	47
December, 95	25	45	297	53	22	25,083	
January, 96	269	71	700	143	172	9,935	
February, 96	616	96	1,357	1,493	382	12,753	
March, 96	1,473	89	3,293	2,045	709	22,000	-
April, 96	2,558	90	4,338	2,094	805	8,837	3,337

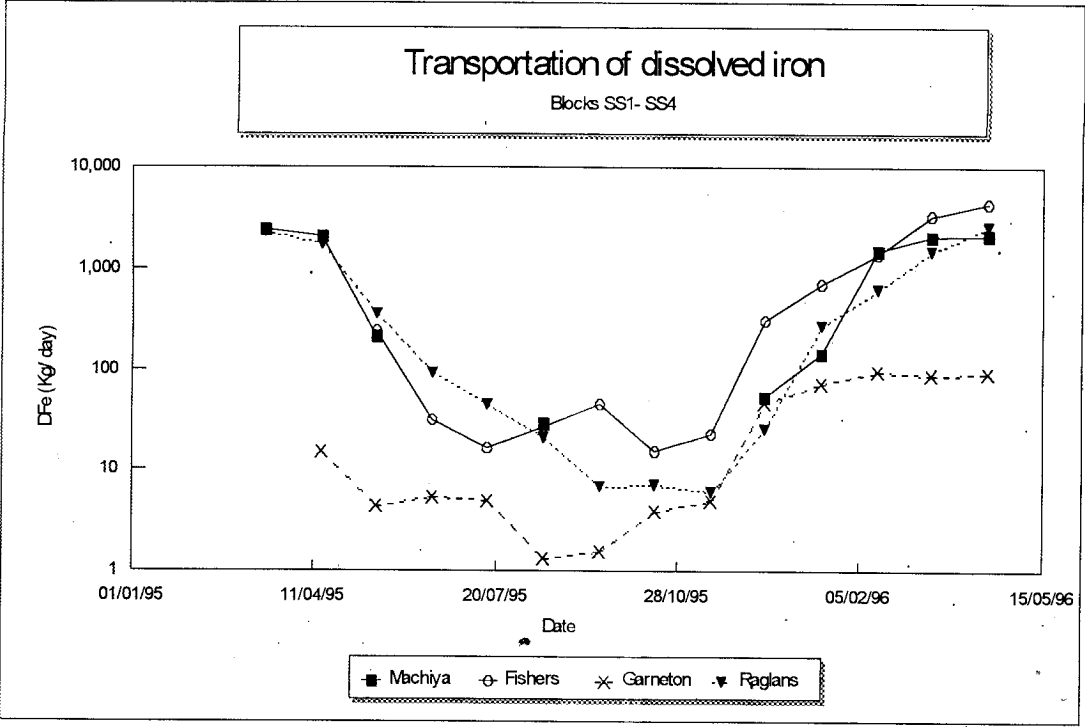


Fig 40 - Seasonal variation in dissolved iron flows at Raglans, Garneton, Fishers and Machiya

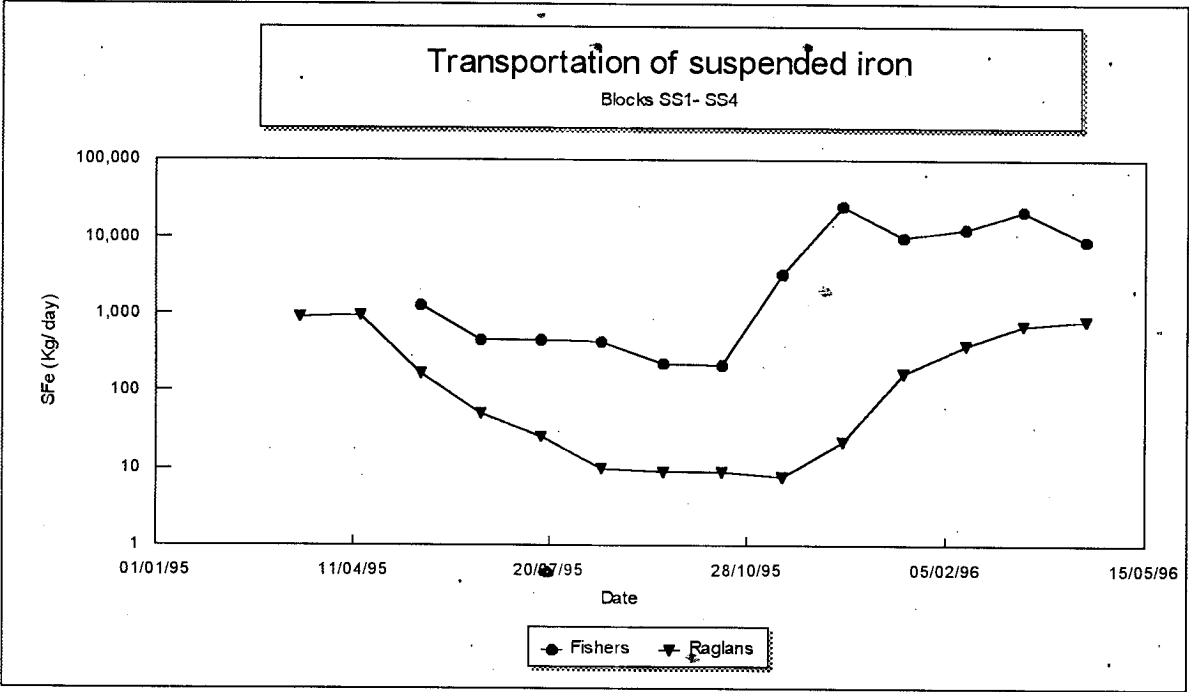


Fig. 41 - Seasonal variation in suspended iron flows at Raglans farm and Fishers farm

### 5.3.6 Manganese

Manganese can be oxidised into the suspended state just like iron. However, the redox potential at which manganese attains the higher more insoluble states is greater than that of iron. Therefore at any given level of the redox potential, a higher proportion of dissolved manganese can exist in equilibrium with atmospheric oxygen than would be the case with iron.

Analysis of the dissolved manganese/ oxidised manganese couples below show that, depending on pH, the manganese concentration could be reduced by oxidising the manganese to one of the three insoluble oxides,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  [Weast, 1974; Latimer, 1939 ].

<u>Couple</u>	<u>Nernst equation</u>	<u>E at</u>
<u>pH = 7</u>		
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 2\text{H}_2\text{O}$	$E = 1.21 - 0.03 \log [\text{Mn}^{2+}] - 0.12\text{pH}$	+055
$\text{Mn}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{Mn}^{2+} + 3\text{H}_2\text{O}$	$E = 1.42 - 0.06 \log [\text{Mn}^{2+}] - 0.18\text{pH}$	+052
$\text{Mn}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \rightleftharpoons 3\text{Mn}^{2+} + 4\text{H}_2\text{O}$	$E = 1.81 - 0.09 \log [\text{Mn}^{2+}] - 0.24\text{pH}$	+067
$\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	$E = 1.23 - 0.06 \log \text{Po}_2 - 0.06\text{pH}$	+081

The concentration of manganese used in the calculation of E at pH 7 is  $10^{-6}$  Mol/ litre. This was the order of magnitude concentration determined in the samples collected at Kafironda. Of the three transitions,  $\text{MnO}_2/\text{Mn}^{2+}$ ,  $\text{Mn}_2\text{O}_3/\text{Mn}^{2+}$  and  $\text{Mn}_3\text{O}_4/\text{Mn}^{2+}$ , the pH at which precipitation of  $\text{Mn}^{2+}$  to the particular oxide becomes energetically more favourable than the other is given by equating the respective redox couples.

$$0.39 - 0.03\log [\text{Mn}^{2+}] = 0.06\text{pH} \dots\dots\dots (6)$$

[for the Mn<sub>2</sub>O<sub>3</sub>/ Mn<sub>3</sub>O<sub>4</sub> transition]

$$0.21 - 0.03\log [\text{Mn}^{2+}] = 0.06\text{pH} \dots\dots\dots (7)$$

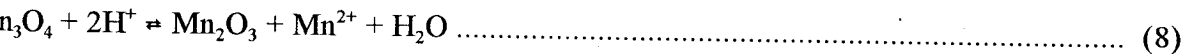
[for the MnO<sub>2</sub>/ Mn<sub>2</sub>O<sub>3</sub> transition]

This gives a pH of 9.5 for the Mn<sub>2</sub>O<sub>3</sub>/ Mn<sub>3</sub>O<sub>4</sub> transition and 6.5 for the MnO<sub>2</sub>/ Mn<sub>2</sub>O<sub>3</sub> transition.

Therefore, in the pH range of rivers encountered during sampling, the manganese would precipitate to the Mn<sub>2</sub>O<sub>3</sub> state.

However mine effluent water is normally discharged at a pH of up to 8.5. The manganese concentration in the plant liquor and effluent is also likely to be higher than 10<sup>-6</sup> Mol/ litre. At Nchanga division, the ZCCM figures for the effluent discharged via the pollution control dam give a dissolved manganese concentration ranging from "less than 0.1mg/ litre" to over 1mg/ litre. The concentration in the Muntimpa dam overflow reported by Hedstrom and Osterman [Hedstrom and Osterman, 1996] is 0.07mg/ litre.

A concentration of 5 mg/ litre of Mn<sup>2+</sup> gives a pH of 8.5 for the transition point for the precipitation of Mn<sup>2+</sup> to the Mn<sub>3</sub>O<sub>4</sub> state rather than the Mn<sub>2</sub>O<sub>3</sub> state. Therefore there is a chance that during neutralisation of plant effluent, the manganese precipitates to the Mn<sub>3</sub>O<sub>4</sub> state. These Mn<sub>3</sub>O<sub>4</sub> particles may later be transported out of the dam. When the pH is reduced so that the Mn<sub>2</sub>O<sub>3</sub> state becomes the thermodynamically stable state, it is possible that the transition could be achieved via reaction 8.



The dissolution of manganese could result in the release of any heavy metals adsorbed on the particles. This has been cited before as a possible mode for the transportation of heavy metal ions which are released to the environment [Hedstrom and Osterman, 1996].

The flows of manganese are summarised in table 8 and figs. 42-44. Fig. 42 shows that whilst there is an overall increase in dissolved manganese flows from Raglans to Machiya, there is an initial rapid increase to the flows monitored at Kafironda and Fishers. Precipitation then becomes dominant to result in the reduced flows monitored at Machiya.

Fig. 43 shows that in block SS2 the difference between the amount of dissolved manganese which is being transferred to the suspended phase and vice versa alternates throughout the year. At times, it appears, there is a nett outflow of dissolved manganese. These are the times when the flow monitored at Fishers is greater than the input from Kafironda and Garneton so that the difference is negative. At other times the difference is positive which means manganese is precipitating within the block. This precipitated manganese may be carried out of the block in the suspended phase or it may settle as sediment. These transfers between dissolved and suspended phase may be linked to the redox conditions indicated in fig. 20 earlier.

Fig. 43 also shows that the peaks in the flows of suspended manganese at Fishers seem to be accompanied by troughs in the nett input of dissolved manganese. This could be because the troughs in the nett input of dissolved manganese are being caused by a re-mobilisation of manganese in the sediment. This manganese might be in the  $Mn_3O_4$  state. On being brought up to more oxidised conditions in the water column, it may be that the transition to the  $MnO_2$  state



is being achieved via reaction 8. This would result in greater flows of both suspended and dissolved manganese at the Fishers site.

Fig. 44 shows that there is three times more manganese in the suspended state which is being taken out of block SS2 than is coming in.

**Table 8. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended manganese monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Dissolved manganese (Kg/ day)					Suspended manganese (Kg/ day)	
Month	Rag DMn	Kaf DMn	GarDMn	Fis DMn	Mac DMn	Rag SMn	Fis SMn
March, 95	45				21	53	
April, 95	29		0.5		16	47	
May, 95	10		0.4	507	28	7	1
June, 95	1	208	0.3	260	6	1	0
July, 95	1	165	0.2	255	5	1	15
August, 95	2	120	0.2	169	3	1	73
September, 95	2	66	0.2	97	5	1	30
October, 95	2	13	0.4	17	4	1	113
November, 95	2	103	0.5	214	6	1	124
December, 95	2	305	0.6	614	24	2	472
January, 96	10	544	2.0	744	70	7	315
February, 96	18	1,104	2.3	828	36	11	498
March, 96	20	1,790	2.0	1,963	737	33	853
April, 96	21	2,146	1.9	1,912	48	41	327

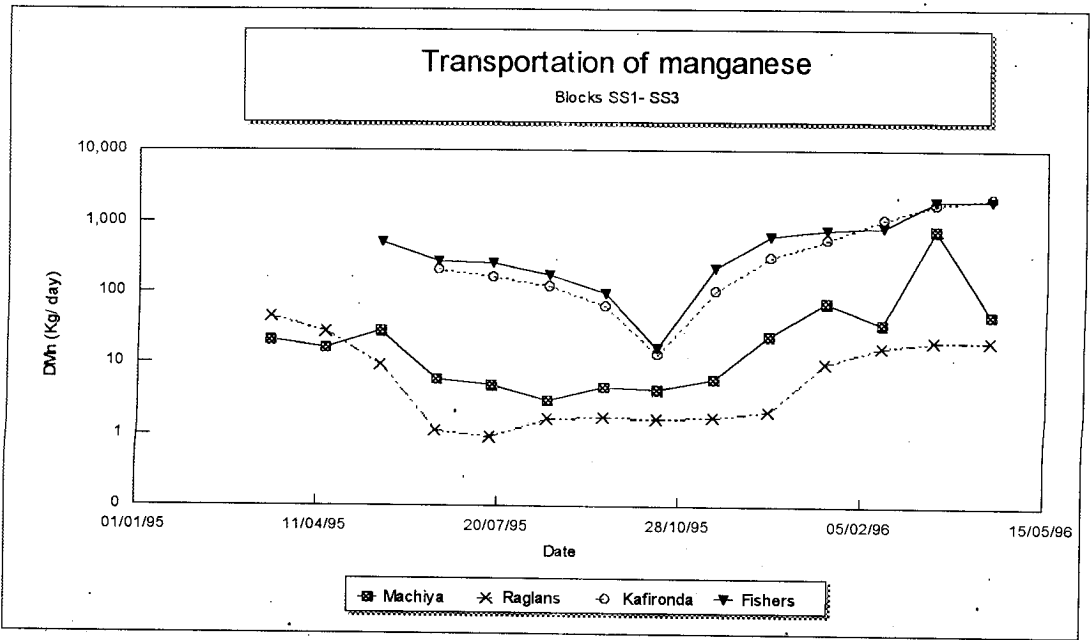


Fig. 42 - Seasonal variation in dissolved manganese flows at Raglans, Kafironda, Fishers and Machiya

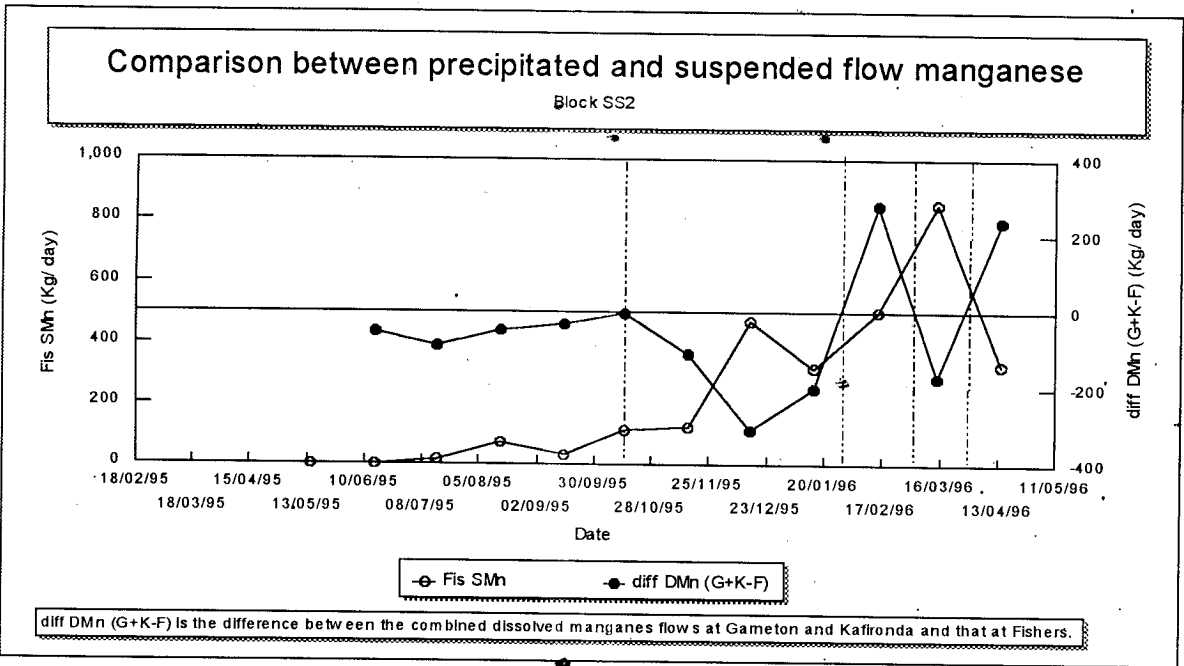


Fig. 43 - Seasonal discrepancy between the input of dissolved manganese from the Mwambashi and Kafue upstream and that monitored at Fishers farm. Also seasonal variation of suspended manganese flows at Fishers farm.

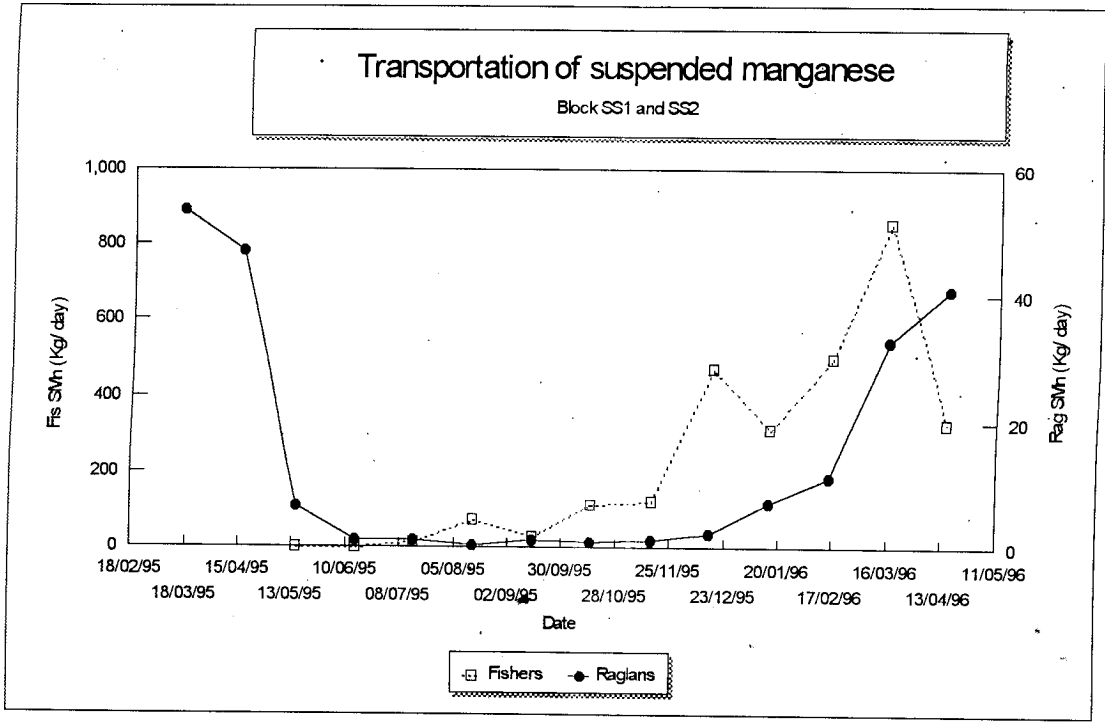


Fig. 44 - Seasonal variation in the flows of suspended manganese at Raglans and Fishers farm.

### 5.3.7 *Copper*

As a copper mineral bearing area, it would be natural to expect this metal even in streams and rivers which are not directly impacted by mining operations. The situation in the Luansobe stream in fig. 19 is a probable case in point. This project was investigating how mining operations have changed the natural chemistry of the metal in the Kafue river basin.

The flows of copper as determined during the sampling are given in table 9 and figs. 45-49. In block SS1, fig. 45 shows that although the dissolved flows at Raglans and Kafironda both show similar seasonal variation, their orders of magnitude are completely different. A distinct minimum at Kafironda occurs at the point of minimum flow in the river just before the start of the rain season. The effluent, shown for both dissolved and suspended states, does not have a marked seasonal variation although both the dissolved and suspended copper in the effluent do show an increase in the rain season.

The log nature of the Y axis in fig. 45 does not fully bring out the difference between the flow at Kafironda and the mine effluent. The actual values for the April 96 flows are 3,991 Kg/ day for the dissolved copper in the flow at Kafironda compared to 477 Kg/ day for the dissolved copper in the mine effluent. To give a possible explanation for the source of the copper measured at Kafironda during the rain season, the suspended copper in the mine effluent is also included on the same graph. It is possible that some of the suspended copper in the effluent may leach out when it reaches the Kafue where the pH may be lower than that at which the mine effluent is being released. Mine effluent is normally released at a pH of over 8 whereas the Kafue river pH during the rain season is usually less than 7.5. If the suspended copper in effluent is in sulphide form, it

could possibly get oxidised to soluble copper sulphate when the river is in an oxidising state [Nkandu et al (1), 1996].

In block SS4, as shown in fig. 46, it is either that most of the copper discharged as effluent is removed from the dissolved phase before it reaches Garneton or the magnitude of this discharge was over-estimated. This was also indicated by fig. 15 in the discussion on sources and sinks.

Fig. 47 covering flows in blocks SS2 and SS3 show that between Kafironda and Garneton on one hand and Fishers on the other, copper is being transferred to the suspended phase. Subject to the comments on the effect of a reducing environment on iron oxides carrying adsorbed copper below, this transfer is substantially complete by the time the river reaches Fishers farm. This is because the flows at Fishers farm are practically the same as at Machiya.

In fig. 47, it can be seen that during the months of August 1995 to October 1995, the dissolved copper flows at Machiya are slightly higher than at Fishers farm. As was shown later in section 5.3.5, the dissolved flows of iron at Fishers farm also rise against the trend during the months of August 1995 to October 1995. This can be attributed to the river becoming more reducing and so converting the metals to the more soluble lower valencies. This could mean that the suspended iron which enters the Kafue river from mine operations or is lying as sediment may have adsorbed some copper. When the environment of the Kafue river becomes reducing, the dissolution of the suspended iron will result in the adsorbed copper also going into solution. This could be why the line for the dissolved copper flows at Machiya in fig. 47 shows a temporary rise. Otherwise continuous precipitation of copper would ensure that the Machiya line should always be below

the Fishers line. If equilibrium had been reached, the Fishers and Machiya lines would have been the same.

Around January '96 and February '96 another situation occurred when the Kafue temporarily became reducing [Nkandu et al (1), 1996]. Fig. 47 shows that, once again, the expected dissolution of copper adsorbed on iron oxyhydroxides brings the Machiya line close to the Fishers line although this time it does not cross it.

Fig. 48 shows some similarity in the behaviour of manganese and copper flows in the suspended phase and the nett input in the dissolved phase. The flow in the suspended phase seems to peak at the time when the nett inflow in the dissolved phase is least. The trough in the nett inflow could be due to increased re-mobilisation of copper from the sediment. It is therefore possible that this behaviour is a result of adsorbed copper on manganese oxides.

Depending on the distance between adjacent monitoring stations and how easily the suspended solids settle, it can be difficult to monitor the movements of suspended solids. Fluctuations in the suspended solids load at one station may be un-noticeable by the time one gets to the downstream station. Fig. 49 is one occasion when these fluctuations are apparent. The first peak in the suspended solids flow at Fishers farm corresponds to the peak in total suspended solids which was noticed at the beginning of the rain season in figs. 26-28 and was observed at stations from Meteton to Machiya. The second peak however seems to have resulted from the discharge of suspended copper in effluent coming from Nkana Division through the Uchi stream. The shortness of the distance, less than 5 Km, between the sampling position on the Uchi stream from the

Fishers farm sampling site made it possible for the escape of solids from Nkana Division to be noticed.

**Table 9. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended copper monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Ga = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Dissolved copper (Kg/ day)					Suspended copper (Kg/ day)		
Month	Rag DCu	Kaf DCu	Ga DCu	Fis DCu	Mac DCu	Rag SCu	Fis SCu	Mac SCu
March, 95	35				1,338	49		7,89
April, 95	18		1		1,011	47		
May, 95	2		1	193	142	6	455	34
June, 95	0	101	0	53	36	1	115	
July, 95	0	78	0	36	31	1	113	
August, 95	0	50	0	25	35	0	101	
Sept, 95	0	27	0	17	22	1	0	
October, 95	0	13	0	11	11	1	21	9
Nov, 95	0	39	1	24	9	1	57	6
Dec, 95	1	172	6	189	43	2	1,164	
January, 96	1	376	6	356	272	8	489	
Feb, 96	2	1,214	6	749	771	13	513	
March, 96	45	2,394	6	2,892	932	30	1,173	
April, 96		3,991	4	3,076	1,388	36	421	



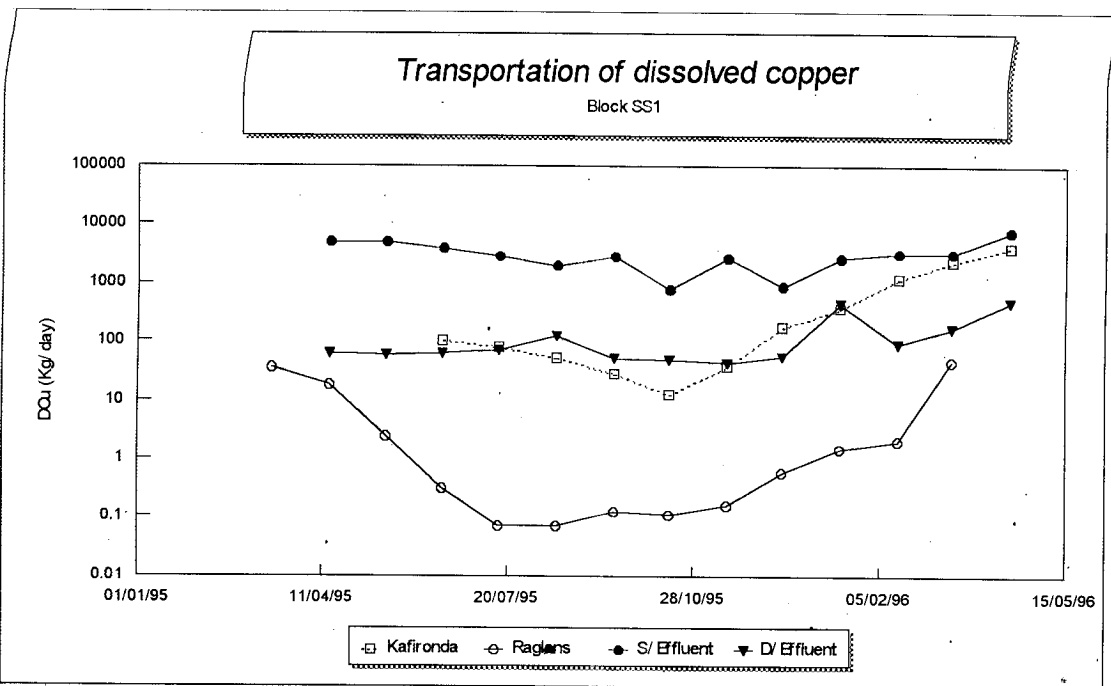


Fig. 45 - Seasonal variation in dissolved copper flows at Raglans and Kafironda and the magnitude of dissolved and suspended copper in mine effluent

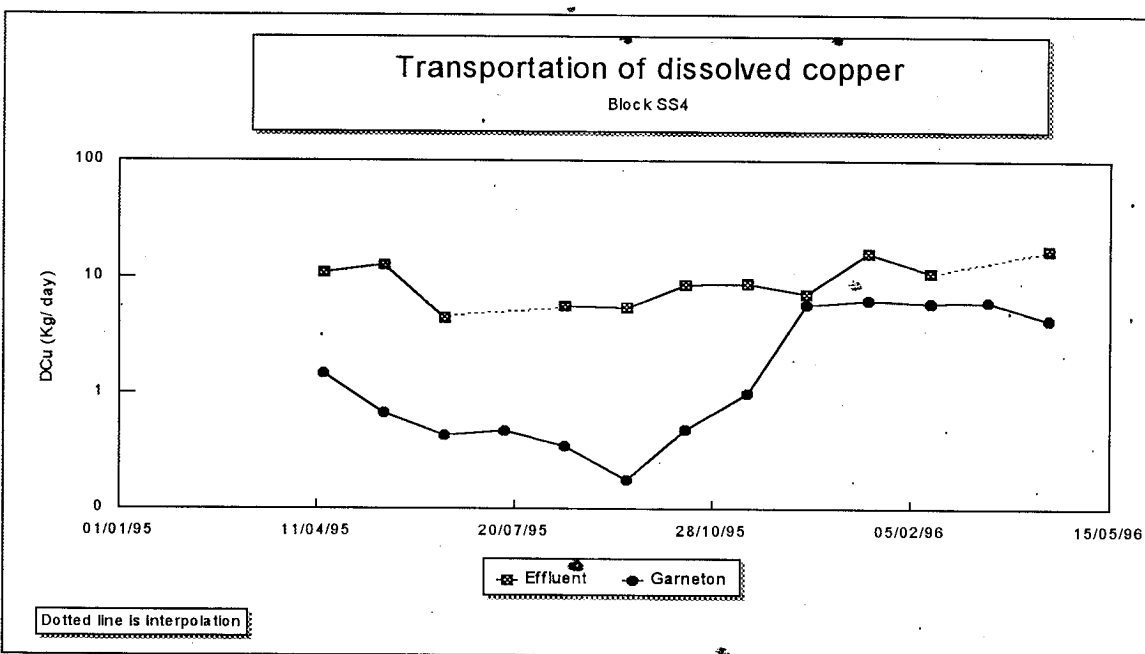


Fig. 46 - Seasonal variation in the flows of dissolved copper in the Mwambashi river and the magnitude of the copper reported as having been discharged into the river as mine effluent.

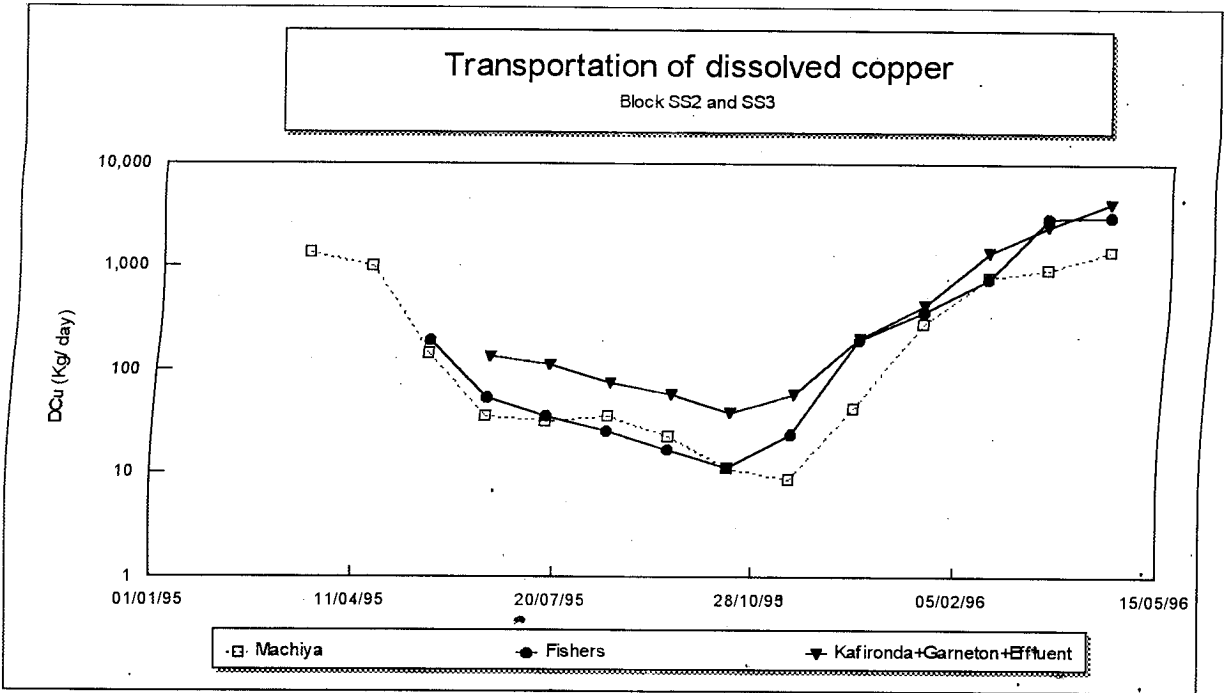


Fig. 47 - Seasonal variation in dissolved copper flows at Fishers farm and Machiya ferry relative to the input from the Mwambashi, mine effluent and the Kafue upstream

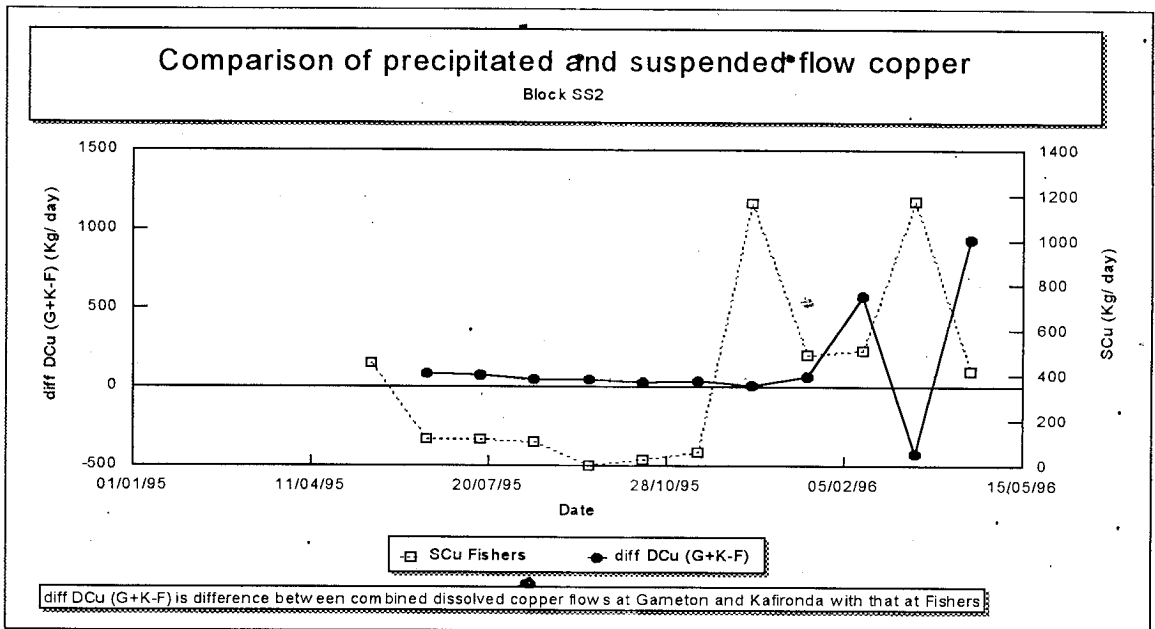


Fig. 48 - Seasonal discrepancy in the input of dissolved\* copper from the Mwambashi and Kafue upstream and that monitored Fishers farm. Also seasonal variation in suspended copper monitored at Fishers farm

## Transportation of suspended solids

Suspended copper

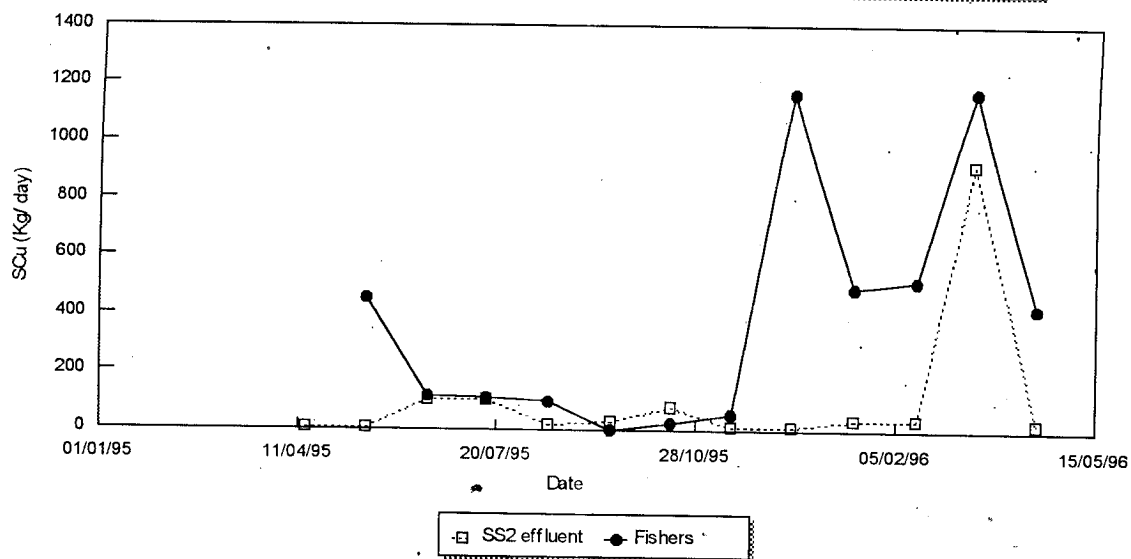


Fig. 49 - Example of how extra-ordinary discharges of mine effluent can temporarily affect seasonal flows monitored in the river.

5.3.8 Cobalt

Cobalt, like copper, is a major mineral in the Copperbelt province. Therefore, like copper, it is expected to be found in the waters of the river basin. Although it is less abundant than copper, it is more soluble than copper in its most common  $\text{Co}^{2+}$  state. The  $\text{Co}^{3+}$  state only exists at very high oxidising potentials. In fact,  $\text{Co}^{3+}$  can liberate oxygen from water. When complexed with ammonia however, the plus three state can exist in the dissolved state at lower oxidation potentials.

The flows of cobalt determined during the sampling are given in table 10 and figs. 50-53. Fig. 50 shows that the cobalt flows at Raglans farm and Kafironda have a seasonal trend. The minimum for Kafironda is distinct and occurs at the point of minimum flow before the onset of the rainy season. The minimum for Raglans farm is however broader. The difference between the mine effluent which is discharged into Kafue river in this sector and the Raglans flow can be several orders of magnitude. The effluent fluctuates about 100 Kg/ day whereas the Raglans flow is below 1 Kg/ day for most of the time and even drops below 0.1 Kg/ day at its minimum.

Fig. 51 shows that, either most of the cobalt discharged in mine effluent in block SS4 never gets to the Garneton site or the discharge has been over-estimated.

Fig. 52 shows that the behaviour of cobalt in block SS2 parallels the behaviour of total dissolved solids for block SS3 as fig. 31 showed. This is in the way cobalt is transferred from the dissolved state to the suspended state during the dry season.

Like copper and manganese, cobalt in block SS2 seems to get re-mobilised during the rain season. Some of this cobalt could be from the sediment although the amount which was removed over the course of the year indicates that either there was nett removal of cobalt from the sediment during the period of sampling or there is another source entering the river between Kafironda and Fishers. Such a source could be un-monitored soil erosion from mine dumps. This can be seen in fig. 53.

**Table 10. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended cobalt monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

	Dissolved cobalt (Kg/ day)					Suspended Cobalt (Kg/ day)		
Month	Rag	Kaf	Gar	Fis	Mac	Rag	Fis	Mac
March, 95	3				18	1		44
April, 95	1		1		13	0		
May, 95	0		1	128	5	0	27	3
June, 95	0	16	0	96	2	0	8	
July, 95	0	10	0	67	2	0	9	
August, 95	0	5	1	43	1	0	17	
Sept, 95	0	2	0	11	2	0	0	
October, 95	0	1	1	5	2	0	16	2
Nov, 95	0	4	2	70	3	0	26	2
Dec, 95	0	18	14	336	6	0	231	
January, 96	0	26	9	330	36	0	106	
Feb, 96	0	64	4	341	20	0	109	
March, 96	1	113	2	237	41	1	152	
April, 96		172	2	176	38	0	67	

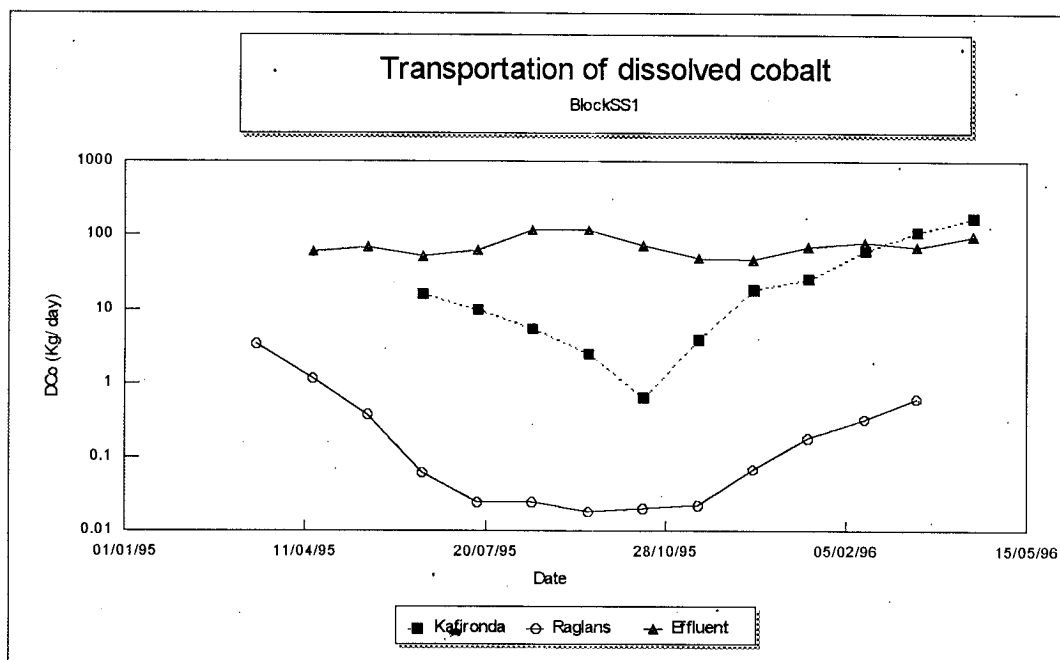


Fig. 50 - Seasonal variation in dissolved cobalt flows at Raglans and Kafironda and the magnitude of mine effluent

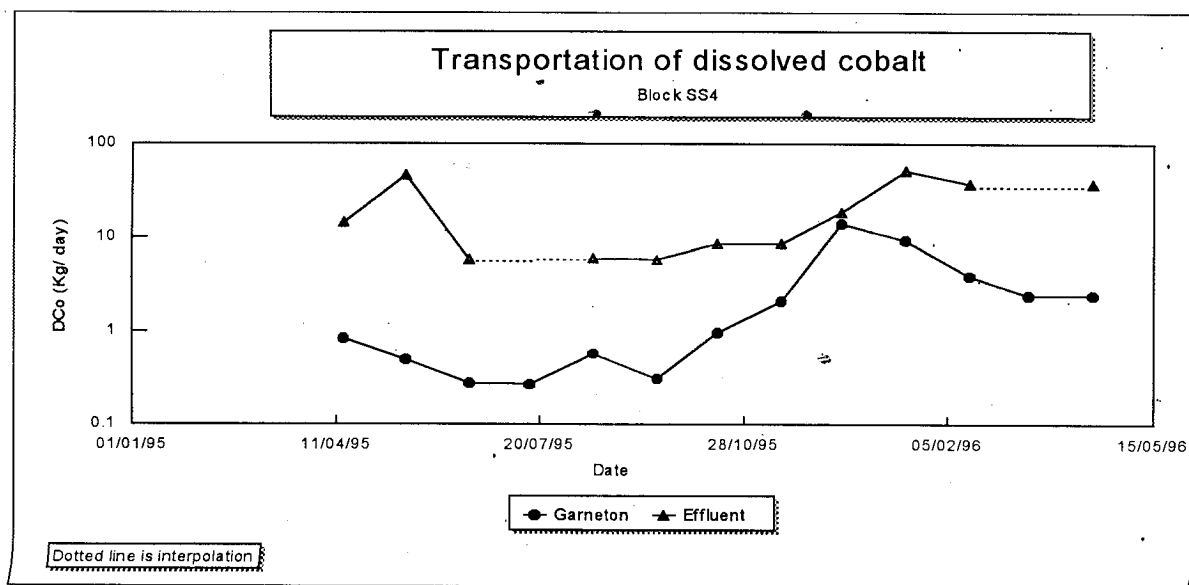


Fig. 51 - Seasonal variation in the dissolved cobalt flows in the Mwambashi and the magnitude of the reported mine effluent discharged into the river.

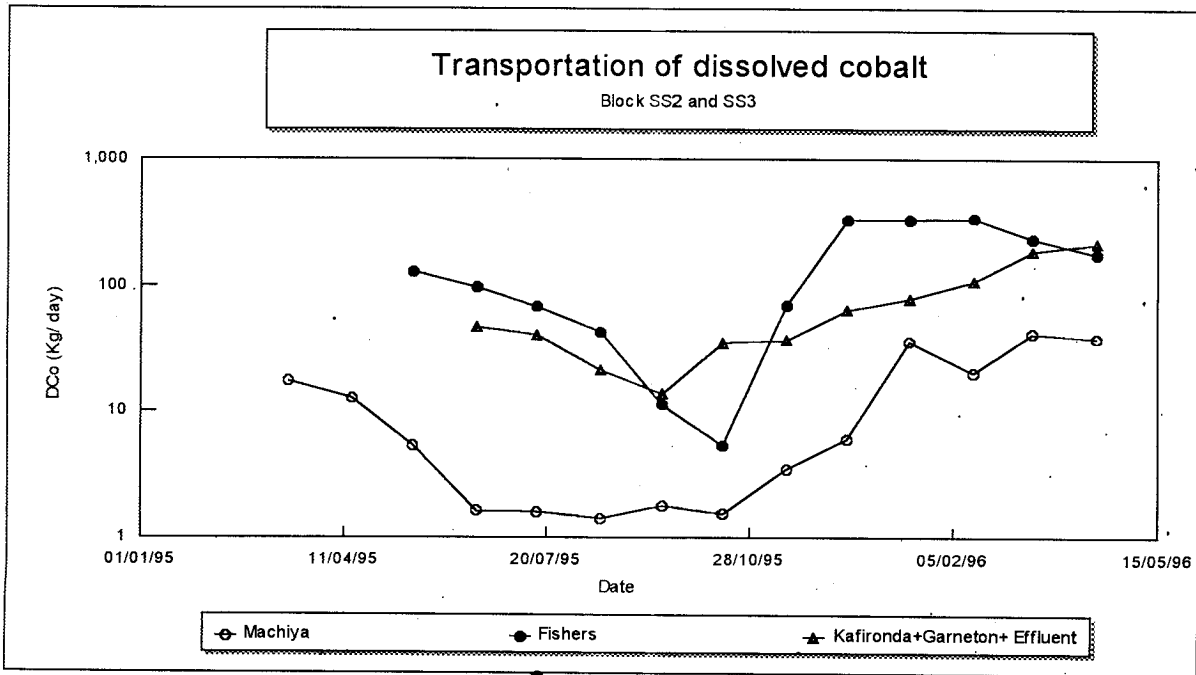


Fig. 52 - Seasonal variation in dissolved cobalt flows at Fishers farm and Machiya relative to the input from the Mwambashi, mine effluent and the Kafue upstream

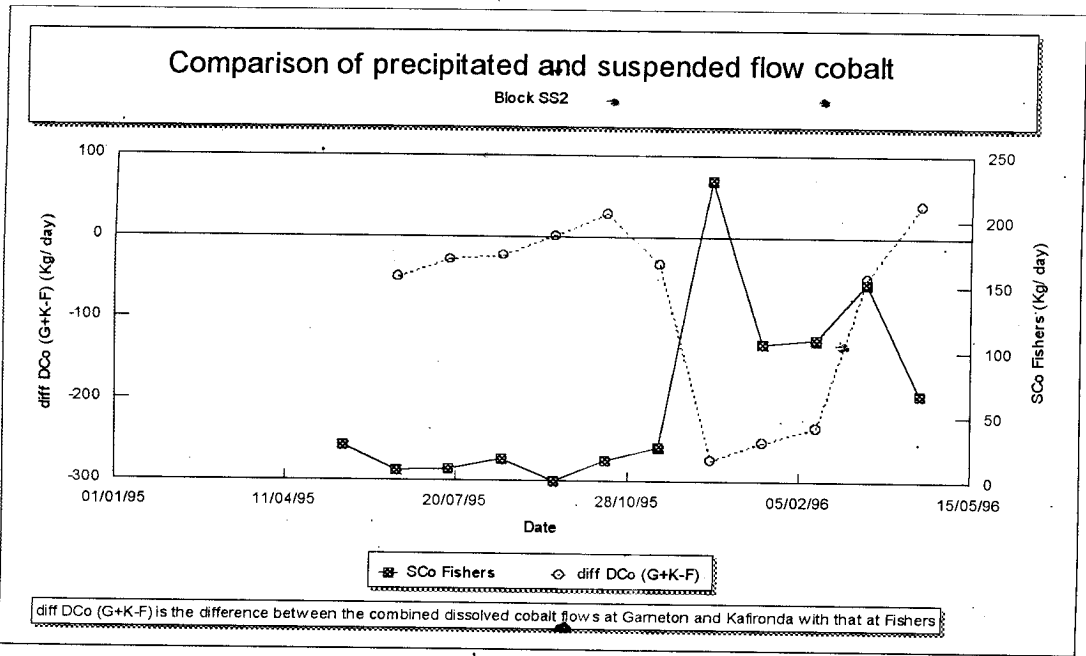


Fig. 53 - Seasonal discrepancy between input of dissolved cobalt flows from the Mwambashi and Kafue upstream and that monitored at Fishers farm. Also the seasonal variation of suspended cobalt flows at Fishers farm.



### 5.3.9 Cadmium

Discussion of this element has been included because of its environmental importance as it is a dangerous toxin. The element is only found in small concentrations. The element is however so toxic that even these small concentrations might prove to be dangerous. Therefore there is an interest in verifying whether mining activities play a major role in changing its availability in the environment. Both the World Health Organisation and the Department of Water Affairs have a maximum limit of only 0.01ppm for potable water. It is however possible that the tiny concentrations at which the metal is found might be difficult to analyse accurately. However these levels might still be above the threshold and so can give rise to serious implications to human health.

The problems with accurate analysis might be the reason why there is such a lack of seasonal balance from the 1994 - 1995 rain season to the 1995 - 1996 rain season for the Raglans, Kafironda and Machiya stations. This is unlike all the other parameters studied in this project. These have showed that although their concentrations changed with the season, their levels in the 1995 - 1996 rain season have been in the same range as they were in the 1994 - 1995 rain season.

Data from earlier reports [Nkandu, 1996] indicated that cadmium concentrations in the Kafue river increased continuously in the region which is roughly equivalent to block SS1 in this study. The question which had been asked in that study was whether the increase continued all the way downstream.

The data collected on cadmium is given in table 11 and figs. 54-59. The available data seems to

indicate that whilst dissolved cadmium in the Kafue river increase from the entry levels at Raglans farm to Kafironda, some of this cadmium together with that coming in via the Mwambashi river precipitates in block SS2. At the start of the rain season, some of this cadmium in the sediment seems to get re-mobilised because the Fishers flow is temporarily greater than the combined Garneton and Kafironda flow. This is also indicated by fig. 58. Trend of troughs in the difference in the dissolved metal flows between the input from Garneton and Kafironda and the output at Fishers coinciding with peaks in the suspended metal flows have in other sections been ascribed to the re-mobilisation of sediment. However this higher flow at Fishers compared to the upstream sites could have been of mine origin via the effluent from Nkana Division which enter the Kafue through the Uchi stream. Cadmium concentrations are not reported in mine effluent.

The activity in blocks SS1, SS2 and SS4 is however overshadowed by that taking place in block SS3. It would appear that there is a major source of cadmium entering the Kafue river between Fishers farm and Machiya. This raises the dissolved cadmium flow during the rainy season from less than 0.5 Kg/ day at Fishers farm to over 15 Kg/ day at Machiya. As Luanshya Division of ZCCM is the only mine whose effluent enters the Kafue river in this stretch it is felt that the source of this cadmium is unlikely to be of mine origin. The area around Kabwe mine however hosts cadmium mineralisation and it is possible the cadmium detected in the Kafue river is coming from there. This could be an important area for future study.

The suspended cadmium flow at Fishers indicates that there is a peak in this flow at the start of the rain season. This seems to be correlated to the peak in total suspended solids which was observed at stations from Garneton to Machiya.

**Table 11. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended cadmium monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

Month	Dissolved Cadmium (Kg/ day)					Suspended Cadmium (Kg/ day)	
	Rag	Kaf	Gar	Fis	Mac	Rag	Fis
March, 95	0.43				1.37	0.02	
April, 95	0.29		0.01		0.35	0.02	
May, 95	0.01		0.00	0.26	0.56	0.00	0.07
June, 95	0.00	0.06	0.00	0.05	0.00	0.00	0.02
July, 95	0.00	0.06	0.00	0.08	0.00	0.00	0.02
August, 95	0.00	0.06	0.00	0.08		0.00	0.03
September, 95	0.00	0.04	0.00	0.04	0.62	0.00	0.00
October, 95	0.03	0.03	0.00	0.05	0.25	0.00	0.00
November, 95	0.00	0.05	0.00	0.03	0.45	0.00	0.09
December, 95	0.00	0.25	0.01	0.50	2.18	0.00	0.41
January, 96	0.01	0.26	0.26	0.31	7.40	0.00	0.27
February, 96	0.03	0.98	0.33	0.08	7.64	0.00	0.16
March, 96	0.00	0.79	0.22	0.00	9.19	0.01	0.19
April, 96		0.75	0.14	0.00	16.02	0.01	0.12

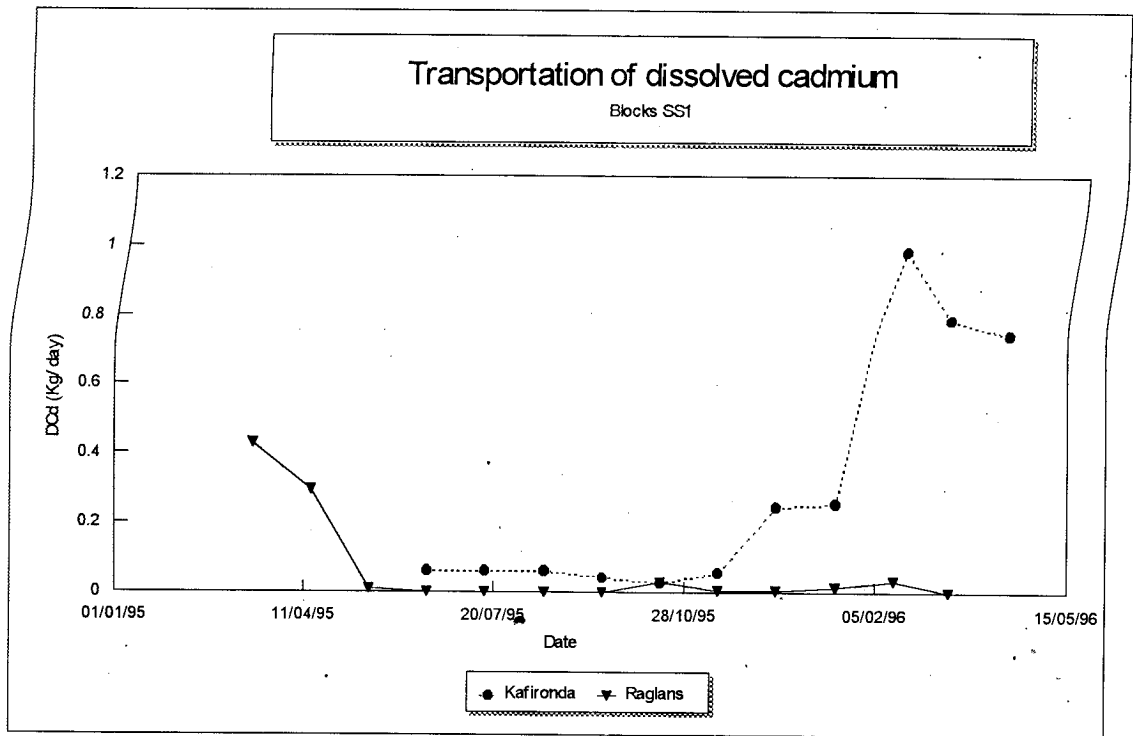


Fig. 54 - Seasonal variation in dissolved cadmium flows at Raglans farm and Kafironda

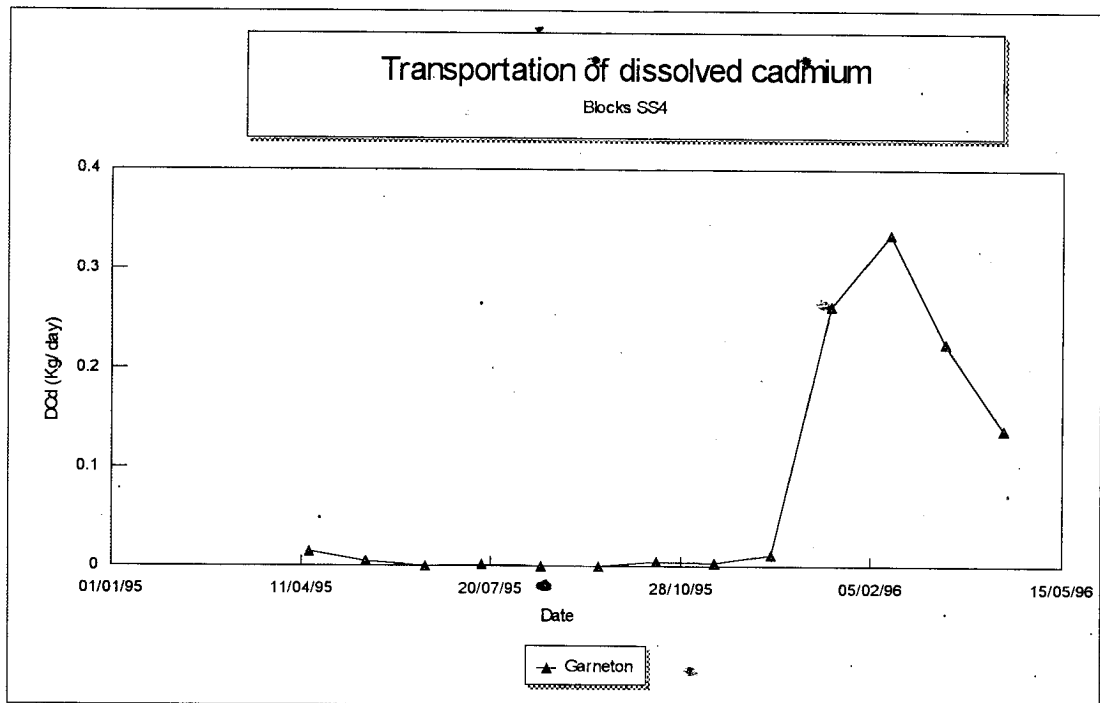


Fig. 55 - Seasonal variation in the flows of dissolved cadmium in the Mwambashi river.

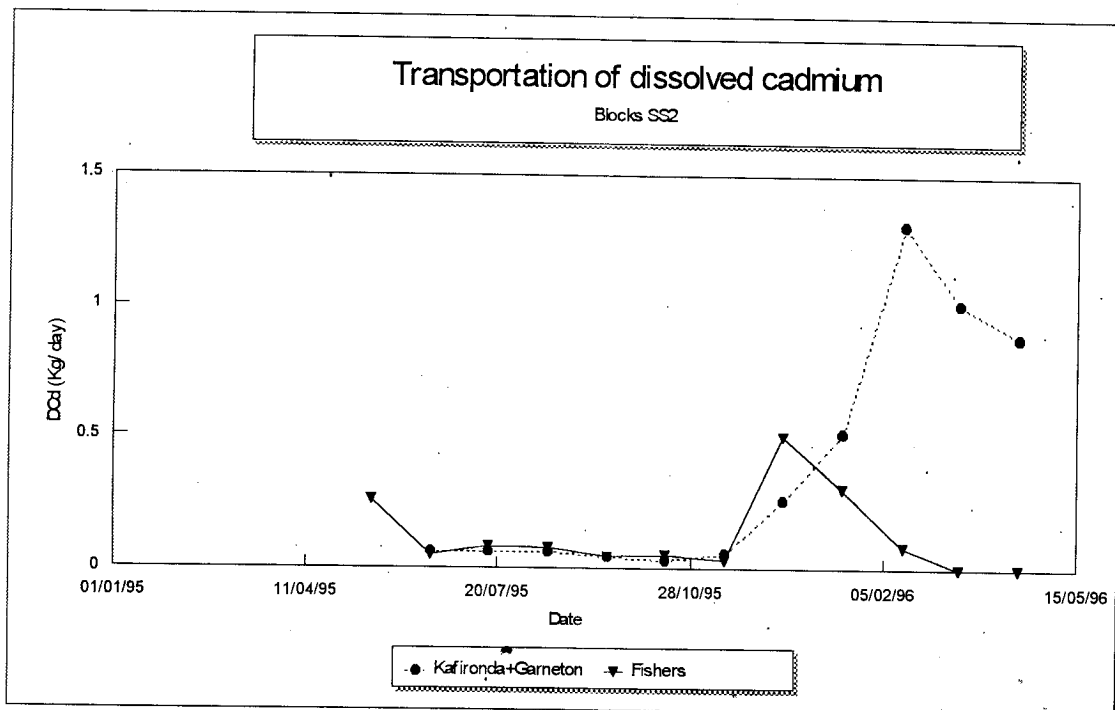


Fig. 56 - Seasonal variation in the flows of dissolved cadmium at Fishers farm relative to the input from the Mwambashi and Kafue upstream

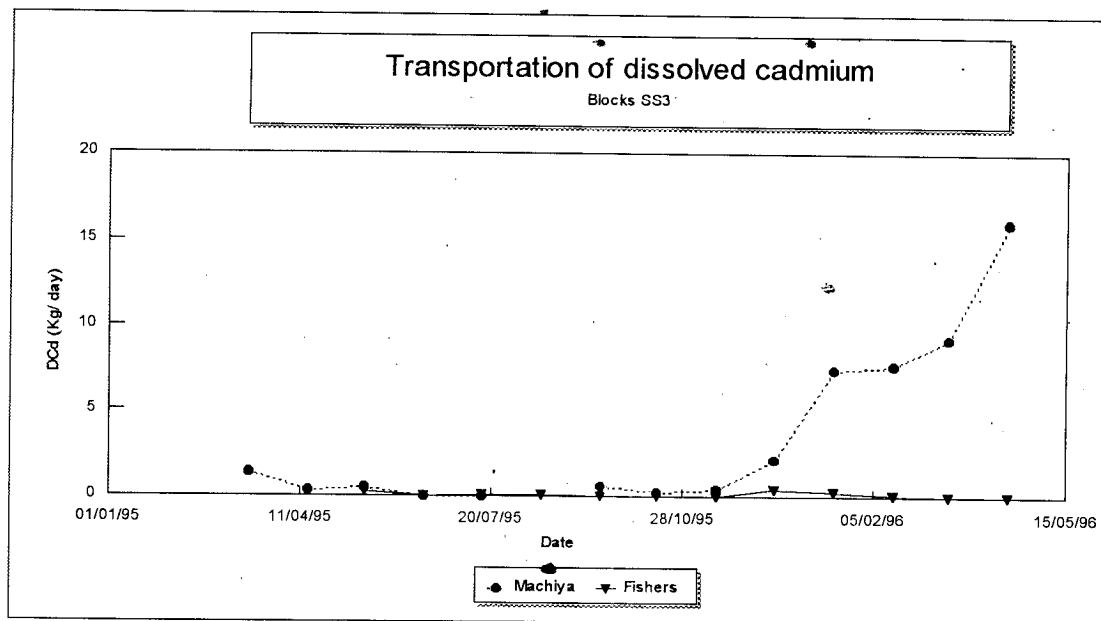


Fig. 57- Seasonal variation in the flows of dissolved cadmium at Machiya ferry relative to the input from Kafue upstream

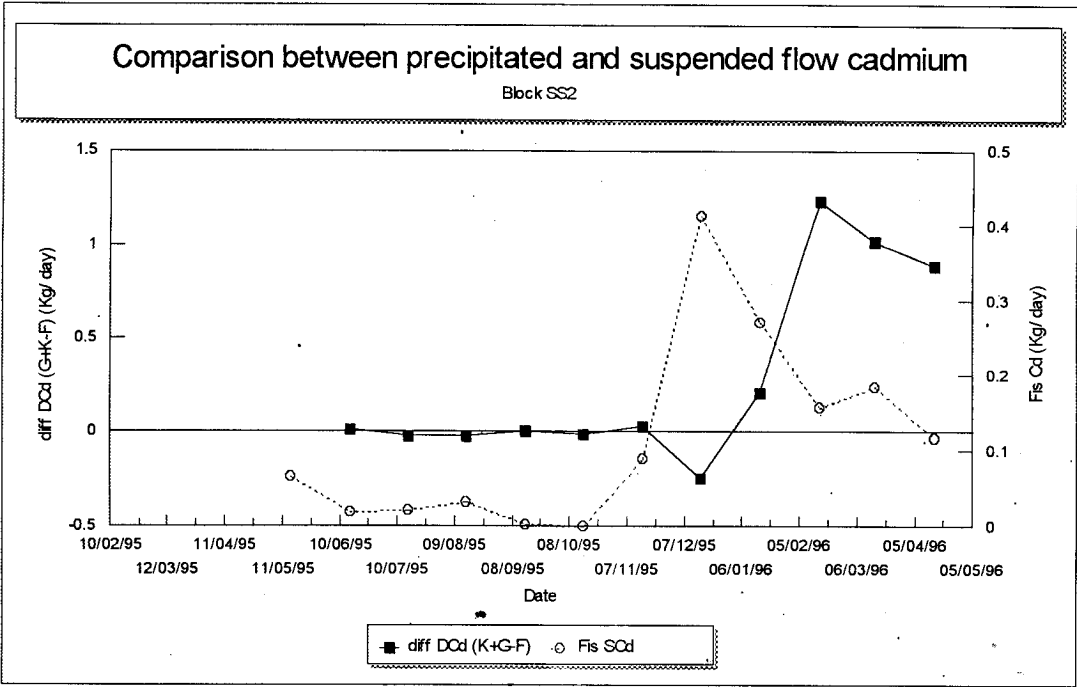


Fig. 58 - Seasonal discrepancy between the input of dissolved cadmium from the Mwambashi and Kafue upstream and that monitored at Fishers farm. Also seasonal variation in suspended cadmium flows at Fishers farm.

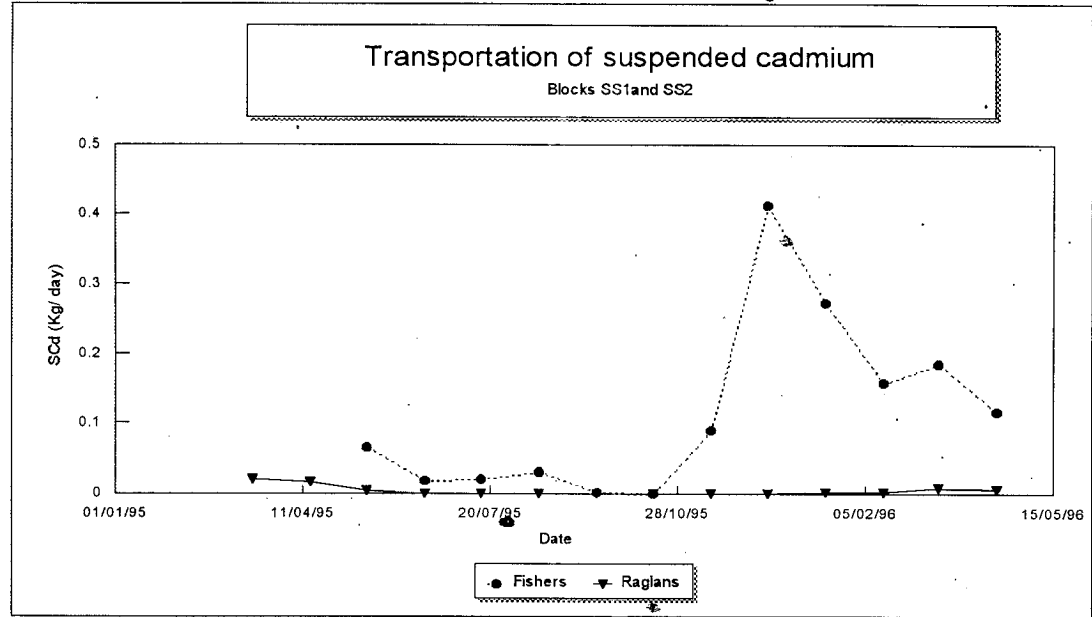


Fig. 59 - Seasonal variation in suspended cadmium flows at Raglans farm and Fishers farm.

5.3.10 Lead

Lead is another potentially toxic metal. The World Health Organisation has given a limit of this metal in potable water of 0.1ppm whilst the Department of Water Affairs gives a limit of 0.05ppm. It was therefore decided that the impact of mining activities on the mobility of this element should be studied. Lead is like iron and manganese in the sense that it can exist in several valencies with the higher valencies being more insoluble [Weast, 1974; Latimer, 1939.]. At atmospheric pressure the transition point between lead dissolved in water and the suspended phase is governed by the equations below.

<u>Couple</u>	<u>Nernst equation</u>	<u>E at pH = 7</u>
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+} + 2\text{H}_2\text{O}$	$E = 1.46 - 0.03 \log [\text{Pb}^{2+}] - 0.12\text{pH}$	+083
$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	$E = 1.23 - 0.06 \log \text{Po}_2 - 0.06\text{pH}$	+081

The lead concentration used in the calculation of E at pH 7 is  $10^{-7}$  Mol/ l. This was the order of magnitude concentration determined in the samples collected at Kafironda. This means that lead was almost at equilibrium with the water/ oxygen couple although a slight precipitation or dissolution of the lead could expected depending on the time of the year as fig 65 shows.

Additionally lead can also be like barium in the sense that it has a fairly insoluble sulphate compound. The relative solubility products of calcium sulphate, lead sulphate and barium sulphate are listed in table 12.

**Table 12: Solubility products of some sulphates.**

Salt	Temperature (°C)	Solubility product (concentrations in Mol/ l)
Calcium sulphate (CaSO <sub>4</sub> )	25	$2.45 \cdot 10^{-5}$
Lead sulphate (PbSO <sub>4</sub> )	18	$1.06 \cdot 10^{-8}$
Barium Sulphate (BaSO <sub>4</sub> )	25	$1.08 \cdot 10^{-10}$

Lead sulphate is therefore about one hundred times more soluble than barium sulphate but a thousand times less soluble than calcium sulphate. Since it has been shown that barium sulphate levels were able to increase continuously from Raglans to Machiya, sulphate levels could only be expected to have an influence on lead levels if dissolved lead flows were more than 100 times those of barium. However, the mass flow rates which were measured for dissolved barium in table 6 are even greater than those of dissolved lead, as shown in table 13. Therefore the flows of dissolved lead could not possibly have been limited by the lead sulphate insolubility.

Fig. 60-64 indicate that there was very little lead coming into the mine area at Raglans. The few points for the flows at Raglans farm which are shown in fig. 60 are those for which the lead concentration was detectable. Fig. 61 shows that very little dissolved lead was coming in via the Mwambashi river as well. In fact the one point where the level seems to shoot up could be due to



analytical error or contamination of the sample somewhere along the line in the process of sample collection, storage or analysis.

After entering block SS1, lead builds up on the way to Kafironda but some of it subsequently gets precipitated out by the time it gets to Fishers farm. There is little difference between the flows of dissolved lead at Machiya and Fishers farm.

Fig. 62 shows a hump in the dissolved lead flows at Fishers farm between the months of July '95 and October '95. A similar situation was observed for iron in fig. 40 and this was attributed to the reducing state of the river at the time. From the similarity of the iron and lead flows, it would appear that the dissolved lead flows are being controlled by its oxidation to the insoluble higher valency oxides. However it has been shown above in the calculation of the Nernst potential for the water/ oxygen and the  $\text{Pb}^{2+}/ \text{PbO}_2$  couples that the  $\text{Pb}^{2+}/ \text{PbO}_2$  couple was almost at equilibrium with the water/ oxygen couple at Kafironda. Therefore precipitation of  $\text{Pb}^{2+}$  to  $\text{PbO}_2$  cannot be the reason for the reduction in dissolved lead flows. In addition, it can be shown that precipitation to  $\text{Pb}_3\text{O}_4$  does not become, energetically, more favourable than the  $\text{Pb}^{2+}/ \text{PbO}_2$  transition until a pH of 8.8. Therefore the precipitation can also not be explained by the transition of  $\text{Pb}^{2+}$  to  $\text{Pb}_3\text{O}_4$ . Therefore it is more probable that the observed similarity in the precipitation of lead and iron is due to the adsorption of the lead onto iron oxyhydroxides.

Fig. 65 is an elaboration of how the  $\text{Pb}^{2+}/ \text{PbO}_2$  couple fared with respect to the water/ oxygen couple at Kafironda during the whole sampling period. When the line for the lead couple is above the water/ oxygen line, then the lead should go into solution. Precipitation would occur if the situation was the other way round. The manganese and iron lines are much lower down. If an

attempt was made to put them on the same graph, the lead and water lines would appear as one.

**Table 13. Average monthly mass flow rates (in Kg/ day) of dissolved and suspended lead monitored at the stated sampling points. [Rag = Raglans farm, Kaf = Kafironda, Gar = Garneton pump station, Fis = Fishers farm, Mac = Machiya ferry]**

Month	Dissolved lead (Kg/ day)					Suspended lead (Kg/ day)	
	Rag	5Gar	Kaf	Fis	Mac	Rag	Fis
March, 95					19.5	0.2	
April, 95	0.4	0.0			3.9	0.2	
May, 95	0.0	0.0		1.5	0.8	0.0	9.0
June, 95	0.0	0.0	12.5	0.2	0.0	0.0	2.0
July, 95	0.0	0.0	12.6	0.1	0.0	0.0	5.0
August, 95	0.0	0.0	12.5	0.5		0.0	5.0
September, 95	0.0	0.0	8.9	0.4	0.1	0.0	0.0
October, 95	0.0	0.0	6.7	0.2		0.0	0.0
November, 95	0.0	0.0	17.0	0.4	0.1	0.0	16.0
December, 95	0.0	0.1	38.5	2.8	2.0	0.0	78.0
January, 96	0.4	0.0	39.8	3.2	2.0	0.0	34.0
February, 96	0.0	42.3	123.0	6.0	9.5	0.0	30.0
March, 96	0.3	0.0	92.9	6.3	5.2	0.1	28.4
April, 96	0.0	0.0	131.1	5.1	5.1	0.1	12.0

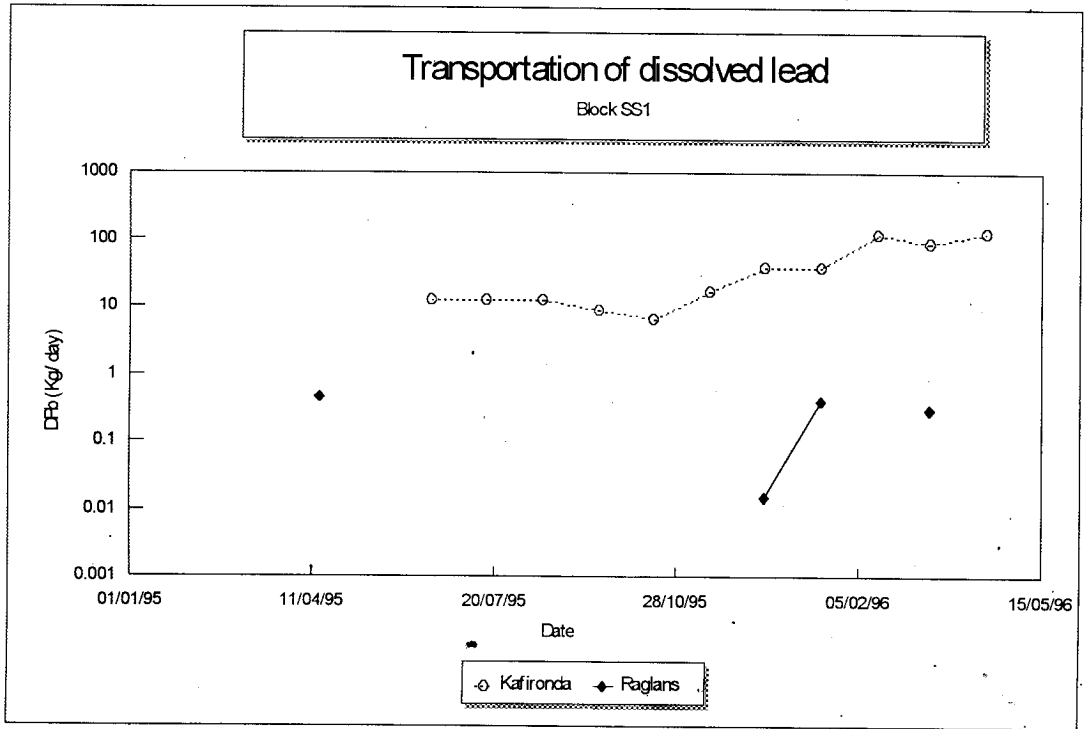


Fig. 60 - Seasonal variation in the flows of dissolved lead at Raglans farm and Kafironda

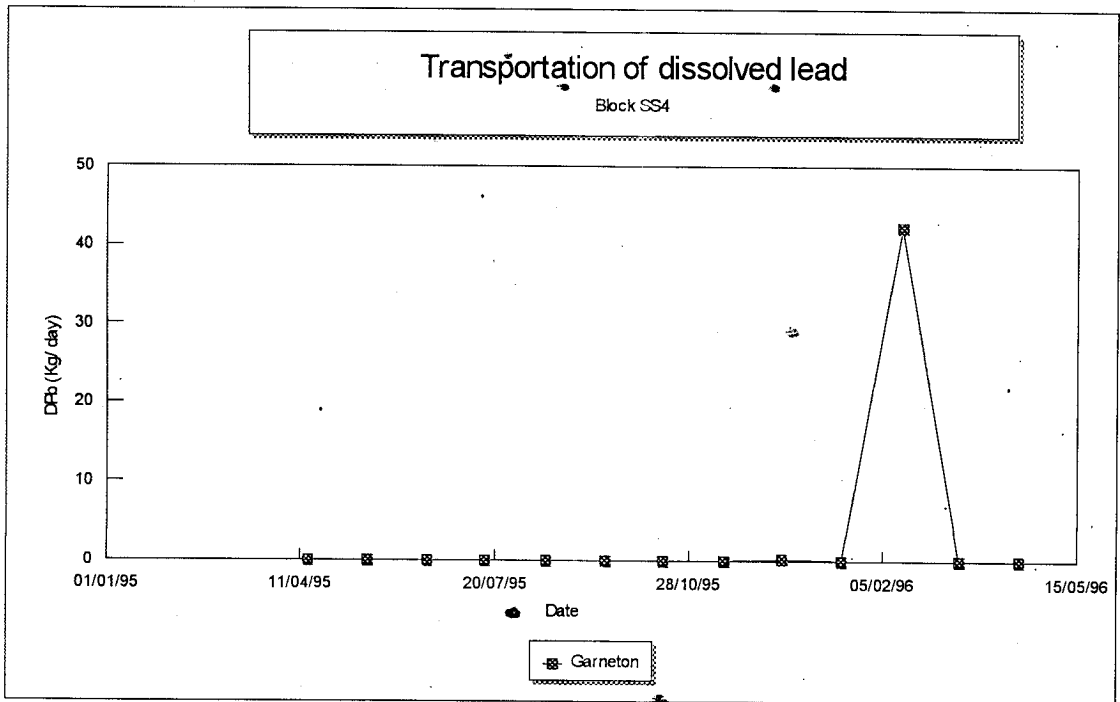


Fig. 61 - Seasonal variations in the flows of dissolved lead in the Mwambashi river

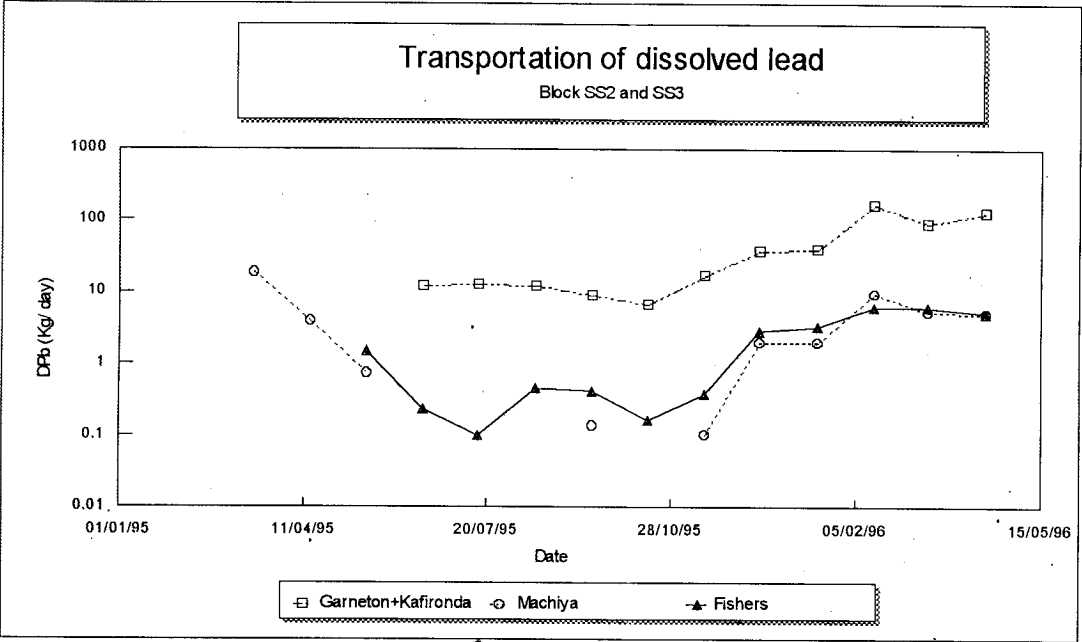


Fig. 62 - Seasonal variation in the flows of dissolved lead at Fishers farm and Machiya ferry relative to the input from the Mwambashi river and Kafue upstream.

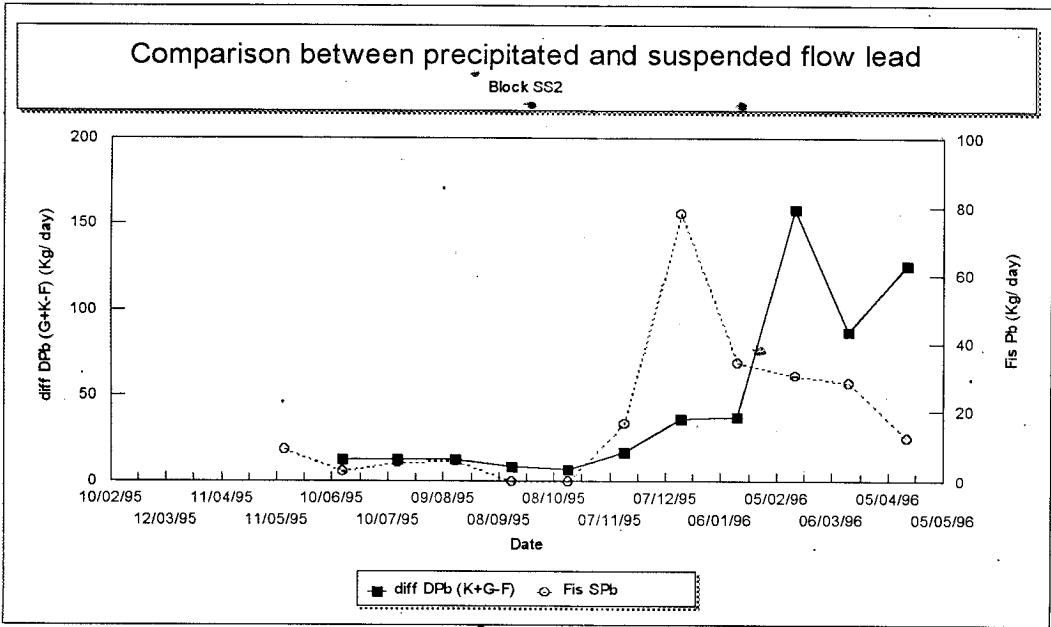


Fig. 63 - Seasonal discrepancy in the dissolved lead flows between the input from the Mwambashi and the Kafue upstream and that monitored at Fishers farm. Also the seasonal variation in suspended lead flows at Fishers farm

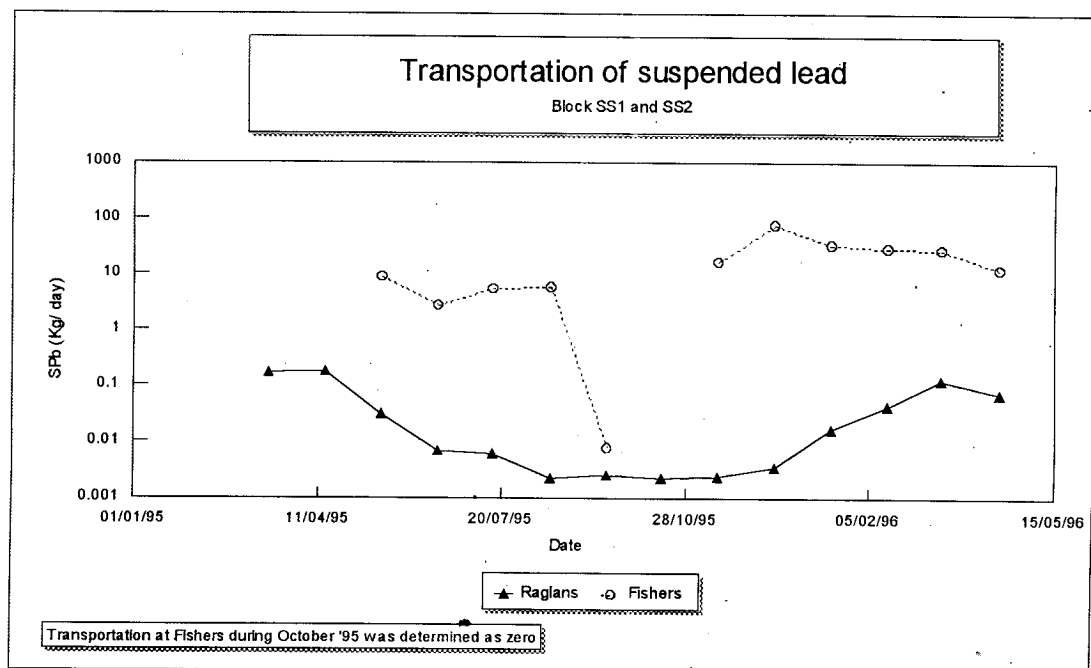


Fig. 64 - Seasonal variation in suspended lead flows at Raglans farm and Fishers farm

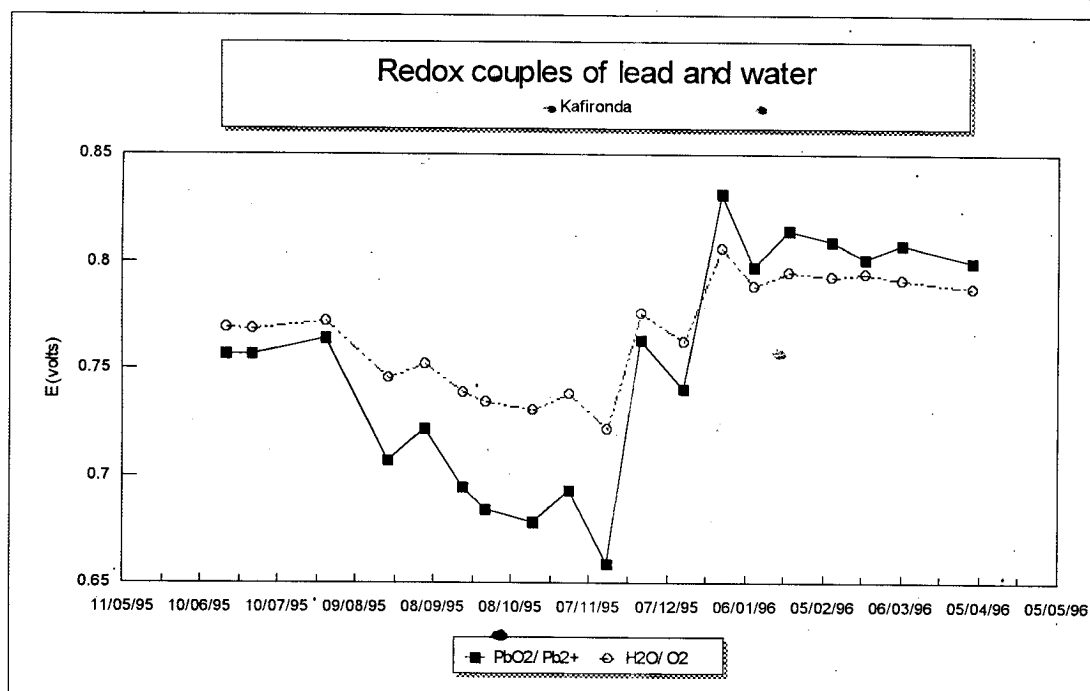


Fig. 65 - Comparison of the water/ oxygen redox couple and the couple for the transition of lead from solution to the suspended state.

## 6.0.0 Conclusions

This study has shown how the mass balance technique can be used to study the circumstances under which the mine effluent are affecting the environment and vice versa. A study of the relative magnitudes of the effluent discharges show that the mine operations which are responsible for some of the biggest effluent discharges into the Kafue river are those situated furthest upstream of the Kafue river. Therefore most of the effect from mining operations was seen in the blocks termed as SS1 and SS4. Blocks SS2 and SS3 were found to be blocks in which the attenuating effects of the environment were beginning to assert themselves and pollution levels were being forced down.

The biggest effects of mine operations on water quality in the Kafue river basin were seen in the Mwambashi river. This is most likely due to the small size of the river relative to the size of the effluent discharged into it. calcium sulphate discharges lead to reductions in alkalinity which is thought to be linked to the precipitation of calcium carbonate by carbon dioxide. As a result not all solids discharged from mine operations can be detected at downstream sampling locations. This has been most marked in the Mwambashi river but these can also be seen in a more attenuated level in the Kafue river.

Chemical precipitation can not account for all the observed reduction in dissolved solids and it is possible there could be biological sinks as well. This could be in such processes as sulphur utilisation by aquatic life forms in protein synthesis and the precipitation of elemental sulphur by anaerobic bacteria utilising sulphate as an oxygen source..

Suspended solids, much of it coming from mine effluent may be causing significant sedimentation in the upstream sections of the river basin during the dry season. However much or all of this subsequently gets re-mobilised during the rainy season.

The patterns of transportation of total dissolved solids and dissolved sulphur are virtually identical and this is attributed to the fact that sulphates are a major component of the dissolved solids. Most of the sulphates are of mine effluent origin.

The low solubility product of barium sulphate does not appear to control either the transportation of dissolved barium or dissolved sulphur. The same seems to apply to dissolved lead and dissolved sulphur.

Iron is transported almost completely in the suspended state. When the river is in an oxidising state, the flows in the dissolved state upstream of the mining areas are in fact higher than within and downstream of the mining areas. During the rain season, the flows within the mining areas are higher than upstream of the mining area. However the flows downstream of the mining areas are lower than in the mining areas indicating that the metal is eventually oxidised out of solution. Manganese seems less sensitive to the redox changes in the river but it too eventually manages to revert to the suspended state by the time the river reaches Machiya. Re-mobilisation of  $Mn_3O_4$  in sediment might cause it to decompose into  $Mn_2O_3$  and  $Mn^{2+}$ . Thus it is noticed that, in block SS2, increases in flows of suspended manganese occur at the same time as increases in dissolved manganese. This decomposition of solid manganese appear to be affecting the transportation of other metals as well.

Of the well known toxins such as lead and cadmium, data indicates that there is an increase in the flows of these metals as the river passes through mine areas, particularly block SS1. Some of the lead transfers to the suspended state in block SS2 and SS3. This transfer seems to depend on the Iron speciation and so the lead could actually be adsorbed onto iron oxyhydroxides. Some cadmium also seems to transfer to the suspended state in block SS2. A big addition to the dissolved cadmium flows is observed in block SS3. The dissolved cadmium flows are raised from about 0.3 Kg/ day at Fishers farm to nearly 20 Kg/ day at Machiya. It is important to discover the source of this cadmium. It could be that there is some cadmium mineralisation in the Kafue basin which is finding its way into the river. Generally though, mining does not seem to play a very significant role in the mobilisation of lead and cadmium in the upper Kafue basin.

#### **7.0.0 Recommendations for further studies**

A repeat of the sampling is recommended to confirm the existence of the processes postulated in this report. Photosynthesis and respiration have been cited as major processes affecting the transport of the elements. Therefore night time sampling would also be particularly useful because the river might behave differently during times of darkness. It could be that there is another cycle occurring on a daily basis in the precipitation/ dissolution of the metal load in the river such as has been observed on a seasonal basis. This would require a re-writing of the daily transportation rates as the rates quoted in this study assumed a constant flow throughout the day.

Data analysis could also be extended to elements not covered in this report.

The source of the big jump in cadmium flows in block SS3 should also be investigated.



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# Appendix 1

## Mine effluent data

### INDEX OF EFFLUENT STREAM AND DIVISION/ MINE RESPONSIBLE

1	No. 2 Channel	Konkola Division [ZCCM]
2	Combined drain	Konkola Division [ZCCM]
3	Pollution control dam	Nchanga Division [ZCCM]
4	Nchanga concentrator discharge	Nchanga Division [ZCCM]
5	Combined Mufulira discharge	Mufulira Division [ZCCM]
6	Luansobe stream	Mufulira Division [ZCCM]
7	Musakashi dam	formerly Chambishi cobalt and acid plant (Nkana Division) now Chambishi Metals PLC
8	Uchi stream	Nkana Division [ZCCM]
9	Wusakili storm drain	Nkana Division [ZCCM]
10	Mindola dam	Nkana Division [ZCCM]
11	New dam	formerly Chambishi cobalt and acid plant (Nkana Division) now Chambishi Metals PLC
12	Muntimpa dam	Nchanga Division [ZCCM]
13	Combined Luanshya discharge	formerly Luanshya Division now Roan Antelope Mining Corporation (Zambia) PLC

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
xii, 95	8,158	29,221	22,087		34,741		62,713				3,776	71,784	10,643
xi, 95	8,158	29,221	9,204		21,497		71,063				2,566	131,385	13,040
oct, 95	8,158	29,221	14,579		29,114		54,944				2,231	6,490	11,496
sept, 95	8,158	29,221	17,388		24,318		56,484				2,023	85,702	7,143
aug, 95	8,158	29,221	9,493		22,619		40,101				611	83,198	12,957
july, 95	8,158	29,221	2,837		19,278		29,882				581	77,870	15,022
june, 95	1,849	30,800	1,976		20,766		25,020				111	139,792	17,730
may, 95	1,860	22,779	9,211		19,348		20,446				144	153,499	21,012
april, 95	4,032	26,752	2,884		27,257		42,431				13,886	5,974	17,244
march, 96	12,445	23,184	29,222		30,360		88,360				21,632	120,828	24,811
february, 96	8,578	30,173	32,614		27,549		127,457				14,011	97,258	21,598
july, 96	11,816	32,473	17,803		35,741		108,311				14,757	85,702	18,420
aug, 96	16,526	38,389	62,138		40,098		60,507				10,868	54,643	14,935
xii, 96	8,158	29,221	17,803		27,130		60,594	ERR	ERR	ERR	6,707	85,702	15,850
Average (Kg/day)													

- = No. 2 Channel
- = Combined drain
- = Pollution Control dam
- = Nchanga Concentrator discharge
- = Combined Mutitira discharge
- = Luansobe stream
- = Musakashi stream
- = Uchi stream
- = Wusakili storm drain
- 0 = Mindola dam
- 1 = New dam
- 2 = Muntimpa dam
- 3 = Combined Luanshya discharge

Total Cobalt

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
April, 95	10.2	32.1	33.5	109.2	4.6		4.9	11.8	0.1	3.9	6.5	17.0	0.6
May, 95	10.2	30.0	3.0	128.4	3.4		23.1	6.1	0.6	3.9	3.4	66.6	3.0
June, 95	10.2	30.0	75.1	259.0	3.9		3.8	78.9	0.4	2.9	3.7	2.0	6.7
July, 95	10.2	30.0	9.8	173.2	3.9		18.3	78.9	0.4	2.8	3.1	23.9	1.4
August, 95	10.2	27.6	8.8	17.3	4.2		72.6	20.0	0.2	1.1	0.9	42.1	1.5
September, 95	2.3	29.9	1.7	353.6	3.1	3.8	80.3	28.4	0.1	1.1	0.7	11.4	2.2
October, 95	2.3	45.4	2.7	29.5	3.1	0.7	38.6	52.2	0.1	1.1	0.1	7.5	3.5
November, 95	2.6	29.2	4.2	545.9	3.1		17.6	52.0	0.3	1.1	0.1	46.9	3.7
December, 95	5.7	35.0	7.0	39.4	4.2		10.6	49.6	0.3	3.9	19.4	2.1	2.1
January, 96	16.9	16.3	36.9	172.0	4.1	6.2	12.2	85.5	0.1	3.9	47.4	11.9	2.8
February, 96	17.3	31.4	42.6	16.6	4.4	6.2	32.7	130.2	0.2	2.6	32.0	10.7	3.4
March, 96	15.2	32.2	26.9	145.6	5.0	15.3	12.3	374.2	0.5	2.6	32.5	23.9	4.2
April, 96	19.1	47.8	123.5	30.1	7.5	9.5	19.9	57.8	1.3	5.8	21.0	44.8	16.0
Average (Kg/day)	10.2	32.1	28.9	155.4	4.2	6.9	26.7	78.9	0.4	2.8	13.1	23.9	3.9

Mass flow rate in effluent discharged by stream

Dissolved Cobalt

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
April, 95	10.2	29.8	11.0	0.9	4.6	6.8	4.9	9.2	0.6	3.9	5.6	4.6	0.3
May, 95	10.2	30.0	2.0	1.0	3.4	6.8	21.9	4.4	0.8	3.9	2.9	39.2	0.7
June, 95	10.2	30.0	3.3	0.9	3.9	6.8	3.8	30.1	0.4	2.6	2.8	0.4	0.6
July, 95	10.2	30.0	2.0	0.9	3.9	6.8	14.6	30.1	0.4	2.6	1.8	8.8	0.7
August, 95	10.2	27.6	5.3	1.0	3.4	6.8	71.6	15.0	0.1	1.1	0.6	4.3	0.7
September, 95	2.3	29.9	1.0	0.9	3.1	3.0	80.3	10.9	0.1	1.1	0.6	4.2	1.1
October, 95	2.3	30.2	0.3	0.2	3.1	0.4	37.8	33.0	0.1	1.1	0.1	7.5	0.8
November, 95	2.6	24.1	0.9	0.7	3.1	6.8	17.4	30.7	0.4	1.1	0.1	7.6	1.2
December, 95	5.7	28.0	0.3	0.0	4.2	6.8	9.7	30.7	0.3	3.9	14.2	0.8	1.0
January, 96	16.9	32.7	3.9	0.6	4.1	6.2	12.2	42.7	0.2	3.9	40.9	7.1	1.5
February, 96	17.3	31.4	3.2	0.2	4.4	6.2	24.6	39.1	0.3	2.6	28.9	6.2	1.3
March, 96	15.2	32.2	4.4	0.6	5.0	15.3	12.3	73.7	0.5	2.6	29.2	8.8	0.8
April, 96	19.1	31.9	19.6	0.5	7.5	9.5	19.9	41.3	0.9	3.9	18.3	15.3	0.9
Average (Kg/day)	10.2	29.8	4.4	0.6	4.1	6.8	25.5	30.1	0.4	2.6	11.2	8.8	0.9

## Total Copper

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
April, 95	21	556	3,008	1,514	25		5	11	0	5	1	9	13
May, 95	21	690	49	4,024	24		5	12	1	5	1	48	15
June, 95	21	630	1,185	1,960	43		4	138	1	4	1	1	82
July, 95	21	680	154	2,035	42		4	138	1	4	1	1	30
August, 95	21	498	483	813	249		2	38	0	1	0	28	22
September, 95	9	434	2	2,320	52	10	1	57	0	1	0	4	7
October, 95	3	605	52	1,116	27	3	1	102	0	1	0	7	38
November, 95	24	661	122	1,785	51		1	31	0	1	0	7	103
December, 95	14	497	198	1,46	46		4	28	0	4	0	57	38
January, 96	59	686	1,562	729	113	27	12	71	0	4	4	1	38
February, 96	24	277	2,451	426	126	14	14	143	0	6	5	18	38
March, 96	15	635	1,192	1,336	131	137	12	981	0	4	2	56	58
April, 96	19	375	5,987	1,425	78	82	5	41	2	5	2	28	107
Average (Kg/day)	21	556	1,265	1,433	77	53	5	138	1	4	1	28	56

## Mass flow rate in effluent discharged by stream

## Dissolved Copper

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
April, 95	10.2	29.8	2.3	0.9	12.6		4.9	5.3	0.6	3.9	0.9	6.2	13
May, 95	10.2	30.0	0.9	1.0	12.4		4.9	7.0	1.2	3.9	0.9	7.7	4.1
June, 95	10.2	30.0	1.5	0.9	16.6		3.8	30.9	0.5	3.2	0.9	0.4	12.0
July, 95	10.2	30.0	2.0	0.9	21.7		3.7	30.9	0.5	3.2	0.9	0.4	2.4
August, 95	10.2	27.6	0.9	1.0	81.0		1.9	22.5	0.1	1.1	0.3	5.3	7.7
September, 95	2.3	29.9	0.3	0.9	15.9	6.1	1.4	28.4	0.1	1.1	0.3	4.3	1.3
October, 95	2.3	30.2	0.3	0.2	13.1	1.2	1.1	24.7	0.1	1.1	0.1	4.2	6.8
November, 95	2.6	24.1	0.9	0.7	14.3		1.0	16.5	0.4	1.1	0.1	7.5	3.1
December, 95	5.7	28.0	0.3	0.0	16.6		3.5	16.5	0.3	3.9	0.1	7.6	7.8
January, 96	16.9	32.7	368.6	0.6	16.4	20.7	12.2	35.6	0.1	5.2	3.0	0.3	2.7
February, 96	17.3	31.4	3.2	0.2	26.2	18.7	13.6	104.1	0.1	5.2	3.7	7.1	14.7
March, 96	15.2	32.2	59.1	0.6	50.0	92.7	12.3	62.4	0.2	2.6	2.2	6.2	9.9
April, 96	19.1	31.9	387.3	0.5	33.5	53.6	5.0	16.5	0.4	3.9	2.2	5.3	8.0
Average (Kg/day)	10.2	29.8	63.7	0.6	25.4	32.2	5.3	30.9	0.5	3.2	1.4	5.3	6.7



ne, 95	101,850	27,588	4,205	57,591	83,777	108,308	3,093	19,178	5,291	10,425	22,766
20,209	77,100	25,421	4,209	47,260	84,800	108,308	3,093	19,178	4,864	139,316	20,175
20,209	73,820	16,661	3,671	45,636	59,412	89,019	768	7,900	1,586	136,768	24,139
20,209	81,785	4,632	3,741	35,805	45,488	97,202	754	7,900	1,542	137,468	27,514
September, 95	82,858	3,669	855	37,167	37,402	90,280	794	9,141	337	250,839	31,708
October, 95	70,642	14,775	2,978	35,929	30,972	124,034	1,658	7,745	367	234,864	39,696
November, 95	106,028	4,681	1,135	50,949	66,190	100,395	1,863	30,198	26,203	8,325	39,568
December, 95	114,122	55,588	3,026	53,148	138,655	121,890	866	38,987	37,756	153,968	46,063
January, 96	117,824	53,518	808	51,368	198,851	215,563	1,419	17,346	25,080	126,134	41,701
February, 96	95,077	30,748	2,762	56,615	169,406	190,723	2,460	18,249	25,152	139,316	36,534
March, 96	106,197	100,747	2,240	68,837	90,785	102,205	8,506	25,361	19,996	94,086	28,638
April, 96	93,734	30,748	2,762	49,369	93,223	108,308	3,093	19,178	12,430	139,316	31,139
Average (Kg/ day)											

Mass flow rate in effluent discharged by stream

Month	1	2	3	4	5	6	7	8	9	10	11	12	13
April, 95	3,295	28,466	33,193	33,010	802	1,313	304	1,313	698	474	45	603	2,934
May, 95	3,295	59,000	3,115	115,813	1,337	1,051	243	1,051	524	193	56	765	14,753
June, 95	3,295	24,600	36,451	44,972	2,607	4,098	191	4,098	219	380	46	59	18,115
July, 95	3,295	34,500	9,993	58,301	2,318	4,098	183	4,098	219	380	45	733	1,658
August, 95	3,295	28,201	486	24,921	3,762	4,184	97	4,184	67	58	19	535	1,470
September, 95	3,723	6,579	160	100,681	5,655	917	84	917	65	360	15	408	4,054
October, 95	1,059	25,704	1,436	3,745	1,869	2,914	82	2,914	52	53	4	678	63,401
November, 95	3,530	17,251	7,569	28,019	2,915	3,073	59	3,073	139	0	6	1,664	6,625
December, 95	4,390	38,797	17,033	2,505	1,716	1,607	273	1,607	123	2,914	217	64	3,538
January, 96	6,269	43,428	67,120	14,117	5,680	2,565	1,068	2,565	67	52	232	1,629	6,548
February, 96	3,850	16,976	132,521	13,424	4,000	15,360	682	15,360	149	0	111	1,168	5,975
March, 96	1,291	26,866	59,404	45,233	2,320	4,082	613	4,082	257	0	110	733	9,839
April, 96	2,247	19,693	403,770	103,282	7,289	8,014	249	8,014	265	53	108	483	59,282
Average (Kg/ day)	3,295	28,466	59,404	45,233	3,252	4,098	317	4,098	219	380	78	733	15,246

## Appendix 2

Accompanying map of the sampling areas

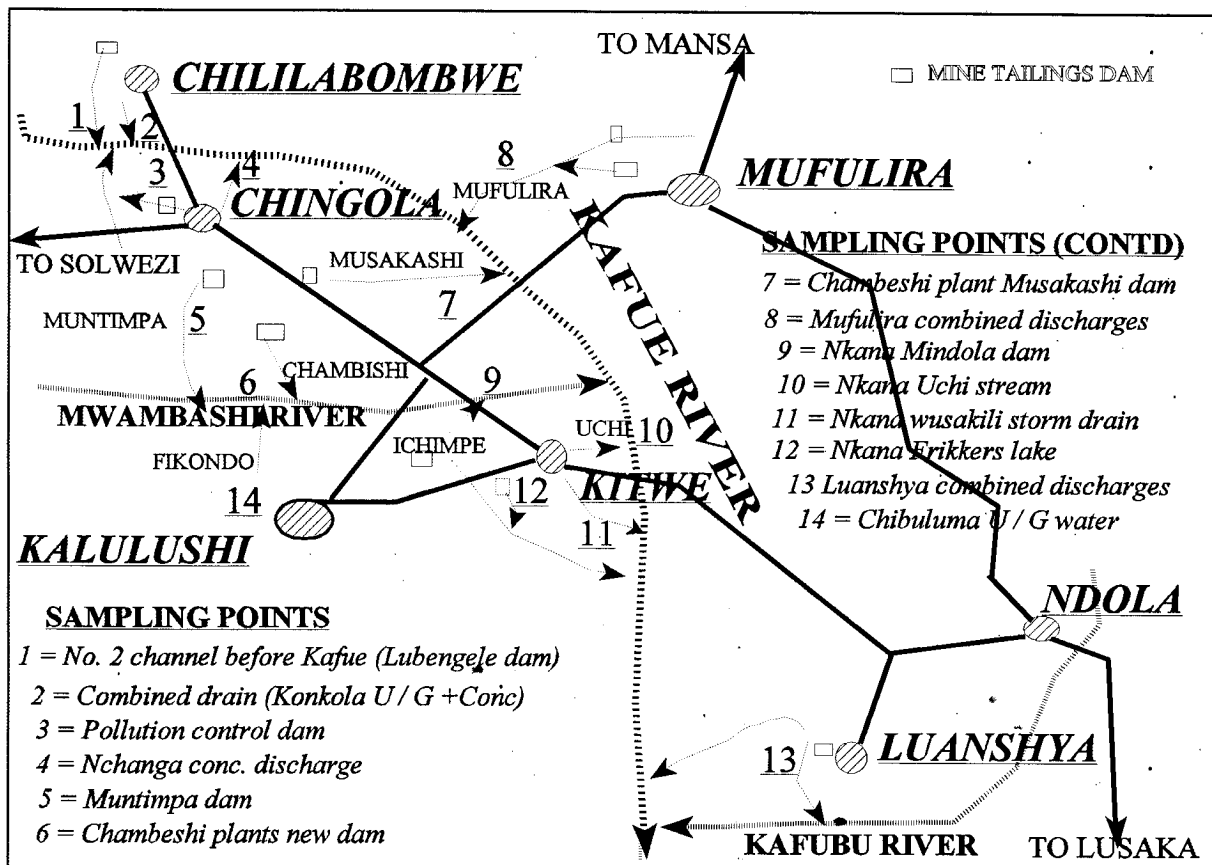


Fig. I - Routes taken by mine effluent to get to the Kafue river

# Appendix 3

Project data

	pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
5	7.63	19.88	0.380	88.5	0.366	13	1.135	1.566
	7.66	16.26	0.397	84.6	0.397		1.301	1.640
	7.59	17.68	0.495	92.4	0.408	11	1.235	1.700
	7.65	15.73	0.372	85.7	0.422	12	1.229	1.750
	7.59	17.96	0.388	80.0	0.463	15	1.285	1.750
	7.86	19.70	0.379	83.7	0.524	13	1.266	1.908
	8.02	20.12	0.373	82.5	0.671		1.270	1.920
	7.72	20.20	0.364	83.0	0.675		1.257	2.060
	7.67	23.04	0.385	86.0	0.682		1.348	2.170
	8.51	22.70	0.398	139.0	0.696		1.024	2.280
	8.03	24.10	0.388	99.3	0.840	10	1.259	2.310
	7.86	25.12	0.517	88.7	1.246	15	1.122	2.200
	7.85	25.67	0.404	92.0	1.073	17	1.210	2.360
	7.75	25.17	0.391	76.0	1.039		1.153	2.420
	7.32	22.86	0.403	63.0	0.899	97	0.692	1.480
	7.52	24.87	0.415	70.5	0.876	12	1.145	1.810
	7.59	24.10	0.425	74.3	0.732	15	1.303	2.020
	7.17	22.15	0.416	56.7	0.418	353	0.651	0.920
	7.08	23.25	0.403	67.8	0.426	60	0.912	0.900
	7.10	23.98	0.407	71.3	0.375	27	0.946	0.960
	7.23	24.34	0.396	74.0	0.378	20	1.176	1.100
	7.27	23.96	0.401	76.7	0.420	15	1.207	1.220
	7.17	23.71	0.412	71.0	0.265	25	1.053	0.920
	7.19	24.35	0.412	77.0	0.302	22	0.977	1.060
	7.09	23.51	0.401	78.3	0.263	26	0.841	0.890
	7.29	23.58	0.474	75.5	0.315	25	1.021	1.000
	7.15	24.28	0.417	74.6	0.229	33	0.923	0.930
	7.23	23.83	0.428	77.7	0.226	70	0.822	0.920
	7.21	24.52	0.487	73.7	0.215	40	1.026	0.970
	7.21	24.85	0.406	79.0	0.197	39	1.020	0.990
	7.04	22.98	0.422	75.8	0.212	35	0.947	0.800
	7.13	23.81	0.517	77.8	0.184	15	0.984	0.930
	7.30	25.09	0.570	83.0	0.188	23	1.163	1.360
	7.31	23.92	0.572	81.0	0.191	15	1.222	1.060

date	(m3/s)	6Fis Fe umol/l	6Fis S mmol/l	6Fis Ba umol/l	6Fis Cd umol/l	6Fis Co umol/l	6Fis Cu umol/l	Aqueous conc umol/l	Aqueous conc umol/l	6Fis Mn umol/l	Aqueous conc umol/l	6Fis Pb umol/l	Aqueous conc mg/l	TSS (mg/l)
-May-95	35.13	0.001	0.970	0.439	0.001	0.716	0.999	0.999	0.999	3.040	0.002	0.002	6.45	
-Jun-95	18.38	0.000	1.101	0.377	0.000	1.660	0.615	0.615	0.615	3.331	0.001	0.001	4.07	
-Jun-95	17.2	0.000	1.129	0.489	0.001	0.426	0.467	0.467	0.467	2.803	0.001	0.001	3.35	
-Jul-95	18.6	0.000	1.226	0.395	0.000	0.565	0.406	0.406	0.406	2.858	0.000	0.000	5.53	
-Jul-95	17.56	0.000	1.375	0.502	0.001	0.904	0.312	0.312	0.312	3.094	0.001	0.001	18.74	
-Aug-95	17.13	0.000	1.687	0.585	0.000	0.743	0.272	0.272	0.272	2.967	0.002	0.002	6.27	
-Aug-95	15.54	0.000	2.433	0.463	0.001	0.273	0.296	0.296	0.296	1.318	0.001	0.001		
-Sep-95	12.68	0.000	2.405	0.561	0.001	0.137	0.228	0.228	0.228	1.638	0.001	0.001	12.12	
-Sep-95	11.14	0.001	2.352	0.488	0.000	0.202	0.264	0.264	0.264	2.257	0.001	0.001	3.68	
-Sep-95	10.3	0.001	2.436	0.526	0.000	0.251	0.313	0.313	0.313	1.500	0.005	0.005	19.07	
-Oct-95	10.42	0.000	3.212	0.566	0.000	0.079	0.231	0.231	0.231	0.299	0.001	0.001	8.43	
-Oct-95	10.33	0.000	6.019	0.724	0.001	0.123	0.165	0.165	0.165	0.380	0.001	0.001	12.83	
-Nov-95	9.37	0.000	4.741	0.605	0.000	0.394	0.228	0.228	0.228	1.533	0.002	0.002	9.88	
-Nov-95	15.28	0.000	4.460	0.631	0.000	1.424	0.326	0.326	0.326	2.949	0.003	0.003	10.14	
-Nov-95	21.96	0.000	3.992	0.595	0.000	0.709	0.253	0.253	0.253	3.458	0.000	0.000	56.47	
-Dec-95	15.88	0.001	3.774	0.561	0.001	0.326	0.214	0.214	0.214	1.045	0.004	0.004	10.21	
-Dec-95	17.14	0.000	2.751	0.467	0.000	0.257	0.214	0.214	0.214	1.948	0.002	0.002	11.12	
-Dec-95	63.82	0.001	1.513	0.410	0.002	2.851	0.947	0.947	0.947	3.604	0.005	0.005	256.93	
-Dec-95	123.25	0.001	1.581	0.355	0.001	0.450	0.565	0.565	0.565	1.929	0.002	0.002	38.14	
-Jan-96	94.13	0.001	1.304	0.355	0.001	0.748	0.733	0.733	0.733	1.875	0.002	0.002	21.72	
-Jan-96	75.93	0.001	1.282	0.352	0.000	0.268	0.500	0.500	0.500	1.758	0.002	0.002	15.13	
-Jan-96	70.31	0.002	1.400	0.356	0.001	1.166	0.804	0.804	0.804	1.802	0.002	0.002	12.79	
-Jan-96	155.49	0.002	0.798	0.320	0.000	0.555	0.617	0.617	0.617	1.225	0.001	0.001	17.97	
-Feb-96	133.16	0.002	0.798	0.327	0.000	0.646	0.951	0.951	0.951	1.278	0.005	0.005	14.80	
-Feb-96	116.64	0.002	0.908	0.298	0.000	0.582	0.977	0.977	0.977	1.500	0.001	0.001	15.01	
-Feb-96	169.73	0.002	0.608	0.317	0.000	0.275	0.996	0.996	0.996	1.048	0.001	0.001	16.60	
-Mar-96	213.17	0.002	0.508	0.366	0.000	0.326	2.125	2.125	2.125	1.766	0.002	0.002	18.89	
-Mar-96	221.16	0.003	0.402	0.326	0.000	0.138	2.046	2.046	2.046	1.580	0.001	0.001	18.41	
-Mar-96	271.85	0.003	0.387	0.312	0.000	0.146	2.487	2.487	2.487	1.893	0.002	0.002	10.26	
-Apr-96	240.36	0.004	0.365	0.305	0.000	0.138	2.455	2.455	2.455	1.820	0.002	0.002	7.92	
-Apr-96	217.71	0.004	0.362	0.280	0.000	0.164	2.439	2.439	2.439	1.691	0.001	0.001	6.60	

Date	Rate (m3/s)	Fe	Mn	Ba	Cd	Co	Cu	Pb
1-May-95	35.13	426.136	0.485	0.154	0.021	8.976	149.864	2.976
3-Jun-95	18.38	278.161	0.278	0.082	0.011	4.895	72.311	1.769
3-Jun-95	17.2							
3-Jul-95	18.6	253.378	7.658	1.914	ERR			ERR
4-Jul-95	17.56	342.495	12.262	0.093	0.014	5.919	74.760	3.619
7-Aug-95	17.13	279.605	25.329	2.730	ERR			ERR
7-Aug-95	15.54	320.638	80.379	0.000	0.023	12.835	75.152	4.383
5-Sep-95	12.68							
1-Sep-95	11.14	238.393	31.607	2.563	0.001	0.001	0.046	0.008
3-Sep-95	10.3							
1-Oct-95	10.42	235.440	125.158	0.000		18.191	23.876	
1-Oct-95	10.33							
5-Nov-95	9.37	334.332	145.986	0.000	0.036	27.229	74.072	15.760
1-Nov-95	15.28							
1-Nov-95	21.96	3260.441	68.691	0.000	0.080	20.114	177.424	10.871
1-Dec-95	15.88	559.835	152.717	0.000	0.057	33.967	110.790	9.915
1-Dec-95	17.14	652.386	73.461	0.000	0.057	22.821	125.866	10.244
1-Dec-95	63.82	13941.376	185.938	0.000	0.196	124.123	1464.474	37.316
1-Dec-95	123.25	2040.119	50.991	0.000	ERR			ERR
1-Jan-96	94.13	1326.577	32.485	0.000	0.040	14.439	177.336	5.537
1-Jan-96	75.93	1078.407	32.894	0.000	0.055	13.551	150.000	5.253
1-Jan-96	70.31	1005.443	26.525	0.000	0.022	13.582	179.087	3.642
1-Jan-96	155.49	1173.712	45.926	0.000	0.020	14.552	144.444	2.742
1-Feb-96	133.16	1027.932	30.016	0.000	0.015	8.966	126.437	4.080
1-Feb-96	116.64	968.884	36.551	0.000	0.014	11.201	125.789	2.068
1-Feb-96	169.73	1136.587	53.308	0.000	0.011	11.531	134.227	1.698
1-Mar-96	213.17	1389.546	52.733	0.000	0.010	9.941	203.209	2.121
1-Mar-96	221.16	1246.290	49.799	0.000	0.010	9.135	170.769	1.300
1-Mar-96	271.85	706.403	27.041	0.000	0.008	5.680	119.593	0.912
1-Apr-96	240.36	484.090	16.597	0.000	0.006	3.794	101.340	0.721
1-Apr-96	217.71	405.148	16.414	0.000	0.006	3.799	87.929	0.542

ate	pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
0-Jun-95	7.68	16.65	0.411	92.7	0.323		1.232	1.754
0-Jun-95	7.69	17.70	0.397	96.5	0.332		1.262	1.79
7-Jul-95	7.69	16.69	0.386	92.0	0.363	48	1.176	1.754
0-Jul-95	7.62	18.40	0.318	89.7	0.370	14	1.135	1.77
0-Aug-95	7.74	20.19	0.380	96.3	0.400	9	1.200	1.87
0-Aug-95	8.08	19.80	0.374	104.5	0.412	16	1.246	1.95
1-Sep-95	7.96	20.24	0.366	92.0	0.422	15	1.267	2.06
0-Sep-95	8.18	21.71	0.385	95.0	0.476	5	1.140	2.18
0-Sep-95	8.25	22.45	0.401	98.0	0.500	14	1.082	2.22
0-Oct-95	8.32	24.05	0.393	94.0	0.514	11	1.280	2.4
0-Oct-95	8.19	24.96	0.479	96.3	0.537	57	1.133	2.54
0-Nov-95	8.47	25.02	0.375	92.7	0.627	9	0.635	2.5
0-Nov-95	7.56	25.05	0.409	74.0	0.539	10	1.086	1.76
0-Dec-95	7.78	24.48	0.425	92.3	0.508	9	1.288	1.97
0-Dec-95	7.06	22.60	0.415	85.3	0.277	70	0.754	0.82
0-Jan-96	7.35	24.52	0.396	81.5	0.288	19	0.989	1.15
0-Jan-96	7.24	23.38	0.426	85.7	0.203	115	0.795	0.9
0-Feb-96	7.28	23.71	0.481	93.0	0.215	45	0.772	1.02
0-Feb-96	7.26	24.19	0.420	90.8	0.188	107	0.657	1.02
0-Mar-96	7.30	24.70	0.426	87.3	0.180	91	0.782	0.97
0-Mar-96	7.15	23.78	0.374	83.5	0.175	65	0.773	0.84
0-Apr-96	7.37	24.93	0.564	88.8	0.163	28	1.052	1.04





pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
7.56	25.80	0.398	78.9	0.211		1.465	1.310
7.65	25.76	0.399	79.1	0.210		1.483	1.360
7.60	25.09	0.401	81.2	0.198	3	1.492	1.330
7.50	24.96	0.383	77.7	0.194	12		1.150
7.59	23.33	0.389	85.4	0.217	14	1.447	1.360
7.71	23.15	0.410	89.3	0.259	39		1.400
7.91	22.88	0.372	96.0	0.283	55	1.378	1.600
8.09	22.40	0.376	95.6	0.290	79	1.458	1.600
8.30	20.94	0.349	94.0	0.357	7	1.491	1.774
8.31	17.99	0.367	93.2	0.379	11	1.454	1.870
8.49	17.49	0.356	95.5	0.375	78	1.282	1.974
8.54	22.04	0.335	99.3	0.456	6	1.262	2.210
8.12	24.45	0.385	80.8	0.539	28	1.312	2.100
8.03	25.21	0.396	74.0	0.626	51	1.142	2.400
8.06	27.60	0.381	78.3	0.719	7	1.213	2.140
8.05	27.45	0.404	96.0	0.607	13	1.215	1.740
7.44	25.76	0.399	69.9	0.313	19	1.016	1.420
7.39	25.19	0.424	75.9	0.246	6	1.393	1.420
7.11	26.29	0.455	67.6	0.174	4	1.452	1.120
7.19	26.16	0.579	75.3	0.173	12	1.649	1.180

Discharge		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc		Aqueous conc	
Rate	(m3/s)	mmol/l	6Fis Fe	mmol/l	6Fis S	umol/l	6Fis Ba	umol/l	6Fis Cd	umol/l	6Fis Co	umol/l	6Fis Cu	umol/l	6Fis Mn	umol/l	6Fis Pb	mg/l	TSS (mg/l)
276.80		0.001	0.377	0.331	0.001	0.016	0.884	0.021	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009	2.23	
254.80		0.002	0.311	0.274	0.000	0.013	1.086	0.015	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	2.70	
201.20		0.002	0.312	0.339	0.000	0.013	1.045	0.019	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	2.73	
227.50		0.002	0.346	0.353	0.000	0.012	1.076	0.017	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	2.83	
200.10		0.003	0.352	0.335	0.000	0.015	1.092	0.019	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	3.60	
116.80		0.001	0.518	0.362	0.000	0.015	0.765	0.021	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	2.33	
41.20		0.000	0.926	0.347	0.000	0.012	0.291	0.351	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.48	
64.80		0.000	0.621	0.328	0.000	0.009	0.433	0.024	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	1.41	
46.60		0.002	0.580	0.311	0.004	0.044	0.812	0.033	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	1.18	
29.30		0.000	0.986	0.449	0.000	0.011	0.222	0.043	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	2.32	
27.80		0.000	0.911	0.304	0.000	0.011	0.203	0.038	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	3.61	
22.00		0.000	0.926	0.347	ERR	0.012	0.291	0.029	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	7.89	
14.80		ERR	1.194	0.510	0.004	0.023	0.274	0.067	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	5.81	
13.30		ERR	1.659	0.604	0.002	0.023	0.152	0.067	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	5.83	
11.50		ERR	2.005	0.779	0.004	0.059	0.138	0.107	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	7.48	
55.10		0.000	2.688	0.830	0.004	0.021	0.141	0.091	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	9.46	
150.00		0.000	2.205	0.660	0.005	0.047	0.331	0.099	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	12.00	
187.30		0.002	0.780	0.371	0.004	0.021	0.751	0.040	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	4.46	
287.80		0.001	0.524	0.333	0.003	0.028	0.590	0.539	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	2.58	
402.80		0.001	0.267	0.262	0.004	0.018	0.628	0.025	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	1.41	

Rate	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l	ug/l
(m3/s)	Fe	Mn	Ba	Cd	Co	Cu	Pb	
276.80								
254.80								
201.20								
227.50								
200.10	177.812	17.477	1.368	0.003	1.819	33.019	0.195	
116.80								
41.20								
64.80								
46.60					0.700	8.438	0.082	
29.30								
27.80								
22.00								
14.80								
13.30	123.450	110.916	2.480	0.005	1.433	8.359	0.090	
11.50	47.512	159.953	2.974	0.004	2.249	6.355	0.070	
55.10								
150.00								
187.30								
287.80								
402.80	95.884	12.619	0.796					

	pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
	7.39	27.49	0.441	74.8	0.122		1.654	0.595
	7.39	26.43	0.384	73.0	0.125		1.700	0.580
	7.37	25.82	0.387	70.1	0.119	9	1.656	0.530
	7.25	26.07	0.382	69.8	0.121	8	1.634	0.590
	7.38	24.51	0.375	66.1	0.134	3	1.615	0.645
	7.29	24.46	0.358	75.8	0.140	4	1.730	0.662
	7.39	23.84	0.383	77.0	0.147	44	1.733	0.700
	7.41	22.30	0.393	75.0	0.154	3	1.646	0.733
	7.37	20.75	0.374	78.0	0.153	8	1.595	0.720
	7.48	21.47	0.367	82.2	0.155	2	1.599	0.758
	7.80	18.32	0.351	96.6	0.158	4	1.543	0.780
	7.83	16.42	0.382	87.7	0.160	4	1.602	0.785
	7.84	16.76	0.369	91.0	0.166		1.505	0.835
	7.67	19.44	0.327	86.5	0.178		1.507	0.860
	7.78	21.41	0.346	101.7	0.196	27	1.456	0.960
	7.84	22.06	0.386	88.8	0.212		1.502	1.025
	7.95	23.85	0.400	95.3	0.235	7	1.538	1.130
	7.99	23.98	0.418	89.0	0.257		1.575	1.230
	7.98	25.67	0.398	83.0	0.280	3	1.474	1.330
	8.29	29.49	0.388	114.7	0.301	5	1.561	1.430
	8.32	27.46	0.413	92.0	0.328	30		1.570
	8.19	25.41	0.392	78.0	0.327	8	1.604	1.570
	8.45	28.94	0.383	120.7	0.322	1	1.544	1.545
	8.17	24.05	0.389	85.3	0.311	8	1.548	1.495
	8.06	27.72	0.418	92.0	0.302	2	1.426	1.330
	8.00	24.86	0.402	85.3	0.306	3	1.623	1.380
	7.91	25.65	0.416	90.0	0.302	3	1.596	1.250
	7.71	25.02	0.433	84.3	0.318	8	1.633	1.180
	7.19	25.99	0.416	71.3	0.208	5	1.377	0.820
	7.25	25.93	0.407	67.3	0.217	1	1.469	0.920
	7.52	25.75	0.429	86.0	0.220	1	1.611	0.990
	7.26	24.69	0.406	72.0	0.179	5	1.362	0.795
	6.94	25.01	0.374	55.4	0.136	1	1.514	0.580
	6.99	25.09	0.377	56.0	0.148	2	1.481	0.660
	7.12	24.49	0.477	59.3	0.179	5	1.540	0.770
	7.00	24.33	0.381	64.8	0.146	2	1.478	0.640
	6.99	24.29	0.399	53.8	0.133	2	1.602	0.580
	6.91	25.38	0.378	60.1	0.114	2	1.571	0.520
	6.94	25.43	0.387	60.6	0.114	3	1.660	0.535
	6.87	24.02	0.407	65.6	0.094	6	1.660	0.440
	6.94	24.81		72.0	0.105	1	1.553	0.475
	7.06	25.94		75.0	0.109	3	1.692	0.520
	7.04	25.29		71.3	0.108	6	1.683	0.520

date	(mbs)	1rag Fe	1rag S	1rag Ba	1rag Cd	1rag Co	1rag Cu	1rag Mn	1rag Pb	TSS (mg/l)
-Mar-95	108.22	0.004	0.014	0.098	0.001	0.009	0.067	0.096	0.096	1.370
-Mar-95	105.84	0.005	0.011	0.118	0.000	0.003	0.051	0.081	0.001	0.937
-Apr-95	99.87	0.005	0.008	0.141	0.000	0.003	0.051	0.078	0.000	1.115
-Apr-95	87.12	0.005	0.010	0.141	0.000	0.003	0.037	0.080	0.001	1.284
-Apr-95	43.30	0.003	0.010	0.092	0.000	0.003	0.032	0.078	0.001	1.410
-May-95	29.95	0.003	0.018	0.142	0.000	0.005	0.020	0.112	0.000	2.005
-May-95	24.53	0.004	0.011	0.130	0.000	0.002	0.020	0.087	0.000	1.237
-May-95	17.80	0.003	0.012	0.141	0.000	0.002	0.027	0.090	0.000	0.902
-May-95	14.36	0.003	0.013	0.117	0.000	0.002	0.014	0.072	0.000	1.102
-Jun-95	7.22	0.003	0.020	0.083	0.000	0.002	0.000	0.045	0.000	1.013
-Jun-95	4.82	0.003	0.027	0.074	0.000	0.002	0.000	0.034	0.000	4.132
-Jul-95	3.90	0.002	0.028	0.075	0.000	0.001	0.000	0.039	0.000	2.345
-Jul-95	3.14	0.003	0.032	0.100	0.000	0.001	0.008	0.079	0.000	4.968
-Aug-95	2.13	0.002	0.034	0.133	0.000	0.002	0.000	0.118	0.000	1.986
-Aug-95	1.86	0.002	0.032	0.162	0.000	0.003	0.014	0.237	0.000	7.144
-Sep-95	1.20	0.001	0.038	0.184	0.000	0.003	0.013	0.331	0.000	3.501
-Sep-95	1.20	0.001	0.041	0.208	0.000	0.003	0.023	0.277	0.000	3.505
-Oct-95	1.13	0.001	0.052	0.207	0.005	0.004	0.016	0.357	0.000	1.506
-Oct-95	1.12	0.001	0.057	0.227	0.000	0.003	0.019	0.275	0.000	2.365
-Nov-95	1.20	0.001	0.050	0.197	0.000	0.004	0.018	0.686	0.000	1.608
-Nov-95	1.20	0.001	0.060	0.211	0.001	0.004	0.031	0.482	0.000	2.696
-Nov-95	1.20	0.001	0.060	0.157	0.000	0.004	0.022	0.288	0.000	4.314
-Dec-95	2.20	0.001	0.081	0.162	0.000	0.003	0.021	0.160	0.000	1.435
-Dec-95	3.01	0.001	0.073	0.163	0.000	0.006	0.016	0.171	0.000	2.768
-Dec-95	2.12	0.002	0.165	0.207	0.000	0.007	0.028	0.115	0.000	1.802
-Dec-95	2.87	0.004	0.371	0.181	0.000	0.005	0.093	0.182	0.000	ERR
-Jan-96	5.48	0.005	0.224	0.218	0.000	0.005	0.039	0.229	0.001	1.967
-Jan-96	6.34	0.010	0.164	0.169	0.000	0.005	0.000	0.302	0.000	2.918
-Jan-96	4.42	0.007	0.126	0.151	0.001	0.004	0.000	0.168	0.000	1.816
-Jan-96	11.21	0.005	0.110	0.125	0.000	0.003	0.040	0.161	0.020	1.788
-Jan-96	25.50	0.004	0.074	0.140	0.000	0.003	0.021	0.187	0.000	5.335
-Feb-96	23.00	0.004	0.072	0.136	0.000	0.003	0.027	0.198	0.001	1.888
-Feb-96	25.74	0.005	0.104	0.114	0.000	0.002	0.018	0.153	0.000	2.359
-Feb-96	40	0.003	0.067	0.106	0.000	0.002	0.000	0.107	0.000	2.175
-Feb-96	50	0.003	0.027	0.098	0.000	0.002	0.020	0.103	0.000	2.150
-Mar-96	57.33	0.003	0.020	0.097	0.000	0.002	0.000	0.089	0.000	2.372
-Mar-96	79.60	0.004	0.016	0.090	0.000	0.001	0.020	0.070	0.000	2.069
-Mar-96	95.71	0.004	0.016	0.095	0.000	0.001	0.009	0.048	0.000	1.809
-Mar-96	111.32	0.004	0.016	0.095	0.000	0.002	0.009	0.047	0.000	ERR
-Apr-96	110.46	0.004	0.015	0.094	0.000	0.001	0.274	0.044	0.001	1.208
-Apr-96	111.38	0.006	0.013	0.000	0.080	0.479	0.000	0.080	0.000	1.960
										1.008

date	(m3/s)	Fe	Mn	Ba	Cd	Co	Cu	Pb
Mar-95	108.22	90.909	5.288	0.352	0.002	0.057	0.183	0.019
Mar-95	105.84	109.123	5.233	0.337	0.002	0.062	0.199	0.019
Apr-95	99.87	115.675	5.571	0.424	0.002	0.064	0.184	0.026
Apr-95	87.12	116.932	6.203	0.448	0.002	0.054	0.186	0.019
Apr-95	43.30							
May-95	29.95							
May-95	24.53	103.107	4.232	0.522	0.003	0.075	0.170	0.017
May-95	17.80							
May-95	14.36	98.312	3.163	0.440	0.002	0.077	0.151	0.018
Jun-95	7.22	101.146	2.182	0.487	0.001	0.036	0.137	0.015
Jun-95	4.82	98.361	3.909	1.931	0.002	0.084	0.180	0.022
Jul-95	3.90							
Jul-95	3.14	95.387	3.984	0.773	0.002	0.086	0.204	0.018
Aug-95	2.13				0.001	0.025	0.101	0.010
Aug-95	1.86	125.478	4.471	0.720	0.001	0.104	0.230	0.024
Sep-95	1.20							
Sep-95	1.20	87.623	10.460	0.545	0.002	0.068	0.252	0.024
Oct-95	1.13							
Oct-95	1.12	93.750	7.730	0.817	0.003	0.095	0.278	0.023
Nov-95	1.20							
Nov-95	1.20	74.564	8.479	2.087	0.002	0.080	0.166	0.022
Nov-95	1.20							
Dec-95	2.20	136.438	11.846	1.487	0.006	0.115	0.242	0.032
Dec-95	3.01	81.169	10.606	0.563	0.002	0.048	0.214	0.025
Dec-95	2.12	79.498	8.525	0.433	0.002	0.062	0.167	0.020
Dec-95	2.87	109.890	5.495	0.534	0.002	0.047	0.222	0.019
Jan-96	5.48	175.939	9.458	0.987	0.006	0.083	0.518	0.040
Jan-96	6.34	193.750	9.722	0.938	0.003	0.066	0.614	0.033
Jan-96	4.42	158.052	5.368	0.582	0.002	0.057	0.272	0.024
Jan-96	11.21	281.261	16.558	1.705	0.005	0.129	0.863	0.060
Jan-96	25.50	152.281	5.203	0.509	0.003	0.075	0.448	0.034
Feb-96	23.00	160.858	4.718	0.564	0.002	0.115	0.343	0.052
Feb-96	25.74	115.070	3.803	0.439	0.002	0.083	0.309	0.025
Feb-96	40	139.333	4.900	1.987	0.002	0.133	0.330	0.033
Feb-96	50	109.000	4.195	0.404	0.001	0.028	0.151	0.014
Mar-96	57.33	112.700	3.690	0.549	0.002	0.093	0.264	0.028
Mar-96	79.60	94.760	4.192	0.307	0.002	0.074	0.208	0.019
Mar-96	95.71	109.558	4.041	0.490	0.001	0.091	0.248	0.033
Mar-96	111.32	74.706	4.182	0.311	0.002	0.065	0.218	0.022
Apr-96	110.46	82.030	3.645	0.235	0.002	0.053	0.210	0.020
Apr-96	111.38	86.035	3.853	0.233	0.001	0.050	0.191	0.015

	pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
5	7.49	20.39	0.380	79.2	0.734	11	1.591	1.746
5	7.56	19.61	0.326	82.9	0.685	13	1.412	1.984
5	7.63	18.74	0.351	90.1	0.670	5	1.377	1.980
5	7.52	18.16	0.361	92.4	0.999	4	1.479	1.750
5	7.72	17.38	0.355	87.3	0.607	13	1.371	2.160
5	7.83	15.08	0.400	81.5	0.557	9	1.344	2.460
5	7.86	15.54	0.394	85.5	0.462	7	1.432	2.510
	7.84	14.06	0.384	95.1	0.434	11	1.308	2.770
5	7.73	17.11	0.335	83.5	0.572	11	1.348	2.800
5	7.73	17.84	0.358	92.0	1.413	8	1.381	1.980
5	7.87	18.81	0.367	90.0	1.324	14	1.418	2.530
5	7.90	19.93	0.368	87.3	1.111	13	1.507	3.050
5	7.90	20.34	0.391	83.5	1.176	12	1.506	3.200
5	7.84	21.01	0.416	72.8	1.418	10	1.568	3.040
5	7.67	22.57	0.372	74.8	2.280	6	1.524	2.060
5	7.95	22.42	0.389	76.8	1.700	9	1.701	2.860
5	7.49	22.60	0.370	64.3	1.328	46	0.865	2.280
5	7.23	21.41	0.371	71.5	0.797	340	0.394	1.290
5	6.83	21.18	0.351	64.3	0.574	240	0.556	0.900
5	6.97	24.57	0.325	64.3	0.685	4	1.409	1.320
5	7.15	23.32	0.319	66.0	0.659	5	1.491	1.500
5	7.09	23.58	0.325	61.5	0.722	1	1.493	1.370
5	7.05	22.95	0.341	61.0	0.598	4	1.467	1.420
5	7.15	22.87	0.356	58.0	0.684	1	1.574	1.420
5	7.13	23.52	0.346	66.6	0.515	2	1.476	1.460
5	7.18	23.00	0.353	64.8	0.572	2	1.536	1.440
5	7.15	23.61	0.345	56.0	0.565	13	1.479	1.420
5	7.17	23.84	0.347	64.0	0.502	8	1.625	1.520
5	7.01	22.39	0.335	60.0	0.422	3	1.412	1.020
5	7.12	23.40	0.369	68.4	0.467	1		1.390
5	7.18	23.17	0.461	65.3	0.458	13	1.476	1.010



Rate (m3/s)	mmol/l 5Gar Fe	mmol/l 5Gar S	umol/l 5Gar Ba	umol/l 5Gar Cd	umol/l 5Gar Co	umol/l 5Gar Cu	umol/l 5Gar Mn	umol/l 5Gar Pb	mg/l TSS
26-Apr-95	4.64	0.001	3.038	0.275	0.000	0.036	0.057	0.023	6.45
05-May-95	1.76	0.000	2.610	0.358	0.000	0.026	0.040	0.036	3.50
12-May-95	2.86	0.000	2.501	0.303	0.000	0.029	0.057	0.032	3.98
18-May-95	3.98	0.000	4.678	0.240	0.000	0.044	0.039	0.021	2.95
31-May-95	2.9	0.001	2.186	0.232	0.000	0.031	0.034	0.038	4.00
15-Jun-95	1.83	0.001	1.653	0.232	0.000	0.033	0.042	0.029	3.87
26-Jun-95	1.78	0.001	1.148	0.244	0.000	0.026	0.045	0.030	3.66
12-Jul-95	1.59	0.001	0.964	0.296	0.000	0.035	0.061	0.028	7.43
03-Aug-95	1.52	0.000	1.656	0.289	0.000	0.063	0.060	0.027	14.10
14-Aug-95	1.63	0.000	7.579	0.443	0.000	0.101	0.035	0.027	22.77
28-Aug-95	1.52	0.000	6.861	0.370	0.000	0.054	0.027	0.031	4.77
15-Sep-95	1.26	0.000	5.052	0.354	0.000	0.049	0.027	0.030	2.90
27-Sep-95	1.17	0.000	5.333	0.357	0.000	0.052	0.026	0.032	3.40
12-Oct-95	1.97	0.000	7.048	0.400	0.000	0.055	0.039	0.043	3.06
26-Oct-95	1.61	0.001	13.972	0.467	0.000	0.169	0.062	0.053	8.18
10-Nov-95	1.16	0.001	9.263	0.368	0.000	0.060	0.036	0.064	2.00
20-Nov-95	2.18	0.000	6.861	0.363	0.000	0.344	0.145	0.058	25.98
06-Dec-95	2.45	0.001	3.680	0.254	0.000	0.275	0.192	0.038	188.69
18-Dec-95	6.29	0.002	2.339	0.236	0.000	0.762	0.257	0.022	145.98
03-Jan-96	11.1	0.001	3.031	0.244	0.004	0.256	0.139	0.043	2.08
19-Jan-96	14.24	0.001	2.713	0.176	0.001	0.089	0.064	0.028	2.15
31-Jan-96	16.23	0.001	3.000	0.210	0.001	0.081	0.062	0.024	1.73
07-Feb-96	10.13	0.001	2.389	0.196	0.003	0.055	0.075	0.028	3.04
14-Feb-96	22.74	0.001	2.838	0.195	0.002	0.056	0.060	0.025	2.95
20-Feb-96	15.67	0.001	1.946	0.165	0.002	0.031	0.062	0.029	1.76
28-Feb-96	26.16	0.001	2.205	0.185	0.001	0.029	0.054	0.024	2.00
06-Mar-96	23.05	0.001	2.099	0.185	0.001	0.029	0.057	0.021	2.56
14-Mar-96	19.03	0.001	1.787	0.202	0.001	0.025	0.070	0.027	1.87
20-Mar-96	12.99	0.001	1.485	0.250	0.003	0.026	0.076	0.028	4.44
26-Mar-96	11.54	0.001	1.737	0.212	0.002	0.035	0.069	0.025	2.74
03-Apr-96	15.45	0.001	1.606	0.218	0.002	0.033	0.057	0.026	2.44

	pH	Temp (C)	Redox (V)	Diss. Oxy (%)	Conductivity (mS/ cm)	Turbidity NTU	Log (filtrate) (liters)	Alkalinity (mequiv./ l)
-95	8.08	29.12	0.395	92.4	0.458	150.0		2.88
95	8.01	28.90	0.372	96.0	0.458	90.0		2.84
-95	8.11	29.43	0.382	100.0	0.451			2.88
-95	8.08	29.60	0.403	95.0	0.472	60.0		2.84
-95	8.06	29.50	0.383	96.0	0.448	100.0		2.8
-95	8.06	29.37	0.387	95.0	0.442	75.0		2.89
-95	8.01	29.89	0.398	99.0	0.457	80.0		2.86
-96	8.10	29.72	0.381	99.0	0.457	100.0		2.84
-96	8.06	29.37	0.394	98.0	0.462	60.0		2.8
-96	8.03	29.29	0.477	98.0	0.443	75.0		2.91