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**ENVIRONMENTAL CONSIDERATIONS IN THE DESIGN  
OF BASE METALS REFINERIES**

**METALS IN RIVERINE SYSTEMS**

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## **EXECUTIVE SUMMARY**

There is a need for engineers involved in the design of base metals refineries to understand the impacts of their designs on the environment. Design engineers should move their focus away from meeting effluent release concentration limits to identifying potential environmental impacts. Further, including waste treatment facilities within the site boundary and producing information suitable for inclusion in a life cycle evaluation and mass integration procedures were required for environmentally conscious design.

It has been estimated that 85% of the life cycle costs of chemical plants are determined during the design phases. Further, an estimated 50% of capital expenditure on new plants is associated with process issues pertaining to environmental management. Formal environmental assessments such as Environmental Impact Assessments are only performed between the Definitive Estimate and the Detailed Engineering phases of projects, or later. This is often too late to significantly incorporate environmental constraints in the core process and remedial waste treatment processes are appended to meet legislative requirements. Early assessment of environmental impacts is required from the information available at the specific stage of the design process. Tools such as Life Cycle Assessment are currently available to evaluate the impact of releases, but these are deficient when considering the impact of releases to riverine ecosystems, specifically metal releases. Hence, there is a need to develop meaningful indicators of environmental performance which can shape minerals process design, from concept- to detailed engineering- stages. This is the focus of this work, specifically for the release of metal-containing aqueous effluents from base metals processing.

### **Predicting Environmental Concentration of Metals in Rivers**

The majority of the work conducted on freshwater systems has concentrated on the behaviour of pollutants in lake systems. This current work examines the behaviour of pollutants in river systems, building on the lakes data which suggest that there was a correlation between the amount of sediment in the water column and the removal of metals from the water column by sedimentation onto particulate matter by first order kinetics. In rivers, especially Southern African rivers, large quantities of sediment are naturally transported in the river systems. The River Compartment Model was developed to predict the steady state environmental concentration profile for metals along the length of a river downstream of a continuous point source effluent release. Building on the results of this

model enables design engineers to better appreciate the impact of metals' release to riverine systems.

### **River Compartment Model**

The River Compartment Model is based on the assumption of first order kinetics for the removal of metals from the water column. This assumption needs to be verified for metals in river systems before the model can be developed further. The shortcomings of the model are discussed in detail.

The use of the model was evaluated in the form of a case study using data from the Zambian Copper Belt region. The outputs of the model provided additional information regarding the environmental impact of a release to the river

### **Affected Stream Length**

The Affected Stream Length refers to the length of downstream river that would be required to mitigate the effect of the increased metal concentrations in the water column as a result of the effluent release, and is thus a measure of the environmental impact of the effluent release. The validity of the Affected Stream Length is dependent on the validity of the River Compartment Model.

The case study illustrated that the Affected Stream Length calculation could be used to identify the metal contained in an effluent which would have the greatest environmental impact. This metric could also be used to compare the environmental impact of a range of effluent streams to predict which effluent would have the greatest potential environmental impact. The Affected Stream Length provides additional information to decision makers adding to the body of information available for environmentally conscious design.

### **Water Model**

Linking an environmental impact to information available at the various levels of design is required to promote the use of environmental considerations in the design decision making process. Greater flexibility in design options is available at the early stages of the design process while the information used to determine the environmental impact during the EIA is only available during the definitive estimate and detailed design stages. To bridge this gap, the Water Model is proposed to summarise information relating to water consumption and effluent release from the process facility for used at all levels of design detail.

This model proposes a steady state network analysis of the water stocks and balances over a process facility. The Water Model contains information that could be used for mass integration methodologies, includes all process areas including waste treatment and is compatible with Life Cycle Assessment methodologies. The model does not implicitly report an environmental impact; rather, it reports the concentrations and flows of effluent streams at the site boundary. This information can be used in conjunction with the River Compartment Model or the Affected Stream Length concept to produce an environmental impact indicator.

### **Significance of this work**

This work has provided a conceptual methodology by which environmental impacts of metal containing effluents to river systems can be evaluated during the design process. The models proposed provide this link for all levels of design. The shortfall in the thesis is that the proposed models have not been validated and that the River Compartment Model is based on results of testwork conducted in lakes. The significance of these shortfalls can only be determined by verification of the assumptions stated for the River Compartment Model.

The significance of the work lies in that the models proposed have demonstrated a methodology that can link design level information to an environmental impact of an effluent release on a river system. Using the Water Model and the River Compartment Model in conjunction allows design engineers to evaluate the performance of process and equipment selection alternatives during the design process, predicting the environmental impact of the proposed alternatives. The models have been developed specifically for metals and thus provide the minerals design community with an indication of the environmental impact early in the design process, before an EIA has been compiled.

## **DEDICATION**

I would like to dedicate this work to my parents Mr Murray Stuart Marr (1936-1994) and Mrs Wendy Ann Marr (nee Stronach).

Dad, I know that you are proud of me and that although you did not express it much while you were with us, I know that you have taken great pride in all the achievements I have accomplished. I was honoured to have a father such as you and although there have been times when I have felt disappointed by you, I know that you did not fail me in anything and gave to me, and my siblings, only of your best. You have given me a picture of a man who I can aspire to be and have shown us the true meaning of a successful marriage. I love and respect you. We all miss the sunshine of your laughter in our lives, but we are also aware that you are not too far away.

Mom, you are love personified. The love you share with us is beyond our full recognition. We are all grateful to have you as our mother. Thank you for your belief in me and the encouragement you have given me through the last two years. Yes, it has been tough on all of us and sometimes I have felt guilty about it, but your belief and faith in me has helped me through. I know that you want to see me in a red gown, but I need to take a break before going for that. Thank you for staying with us and I know that you will see your dream of me become a reality. I love you and want you to know that I do.

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University of Cape Town

## TABLE OF CONTENTS

	<b>Page</b>
<b>EXECUTIVE SUMMARY</b>	<b>II</b>
<b>DEDICATION</b>	<b>V</b>
<b>ACKNOWLEDGEMENTS</b>	<b>VI</b>
<b>TABLE OF CONTENTS</b>	<b>VII</b>
<b>LIST OF FIGURES</b>	<b>XI</b>
<b>LIST OF TABLES</b>	<b>XII</b>
<b>CHAPTER 1 – INTRODUCTION</b>	<b>1</b>
1.1 Freshwater in Southern Africa	2
1.2 Environmental Considerations in the Design of Process Plants	5
1.3 Water in the Minerals Industry	7
1.4 Hypothesis	9
1.5 Thesis Structure	10
1.6 Significance of this Thesis	12
1.7 Closure	12
<b>CHAPTER 2 – METALS IN THE ENVIRONMENT</b>	<b>13</b>
2.1 Riverine Ecosystems	13
2.1.1 Catchment Signatures	13
2.1.2 River Catchment Management	14
2.1.3 Ecological Stream Flow Requirement	15
2.1.4 Water Quality Variables affecting Riverine Ecosystems	17
2.2 Environmental Modelling	18
2.2.1 Multimedia Fate and Transport Models	20
2.2.2 Fate and Transport Component of the Model	22
2.2.3 Descriptive Models of River Ecosystem Functioning	23
2.3 Freshwater Indicators	25
2.3.1 Physiochemical Freshwater Indicators	26
2.3.2 Biological Freshwater Indicators	27
2.3.3 Integrated Freshwater Indicators	29
2.3.4 Freshwater Indicators for the Design of Metals Refineries	30
2.4 Aquatic Toxicity and Persistence	31
2.4.1 Aquatic Toxicity	31

2.4.2	Persistence	32
2.4.3	Bioaccumulation	32
<b>2.5</b>	<b>Metals in Aquatic Ecosystems</b>	<b>33</b>
2.5.1	Biological Effects of Metals	33
2.5.2	Factors Affecting the Fate of Metals in Aquatic Systems	35
2.5.3	Metals Persistence	37
2.5.4	Bioavailability of Metals in Aquatic Ecosystems	38
2.5.5	Deficiency, Tolerance and Acclimation	40
2.5.6	Bioaccumulation	41
2.5.7	Toxicity	42
<b>2.6</b>	<b>Criteria to Evaluate Ecotoxicity Indicators</b>	<b>43</b>
<b>2.7</b>	<b>Modelling Metal Toxicity and Persistence</b>	<b>43</b>
2.7.1	Ecotoxicity	45
2.7.2	Multi-species Toxicity	47
<b>2.8</b>	<b>Closure</b>	<b>48</b>
<b>CHAPTER 3 – DESIGN OF BASE METALS REFINERIES</b>		<b>50</b>
<b>3.1</b>	<b>Design of Chemical Plants</b>	<b>50</b>
3.1.1	Design of Chemical Plants	50
3.1.2	Design of Base Metals Refineries	54
3.1.3	Environmental Initiatives in the Minerals Industry	56
3.1.4	Water Use in Base Metals Refineries	57
<b>3.2</b>	<b>Environmental Considerations in the Design of Process Plant</b>	<b>59</b>
3.2.1	Including Environmental Impacts as Design Objectives	59
3.2.2	Predicting Environmental Impacts during Design	60
3.2.3	Importance of Site- and Catchment-Wide Considerations	61
<b>3.3</b>	<b>Life Cycle Assessment</b>	<b>61</b>
3.3.1	Life Cycle Assessment in the Design Process	63
3.3.2	River Systems in Life Cycle Assessment	64
3.3.3	Metals in Life Cycle Assessment	65
<b>3.4</b>	<b>Review of the Hypothesis</b>	<b>65</b>
3.4.1	Environmental Considerations in Design	66
3.4.2	Riverine Ecosystems	66
3.4.3	Result of Hypothesis Testing	67
3.4.4	Restating of the Hypothesis	67
<b>3.5</b>	<b>Closure</b>	<b>68</b>
<b>CHAPTER 4 – MODEL DEVELOPMENT</b>		<b>70</b>
<b>4.1</b>	<b>Water Flow Model for Design Applications</b>	<b>70</b>
4.1.1	Systems Boundary	71
4.1.2	Inputs and Outputs	72
4.1.3	Water Stocks and Balances	73
4.1.4	Network Analysis for Water flows	74
4.1.5	Benefits of the Water Model in Design	78
4.1.6	Water Indicators for Design	79
<b>4.2</b>	<b>The River Compartment Model</b>	<b>81</b>
4.2.1	Assumptions	82

4.2.2	System Description	82
4.2.3	Compartment Balances	83
4.2.4	Metal Fluxes to Sediment	86
4.2.5	Sediment Metal Content	87
4.2.6	Estimating the Environmental Impact	89
4.2.7	Affected Stream Length	91
4.2.8	Model Inputs	92
4.2.9	Model Outputs	92
<b>4.3</b>	<b>Closure</b>	<b>98</b>
 <b>CHAPTER 5 – EVALUATION OF THE RIVER COMPARTMENT MODEL</b>		 <b>100</b>
<b>5.1</b>	<b>Case Study Area</b>	<b>101</b>
5.1.1	Mining Activities in Mwambashi Catchment	101
5.1.2	Measured Environmental Metal Concentrations	102
5.1.3	Rainfall and Evaporation	103
<b>5.2</b>	<b>Case Study</b>	<b>104</b>
5.2.1	Assumptions	104
5.2.2	Results	105
5.2.3	Affected Stream Length	109
5.2.4	Metal Flux to Sediment	111
5.2.5	Metal Sediment Content	111
<b>5.3</b>	<b>Discussion of Case Study Results</b>	<b>114</b>
5.3.1	Metal Environmental Concentrations	115
5.3.2	Affected Stream Length	116
5.3.3	Metal Sediment Content	117
<b>5.4</b>	<b>Application of the Affected Stream Length</b>	<b>118</b>
5.4.1	Using the Affected Stream Length Estimate in Design	119
5.4.2	Criticising the Affected Stream Length Estimate	119
5.4.3	Evaluating the Affected Stream Length Estimate	120
<b>5.5</b>	<b>Evaluating the Proposed Models</b>	<b>122</b>
<b>5.6</b>	<b>Closure</b>	<b>124</b>
 <b>CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS</b>		 <b>126</b>
<b>6.1</b>	<b>Testing of the Hypothesis</b>	<b>126</b>
6.1.1	Environmental Considerations in Design	126
6.1.2	Result of Hypothesis Testing	127
<b>6.2</b>	<b>Restating the Hypothesis</b>	<b>127</b>
6.2.1	Riverine Ecosystems	128
6.2.2	Metals in Freshwater Aquatic Ecosystems	129
6.2.3	Predicting Environmental Concentration of Metals in Rivers	130
6.2.4	River Compartment Model	130
6.2.5	Affected Stream Length	132
6.2.6	Water Model	134
6.2.7	Testing the Restated Hypothesis	135
<b>6.3</b>	<b>Recommendations for Further Work</b>	<b>136</b>
6.3.1	Environmental Impact of Metals in the Freshwater Ecosystems	136
6.3.2	River Compartment Model	137
6.3.3	Affected Stream Length	138

6.3.4	Water Model	139
6.4	Closure	140
<b>REFERENCES</b>		<b>142</b>
<b>APPENDICES</b>		<b>155</b>
<b>APPENDIX A – SUPPLEMENTARY LITERATURE</b>		<b>156</b>
A.1	Water Quality Variables	156
A.2	Modelling Metals in Aquatic Systems	161
A.3	Physical and Biological Factors Affecting Metal Bioavailability	165
A.4	Freshwater Indicators in LCA	168
A.5	Environmental Modelling	183
<b>APPENDIX B – CASE STUDY</b>		<b>191</b>
B.1	Case Study Measure Environmental Concentrations	191
B.2	Case Study Model Results	193

University of Cape Town

## LIST OF FIGURES

Figure 1.1: Mean Annual Rainfall and Runoff for Selected Countries (Davies et al., 1993) ....	3
Figure 2.1: Effect of Decreasing the Water Flow in a Riverine System (Davies, 2002) .....	17
Figure 2.2: Schematic Representation of a Catchment .....	21
Figure 2.3: Fate of Metals in the Aquatic Environment (di Toro <i>et al.</i> , 2001a). .....	36
Figure 2.4: Transformation of Metals in Aquatic Environments (Chapman, 1996).....	37
Figure 2.5: Dose Response Curve (Janssen <i>et al.</i> , 2000, Chapman and Wang, 2000).....	41
Figure 3.1: The Design Process (Cano-Ruiz and McRae, 1999).....	51
Figure 3.2: Process Design Constraints (adapted from Sinnott <i>et al.</i> , 1983) .....	52
Figure 3.3: Framing of Chemical Process Design (Cano-Ruiz and McRae, 1999) .....	54
Figure 4.1: Representation of Site and Process System Boundaries for the Water Flow Model .....	72
Figure 4.2: Network Diagram for Water Balance Model .....	76
Figure 4.3: Diagram of a River Compartment .....	83
Figure 4.4: Water Column Metal Concentration at Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days.....	93
Figure 4.5: Water Column Metal Concentration at Metal Half-Live of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L.....	94
Figure 4.6: Metal Flux to Sediment at Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days ....	95
Figure 4.7: Metal Flux to Sediment at Metal Half-Live of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L.....	96
Figure 4.8: Metal Content in Sediment at Sediment Residence Time Ratios of 1.2, 2.5, 5, 10, 50, and 100.....	96
Figure 4.9: Metal Content in Sediment at Sediment Residence Time Ratios of 10 and Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days .....	97
Figure 4.10: Sediment Metal Content at Metal Half-Live of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L.....	98
Figure 5.1: Mwambashi Catchment Area (Simukanga et al., 2002).....	102
Figure 5.2: Predicted Environmental Concentration for Effluent D1.....	106
Figure 5.3: Predicted Environmental Concentration for Copper .....	107
Figure 5.4: Predicted Metal Environmental Concentration for Cobalt.....	107
Figure 5.5: Predicted Metal Environmental Concentration for Zinc .....	108
Figure 5.6: Predicted Metal Environmental Concentration for Cadmium .....	108
Figure 5.7: Predicted Sediment Metal Content* for Effluent D1 .....	112
Figure 5.8: Predicted Dry Season Sediment Metal Content* for Copper .....	112
Figure 5.9: Predicted Dry Season Sediment Metal Content* for Cobalt.....	113
Figure 5.10: Predicted Dry Season Sediment Metal Content* for Zinc.....	113
Figure 5.11: Predicted Dry Season Sediment Metal Content* for Cadmium .....	114

## LIST OF TABLES

Table 1.1: Breakdown of Freshwater Consumption by Sector.....	1
Table 1.2: Coefficient of Variation in Mean Annual Runoff for Selected Areas (Davies et al., 1993).....	3
Table 1.3: Water Usage by Sector for South Africa (GRID-Arendal, 1999).....	4
Table 2.1: River Flows: Their Importance to Ecosystem Functioning (King et al., in press) .	16
Table 2.2: Water Quality Variables Effecting Riverine Ecosystems (Dallas and Day, 1993, Dallas et al., 1994, Davies and Day, 1998) .....	18
Table 2.3: Metals Classified according to their Toxicity and Availability in Natural Aquatic Systems (Dallas and Day, 1993) .....	34
Table 2.4: Examples of the Biological Functions of some Essential Metals (Parametrix, 1995, Dallas and Day, 1993, Chapman and Wang, 2000).....	34
Table 2.5: Physical and Chemical forms of Metals in Aquatic Systems (Allen, 2000).....	39
Table 3.1: Types of Design Estimates (Douglas, 1988).....	53
Table 3.2: Level of Information for Design Estimates .....	55
Table 3.3: Water Use in Base Metals Refining.....	58
Table 3.4: Rio Tinto Guidelines for Water Management (Leiner et al., 1998).....	60
Table 4.1: Metal Concentration Limits for Emissions to Aquatic Ecosystems (Dallas and Day <sup>+</sup> , 1993, DWAF <sup>#</sup> , 1996,.....	81
Table 4.2: Half-life times from freshwater mesocosm experiments (Diamond et al (1990), cited by di Toro et al., 2001a) .....	86
Table 4.3: Concentration Profile Reactions for Various Orders of Reactions.....	91
Table 5.1: Metal Concentration in the Mwambashi Catchment during the Dry Season (Simukanga, 2002).....	103
Table 5.2: Rainfall and Evaporation Data for the Mwambashi Catchment.....	103
Table 5.3: Simulated Effluent Release to the Mwambashi Catchment .....	104
Table 5.4: Affected Stream Length using Environmental Concentration as Target Concentration .....	109

## CHAPTER 1 – INTRODUCTION

The design of chemical or minerals process plants involves a series of decision-making exercises. Process engineers begin with an infinite design space of possibilities, and, through the design process, make decisions that progressively constrain that decision space. Decisions made during the design process manifest themselves in the final cost of the operating plant, which are not solely financial, but also socio-political and environmental. Environmental issues have become increasingly important in the global context. In the opinion of leading scientists from 50 countries taking part in a UNEP survey, Climate Change, Freshwater Scarcity, Desertification/Deforestation and Freshwater Pollution were identified as the top four issues facing humanity in the 21<sup>st</sup> century (UNEP, 2001). This thesis provides a basis for the understanding of freshwater-related impacts by reviewing these in the context of the design of base metals refineries (including minerals beneficiation, smelters and metals finishing). The thesis attempts to provide a link between information available during the design of these operations and the manifestation of water-related impacts in the catchment in which they are placed. This work uses Southern Africa as a contextual study area, but has wider applicability, as the issues regarding freshwater are global in scale and significance.

Increasing demand for freshwater is occurring in three key areas; human needs for safe drinking water and sanitation, agricultural needs for increasing production to meet population growth, and industrial needs to provide more goods and services for a growing population. Agriculture is an inefficient water user with inefficiencies of up to 85% for water consumed during irrigation. Agriculture is also the largest polluter of freshwater in developed and developing countries because of excessive fertiliser use and poor land management practices (WBCSD, 1999). The water consumption per sector is presented in Table 1.1.

**Table 1.1: Breakdown of Freshwater Consumption by Sector**

Sector	Global Consumption (%)	South African Consumption (%)
Agriculture	70	76
Industry	20	10
Residential/Commercial	10	14

Though industrial use is small by comparison to agriculture, it remains highly significant and merits consideration – both in terms of the quantity used, but also in terms of the real potential for industrial activity to pollute fresh water resources. This is particularly true of the minerals and metals industries, which are the focus of this thesis.

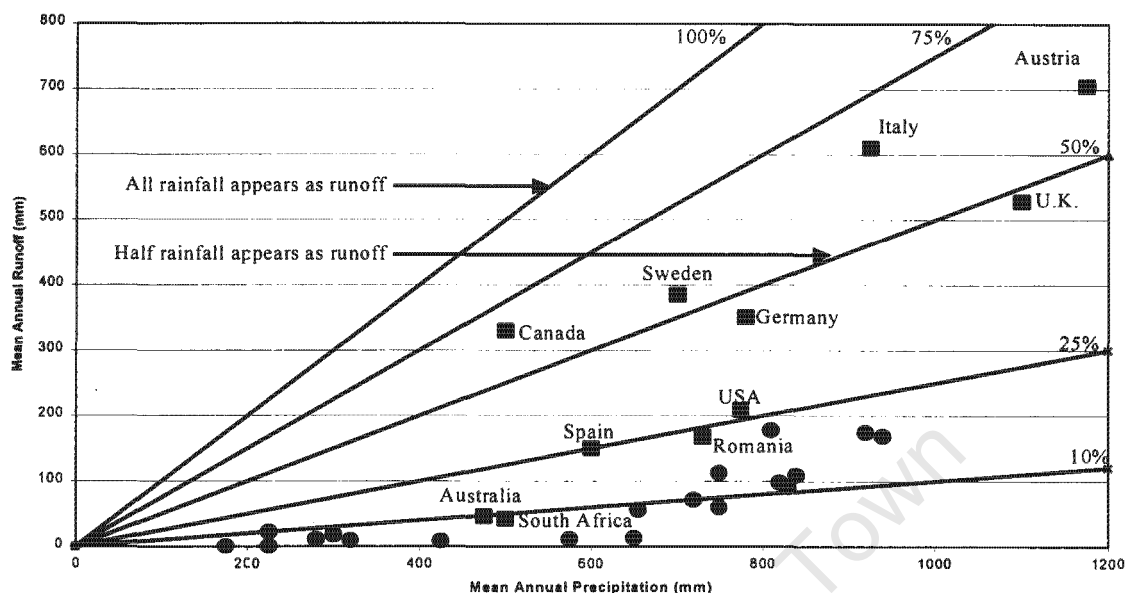
The majority of the research conducted on the behaviour of metals in freshwater systems has concentrated on lakes. Freshwater lakes occur in areas where the mean annual rainfall is greater than the mean annual evaporation rate. In water stressed countries, such as South Africa, the annual rainfall is lower than the annual evaporation rate over the majority of the country. There is only one small area of South Africa where the mean annual rainfall is greater than the mean annual evaporation rate. This is the site of South Africa's only true freshwater lake - Lake Funduzi (Davies and Day, 1998). In water-scarce countries, rivers are the major source and occurrence of surface freshwater.

### **1.1 Freshwater in Southern Africa**

Ashton et al. (2002) review the status of water availability in Africa and state "*virtually every country faces severe and growing challenges in their rapidly escalating demand for water that is driven by burgeoning populations*". The authors link resource depletion and pollution to the dwindling supplies, and demand increases are being exerted from population growth coupled to rapid industrialisation, mechanisation and urbanisation. Southern Africa is a semi-arid region, with a mean annual rainfall (500mm) below the world average (750mm), and high evaporation rates. There are marked climatic gradients across the subcontinent and these have resulted in a variety of different aquatic ecosystems, with organisms adapted to different water quality regimes and flow patterns. Figure 1.1 presents the relationship between Mean Annual Rainfall and Mean Annual Runoff for selected countries. The square points mark the various countries while the round points mark major South African catchments.

Southern African rivers have strongly seasonal flow with considerable year-to-year variability in runoff (coefficient of variation for mean annual runoff > 117% for South Africa), (Davies et al., 1993). The coefficients of variation in mean annual runoff for selected areas are compared in Table 1.2.

**Figure 1.1: Mean Annual Rainfall and Runoff for Selected Countries (Davies et al., 1993)**



**Table 1.2: Coefficient of Variation in Mean Annual Runoff for Selected Areas (Davies et al., 1993)**

Country	Coefficient of Variation in Mean Annual Runoff (%)
USA	38
Canada	20
Europe	22
Victoria (Australia)	53
Australia and New Zealand	50
Africa	25
Asia	27
South Africa	117

Both the Geo2000 report (UNEP, 2001) and the Stockholm Environmental Institute report "Comprehensive assessment of the freshwater resources of the world" (SEI, 1997) predict that, by the year 2025, South Africa will be severely water stressed, with demand exceeding supply. The UNEP NGO, GRID Arendal, produced a "State of the Environment" report for the South African Department of the Environmental Affairs and Tourism (DEAT) in 1999. This report predicts a 51.7% increase in the demand for fresh water in Southern Africa over the next 30 years. Population growth, increased economic activity and changes in land use were stated as the major contributors to the

increased demand. The current and predicted water usage by sector are summarised in the Table 1.3:

**Table 1.3: Water Usage by Sector for South Africa (GRID-Arendal, 1999)**

Sector	Contribution to GDP	1996 (10 <sup>6</sup> m <sup>3</sup> per annum)	2030 (10 <sup>6</sup> m <sup>3</sup> per annum)	Percentage Increase
Urban and Domestic		2 171	6 936	219.5%
Mining and Industrial	37%	1 598	3 380	111.5%
Irrigation and Afforestation	6%	12 344	15 874	28.6%
Environmental		3 932	4 225	7.5%
Total		20 045	30 415	51.7%

The scarcity of water is also exacerbated by pollution of the surface and groundwater resources. Typical pollutants of South Africa's freshwater environment include industrial effluents, domestic and commercial sewage, acid drainage from mining and minerals' processing, agricultural runoff and litter. The major water quality problems in South Africa are a result of salinisation (and related ecotoxicological effects), enrichment by plant nutrients, microbiological proliferation, particulate sedimentation and silt migration, and acidification. This last gives rise to increasing metals' mobilisation, with the direct effect of increased eco-toxicity of freshwater resources. Water quality problems resulting from the activities of the mining and minerals industry include the toxicological effect of metals in aquatic ecosystems, acid mine drainage, cyanide releases, siltation and water consumption (Aston et al., 2002).

In 1991, the management of water resources, and particularly the control of surface water quality through the control of discharges in South Africa, was revised to include consideration of the assimilative capacity of the receiving stream (Dickens and Graham, 1998). The discharge controls were implemented by the introduction of acceptable values of water-quality parameters designed to provide protection for the downstream river environment. Management of effluent discharges into surface waters with the objective of preserving the integrity of the downstream aquatic resources has since been implemented (Dickens and Graham, 1998). Protecting the needs of the environment requires tools that can be used to monitor environmental conditions as well as for setting ecological objectives to ensure either proper or sustainable management

of the water resources (Dallas, 2000). In the design of chemical process plants, tools are required to predict the environmental consequences of effluent discharges to surface waters.

South Africa's National Water Act (Act 38 of 1998) (DWAF, 1998) recognises that basic human and environmental needs should be met, and that the exploitation of water in all aspects (quality, quantity and reliability of supply) must be sustainable in the long term. This Act has removed the privileged position that agriculture, mining and industry have held regarding water use under the previous Water Act. Competition for a restricted water supply has increased, requiring new operations to justify their access to water sources. Accountability for water use has increased and water licenses have been issued and will be reviewed on a regular basis (typically 5 years for agricultural users, 10-20 years for industry, and 40 years for forestry). Licenses can be withdrawn for re-allocation to other users should the water accountability or consumption be found to unacceptable by the reviewing committee.

The pressure on industry to reduce its consumption of freshwater is increasing. Accountability for the utilisation of the water resources by current users is being scrutinised in order to free up water resources for other users. This pressure to reduce water consumption and the impacts of effluent discharges to freshwater systems has prudent decision analysis during the design process to reduce the impact of new chemical process plants on the freshwater resources.

## **1.2 Environmental Considerations in the Design of Process Plants**

Environmental considerations in the design of chemical plants should be based on a foundation of Environmental Sustainability. Sustainable Development has become a high profile subject in South Africa following the World Summit on Sustainable Development held in Johannesburg during October 2002. A multitude of definitions for sustainable development have been presented in literature. For this thesis, the Goodland and Daly (1996) definition will be used. Sustainable development is defined as "*development without growth in throughput of matter beyond regenerative and absorptive capacities*". This definition is particularly applicable to freshwater aquatic systems as both the absorptive and regenerative aspects are highlighted and these have

been identified as being amongst the most challenging environmental issues facing humanity in the 21<sup>st</sup> century.

It is widely recognised that early consideration of environmental matters during design is needed to obtain good environmental performance at least cost. It has been estimated that about 85% of the life cycle cost, financial and environmental, are determined by decisions made in planning and design phases (Blanchard, 1991). Cano-Ruiz and McRae (1999) breakdown the proportion of expenditure for selected aspects of process plant costs and express them as fraction of sales revenue. Plant and equipment comprise in the order of  $\pm 9\%$  of sales revenue, Research and Development  $\pm 4\%$  and Environmental aspects  $\pm 4\%$ . The environmental costs are detailed further with the authors reporting that pollution control operating costs constitute  $\pm 50\%$  of environmental costs, with pollution control capital expenditures and hazardous waste site remediation each contributing  $\pm 25\%$ . It has been reported that an estimated 50% of the capital costs for new chemical plants are devoted to handling wastes (Cano-Ruiz and McRae, 1999). The authors suggest that the inclusion of the waste treatment infrastructure within the analysis boundaries, integration of mass exchange processes, adopting a life cycle analysis framework for considering environmental impacts, and shifting the emphasis from effluent concentration to environmental impacts should be adopted during the framing of the design problem.

It should be recognised that the effect of process plants on the environment is not solely local in effect. Environmental legislation generally concentrates on preventing set guidelines being exceeded at the site facility boundary. As a rule, emissions to the environment are not currently considered in terms of their total impact on the receiving system. Environmental performance should be viewed from a holistic perspective to evaluate the full impact of the release on the receiving body. In terms of freshwater systems, the receiving body could either be a river system or a lake. Both systems form part of a catchment or watershed and it is thus important to view water-related impacts on a catchment scale rather than solely on a site level. This suggests that, even at the design stage of new projects, there is a need to integrate "site-wide" impacts with their extension to catchment scale. Considering catchment-scale effects requires that other users of the catchment need to be considered when making decisions related to utilisation of a water resource consumptively or for dissipative purposes.

The above discussion suggests that in order to effectively consider environmental aspects during the design of process plants, the approach should:

- Include waste treatment infrastructure within the analysis boundaries,
- Facilitate integration of mass exchange processes,
- Be adaptable to a life cycle analysis framework for considering environmental impacts, and
- Shift the emphasis from effluent concentration to environmental impacts.

The difficulty of establishing these metrics for base metals operations lies in establishing links between effluent concentrations and environmental impacts. This is especially true in determining the life cycle impact of metals in aquatic ecosystems. In order to develop the link between environmental concentrations of metals and their environmental impact, a review of the current knowledge relating to metals in aquatic ecosystems is presented. The current advances in understanding of riverine systems are reviewed to determine how the behaviour of metals in aquatic systems can be related to environmental impacts. Having established this basis, the environmental impact of metals in riverine systems can be related to release of effluents to these systems. This allows the final step of relating information available at the design stage of base metals refineries to effluent release from proposed refineries.

### **1.3 Water in the Minerals Industry**

Mine derived pollution is one of the major causes of water degradation in many parts of the world (van Zyl et al, 2002). Potential sources of pollution from a mine or minerals processing site include mine water discharge, leachate or runoff from waste disposal facilities and the intentional or accidental release of process streams to surrounding areas. Ashton et al (2002) reviewed the use of water in the minerals industry. Their review focussed mainly on the mining aspects of water related environmental impacts. This work concentrates on processes downstream of the mining operation and includes minerals beneficiation, smelter and metals finishing operations.

Ashton et al (2002) identify five areas of impact that mining and minerals processing have on water systems. These are acid mine drainage, release of metals, cyanide, siltation and water use. The set of impacts that a specific mining operation will have on

the environment, and specifically the aquatic environment depend on (Ashton et al, 2002):

- The type of rock and ore being mined and processed,
- The type of mining operations and the scale of operations,
- The efficiency and effectiveness of any environmental management systems deployed by the management.
- The sensitivity of the receiving environment (including water scarcity).

van Zyl et al (2002) describes acid mine drainage as the "*the most serious and pervasive environmental problem facing the minerals industry today*". The degree of acid mine drainage generation and impacts are site specific and determined by the geology and climate regime in conjunction with the mining, processing and waste handling methodology. The early recognition of the potential for acid mine drainage is essential for successfully managing the potential environmental impacts. Tests can be conducted during the evaluation, design or testwork phases of the mine development to characterise the mine rock to define the potential for acid mine drainage formation (van Zyl et al, 2002). Although the importance of acid mine drainage is recognised, this subject has not been included in this work since acid mine drainage is generated more from mining activities than surface refining activities. Further discussion on acid mine drainage can be found in Ashton et al.(2002).

The aspects relating to cyanide from mineral operations is specific to the gold mining industry and are not discussed in this work which focuses on the base metals industry.

Siltation is the process whereby fine solids particles build up on the bed of a river or lake and is the result of an excessive load of suspended solids in a river system (Ashton et al., 2002). Mining operations produce large quantities of dust and finely powdered rock. These materials are dumped after the valuable metals have been removed. The storage of tailings material is commonly performed in the form of tailings dams. Losses of material from tailings dams through wind bourn dust or erosion by rainfall runoff can result in these installations contributing to the sediment load in rivers (Ashton et al., 2002). The sediment balance in rivers is sensitive and any changes in flows or sediment loads do have impacts on the river system. River disposal of tailings has been used in projects to reduce the terrestrial footprint of the plant. This practice has been used in the past but has been discontinued over most of the world. Three operations in

Australasia presently use river disposal of tailings material viz. Ok Tedi, Grasberg and Porgera mines. In these cases, the lack of suitable land and high regional rainfall resulted in a choice between not exploiting the deposits or river disposal. The ecological consequences of these operations are discussed in van Zyl et al. (2002). The impacts of the Australasian operations on the rivers system have had far reaching environmental and socio-economic consequences for the river systems. Increased sediment loading and deposition, elevated metal and other mineral levels, acid drainage from over bank deposition and other biological consequences such as loss of riparian vegetation, riparian forest dieback, loss of sensitive species, reduced photosynthesis etc. result from increased sediment discharge into a river system (Ashton et al., 2002, van Zyl et al., 2002).

The focus of this work concerns the remaining two impacts of mining on water systems, the release of metals to river systems and, to a lesser extent, water use. These topics are discussed in Chapter 2 of this thesis.

#### **1.4 Hypothesis**

This thesis seeks to evaluate the following hypothesis:

***The design of base metals operations for effective and efficient water usage and management requires consideration of both site- and catchment-wide effects of metal releases to freshwater aquatic systems, and their incorporation into the design process through suitable performance measures.***

This will be explored by:

- Establishing an understanding of the processes which take place within a catchment and freshwater bodies,
- Following the fate of metals releases to freshwater systems,
- Evaluating the relationship between the effect of a metal in a freshwater body and the environmental concentration of the specific metal,
- Establishing a mechanism to related the environmental concentration of a metal to the release of metal containing effluents into aquatic systems, and
- Exploring methodologies to incorporate these in the design process.

This hypothesis is re-evaluated in Chapter 3 following the review of the literature.

## **1.5 Thesis Structure**

The thesis is presented in six chapters. These Chapters are described in the following paragraphs.

### **Chapter 1 – Introduction**

This chapter introduces the study topic of Freshwater related environmental impacts and their consideration during the design of Base Metals Refineries. The context of environmentally conscious design is set as the basis for this work. The requirements for environmentally conscious design are proposed. The environmental impacts on water systems as a result of the mining and minerals industry is briefly discussed. Finally, the hypothesis for this thesis is stated and the layout of the thesis detailed.

### **Chapter 2 – Metals in the Environment**

This chapter discusses water variables from a riverine ecosystem perspective. Environmental Modelling is briefly reviewed with the fate and transport aspects of these models and their application to the modelling of riverine systems.

The discussion moves to Freshwater Indicators covering both physiochemical and biological indicator systems. Indicators for the monitoring of industrial performance are introduced. Finally, the persistence and toxicity of metals in aquatic ecosystems is discussed considering factors that affect the fate of metals in aquatic systems. The discussion focuses on freshwater rather than incorporating all aquatic habitats. The modelling of metals in aquatic ecosystems is introduced together with considerations of how indicators can be represented in the design phase of process design projects.

### **Chapter 3 – Design of Base Metals Refineries**

This chapter discusses the design of base metals refineries in order to establish the level of information available at the design stages. The use of water in base metals refineries is discussed. Life Cycle Assessment is introduced as one of the tools available to evaluate process level information available at the design stages of metallurgical plant

and predict environmental impacts of releases from these plants. The shortcomings of Life Cycle Assessment regarding metals and river systems are briefly highlighted.

Finally, the hypothesis is evaluated in terms of the information available in the literature and is found to be correct. The hypothesis is restated in terms of the literature and evaluated through the remainder of the thesis.

#### **Chapter 4 – Model Development**

This chapter proposes two system models that could be used together to meet the requirements of environmentally conscious design. The first model tracks water quantity and quality within a site boundary and can be used during design to compare the water consumption of proposed process routes. The second model is a River Compartment Model, comprised of a simple fate and transport model of a release of a metal containing industrial effluent into a river. The concept of an “Affected Stream Length” is introduced as a proxy indicator of environmental damage within a catchment, and its relevance and appropriateness discussed. The models are evaluated in a parametric study to determine the factors which have the greatest effect on the model output.

#### **Chapter 5 – Evaluation of the River Compartment Model**

The value of the River Compartment Model is explored with the assistance of an environmental monitoring program within the Zambian Copper Belt. Though not a South African study, the local hydrogeology is similar in both countries, and it is anticipated that the interpretations developed through this case study will have some regional applicability. In particular, the model is used to explore to what extent the proposed “Affected Stream Length” metric provides information on environmental impacts that is different to that based solely on emission-level information, which is the common basis for understanding the environmental effects of minerals process design choices. It is argued that consideration of such catchment-level impacts is necessary, even at the design stage, and some suggestions are offered on how this might be achieved given the limited information available during design.

The basis of the models and the Affected Stream Length are discussed in terms of the principles of environmentally conscious design.

## **Chapter 6 – Conclusions and Recommendations**

The findings of the work are discussed in relation to the restated hypothesis. The hypothesis was tested and was found to be true. Therefore, we failed to reject the proposed hypothesis and concluded that site and catchment wide environmental impacts were required for the effective management of water during the design process.

The results of the thesis are discussed. The two proposed models, the River Compartment Model and the Water Model are discussed in terms the validity of their assumptions and proposed methodologies. Recommendations for verification and further development of the models are presented.

### **1.6 Significance of this Thesis**

The significance of the work is in the models proposed providing a methodology which can link design level information to an environmental impact. Using the Water Model and the River Compartment Model in conjunction allows design engineers to evaluate the performance of process alternatives during the design process and predict the environmental impact of the proposed processes. This allows environmental impact orientated information to be used as additional information in design decision-making. The models have been developed specifically for metals and thus provide the minerals design community an indication of the environmental impact early in the design process, before an EIA has been compiled. These models specifically consider river systems, adding to the suite of environmental management tools available to design engineers and plant operators.

### **1.7 Closure**

Before a link between the design level information and environmental impacts to riverine systems can be established, we need to explore both the behaviour of metal in aquatic ecosystems and the level of design information which is available to predict these environmental impacts. Chapter 2 discusses the behaviour of metals in the environment to establish a mechanism which can be modelled as an impact indicator. The design context of this work is discussed in Chapter 3 before the stated hypothesis is evaluated against the reviewed literature.

## CHAPTER 2 – METALS IN THE ENVIRONMENT

Having highlighted the importance of environmental impacts and their early consideration in the design of base metals refineries, this chapter explores two of the major impacts of the mining and minerals industry on water systems, the release of metals to river systems and water use. The complexities involved in studying and modelling the fate and ecological effects of metals in aquatic environments are discussed. The behaviour of metals in the freshwater aquatic environment is discussed with a view to establishing those mechanisms that are relevant to metals dispersion between aqueous and other phases, and can be modelled and used as decision-making tools in the design process. The modelling of environmental systems, specifically riverine ecosystems, and pertinent indicators for freshwater systems, are discussed briefly to establish a basis upon which decisions in the design process can be based. Finally, a review of aquatic toxicity parameters is presented followed by a review of the behaviour and toxicological effects of metals in aquatic ecosystems.

### 2.1 Riverine Ecosystems

Davies *et al.* (1993) discusses the ecological functioning of riverine systems. For the purposes of protecting and maintaining aquatic ecosystems, prevention, rather than mitigation of environmental impacts, needs greater emphasis. Aquatic ecosystems include numerous species, habitats and processes, all of which are interlinked and interdependent, and which require protection if healthy ecosystem structure and functioning are to be maintained. The complexity of determining the effects of changes in water quality on aquatic ecosystems is increased by many cause and effect relationships, which are poorly understood or completely unknown at present (Dallas and Day, 1993, Dallas *et al.*, 1994, Davies and Day, 1998).

#### 2.1.1 Catchment Signatures

South Africa is diverse in climate, geomorphology, geology and soils, and aquatic biotas, and so the different regions exhibit considerable differences in natural water quality, even when unaffected by human activity (Dallas and Day, 1993). River biotic communities vary regionally within South Africa and in accordance with the level of catchment disturbance.

Recently, river scientists and limnologists identified that the regional variations observed at family level was more significant than originally thought. King and Schael (2001) identified the "invertebrates to species" level for a number of rivers in the Western Cape, South Africa, and found that each catchment produced a unique biotic community at species level. They termed this uniqueness of the invertebrate community a catchment signature. Regional signatures were expected due to variations in climate, vegetation and geology, but a catchment signature was not anticipated. Catchment signatures highlight the uniqueness of each catchment community and the realisation that each catchment is important and needs to be conserved from a biodiversity perspective. Every catchment thus needs to be considered in a conservation strategy and no catchment can be considered dispensable (King, personal comm., 2002).

The implications of catchment signatures is that river management, and specifically catchment management, need to be considered in the design process from the perspective of water abstraction and release of effluents. These considerations could have a marked influence on decisions made during the design process provided the decision makers can be adequately informed.

The National Water Act of South Africa identifies the catchment as the lowest meaningful level of management. The establishment of Catchment Management Agencies provides a forum for all stakeholders to contribute to the management of the river catchment. Proposed industrial activity in a catchment will require the acceptance of other users in the catchment, especially if the proposed activity could result in an alteration in the functioning of the catchment (Davies and Day, 1998).

### **2.1.2 River Catchment Management**

Holistic approaches to river catchment management are essentially processes that allow aquatic scientists from many disciplines to integrate data and knowledge. Each specialist develops an understanding of flow-ecosystem relationships, and then works within an overarching process of the holistic approach, to reach consensus on environmental flows with the other team members. The output is a description of a flow regime, in terms of frequencies, timing and duration of different magnitude flows, needed to achieve and maintain a specific river condition (King *et al.*, in press).

The management of the condition of a river and its catchment require that the following be considered (King *et al.*, in press):

- All major abiotic and biotic components that constitute the ecosystem should be managed;
- The full spectrum of instream flows, and their temporal and spatial variability, constitutes the river flow to be managed.

In terms of a disturbance being imposed on the river system by the activities of a minerals processing plant in a catchment, these variables also need to be managed. The above points can be summarized as water quantity issues reflected in the water use by a minerals plant and the water quality issues relating to physiochemical and biotic elements of river systems that can be affected by both the water use and releases of effluents to the river.

To maintain an ecological functioning, a river system requires a series of flows that maintain the river channel and provide ecological cues to the biotic elements of the system. These flows vary seasonally and are impacted by water abstraction from a river system, or water return to the system, and are described as ecological stream flow requirements

### **2.1.3 Ecological Stream Flow Requirement**

Un-impacted river systems experience a range of flows during the annual seasons. To understand the effect of water abstraction from a river system, an understanding of the ecological flow requirements of a river system is required. Once the ecological flow requirements have been established, the water available for "harvesting" from a catchment can be established. The Flood Pulse Concept proposed by Junk *et al.* (1997) recognises that riverine systems require a range of flows to maintain a healthy ecological functioning. King *et al.* (in press) discuss the flows required and describe the discharge flow patterns. The ecological importance of these flow regimes are summarised in Table 2.1.

Evaluation of the effects of flow reductions, or increases, on riverine ecosystems has been the focus of hydrological investigations in recent years. South African and Australian river scientists are working towards defining the ecological flow requirements in their respective countries. Recent findings indicate that between 79 and 92% of the

“normal” hydrological flow is required in the river to prevent any damage to the health of the system functioning (King, 2002, personal comm.).

**Table 2.1: River Flows: Their Importance to Ecosystem Functioning (King et al., in press)**

Flow	Importance to Ecosystem
Low flows	These daily flows occur outside the high-flow peaks. They define the basic hydrological nature of the river: its dry and wet seasons, and degree of perenniality. The difference in magnitudes in low-flow and the dry and wet seasons create more or less wetted habitat and different hydraulic and water quality conditions, which directly influence the balance of species at any time of the year.
Small Floods	Small floods are ecologically important in semi-arid areas in the dry season. They stimulate spawning of fish, flush out poor quality water, mobilise and sort gravels and cobbles thereby enhancing physical heterogeneity of the riverbed, and contribute to flow variability. They re-set a wide spectrum of conditions in the river, triggering and synchronising activities as varied as upstream migrations of fish and germination of riparian seedlings
Large Floods	Large floods trigger many of the same responses as do small ones, but additionally provide scouring flows that influence the channel form. They mobilise coarse sediments, and deposit silt, nutrients, eggs and seeds on flood plains. They inundate backwaters and secondary channels, and trigger bursts of growth in many species. They re-charge the soil moisture levels in the banks, inundate floodplains, and scour estuaries thereby maintaining links with the sea.
Flow Variability	Fluctuating discharges constantly change conditions through each day and season, creating mosaics of areas inundated and exposed for different lengths of time. The resulting physical heterogeneity determines the local distribution of species: higher physical diversity enhances biodiversity

The effects of changes in flows of a riverine system can be estimated by employing holistic river management methodologies such as the Building Block Methodology discussed by King and Louw (1998) and the updated methodology, DRIFT, as described by King *et al.* (in press). These methodologies determine in-stream flow requirements that describe, in space and time, the minimum amount of water that it is believed will facilitate maintenance of the river at some pre-defined desired state. The ecological effect of decreasing the flow in a riverine system is exceptionally complex and results in interactions between biota, inorganic salts, nutrients, temperature, dissolved gases, pH, toxic pollutants, particulate organic matter and the sedimentary status of the channel. Figure 2.1 summarises some of the interactions and consequences of decreasing the volume of water in a river system. A similar diagram can be constructed for increases in flow down a river system.



effects of water quality on a very limited number of aquatic organisms, which results in a significant level of analytical uncertainty (Dallas and Day, 1993).

**Table 2.2: Water Quality Variables Effecting Riverine Ecosystems (Dallas and Day, 1993, Dallas et al., 1994, Davies and Day, 1998)**

Water Quality Variables	Major Effects
Physical Factors	
Temperature	Determines metabolic rate, Determines availability of nutrients and toxins, Determines oxygen saturation level, Changes provide ecological cues for breeding, migration, etc
Turbidity and suspended solids	Turbidity determined degree of penetration of light, hence vision, photosynthesis, Suspended solids reduce penetration of light, smother and clog surfaces (e.g. gills) and adsorb nutrients, toxins, etc.
Chemical Factors	
pH	Ionic balance, Chemical species and their availability, Gill functioning
Conductivity, salinity, TDS, individual ions	Osmotic balances, Ionic balances, Water balances
Nutrients	Not toxic per se: cause eutrophication and thus affect community structure
Organic enrichment	Reduction in oxygen concentration, Increase nutrient levels
Dissolved oxygen	Respiration
Biocides	Usually target specific groups (eg molluscs, insects, plants) and thus alter community structure
Trace metals	Many essential at low concentrations, Some mutagenic, teratogenic, carcinogenic, Some metabolic inhibitors

These water quality variables are discussed further in relation to freshwater indicators in Chapter 2.3 and in relation to the fate and transport of metals in freshwater aquatic systems in Chapter 2.5. Before engaging in these issues, the modelling of environmental systems is discussed to provide a background to the development of a model to describe the environmental impacts of metals in river systems.

## 2.2 Environmental Modelling

The sheer complexity of the internal system behaviour of environmental systems results from the dynamic and multidimensional interactions, and the external actions - physical, chemical and biological. Malkina-Pykh (2000) discusses the difficulties posed to

modellers of environmental systems and concludes that the rule of “as simple and as highly aggregated as possible and as complex and disaggregated as necessary” should be followed in modelling ecosystems.

One approach to modelling of such environmental systems is an integrated modelling approach which captures as much as possible of the cause-effect relationships and describes them as operators of transition, or input-output functions - the typical black or grey box models. The black box approach to the ecosystem focuses on the components that reflect the ecosystem’s response to stressors, treated the whole ecosystem as a single unit, without any consideration of the internal processes. The grey box ecosystem model provides some insight to the ecosystem processes which are featured by chains of causality, highlighting stressors, abiotic variables, responsive to stressors, and quality variables responsive to abiotic variables (Malkina-Pykh, 2000).

Landis and McLaughlin (2000) discuss ecological systems as an example of a complex system citing three conditions of complex systems:

1. Non-linear feedbacks
2. Time-lags
3. At least three things happening together with interactions

Ecological systems meet each of the necessary characteristics for complex dynamics to occur. Complex systems are neither completely deterministic nor stochastic, though different components may have each of these characteristics. Unlike in typical toxicity tests, the causes and effects of the events in a complex system are not proportional or proximate. A small change in a population may result in a cascade effect, leading to changes in population size and even extinction of other species. In complex systems, the parts are linked together with varying intensities. Complex systems undergo irreversible processes and are dynamic, not in equilibrium, and thus not classically stable. They are best described as constantly moving targets which can demonstrate a variety of dynamics, from a quasi stable state, to cycles, to chaotic domains. The observed dynamics also depend upon the slice of the multivariate space being measured. One set of system variables may seem stable, whereas other aspects of the system may be cycling or even exhibiting chaotic dynamics (Landis and McLaughlin, 2000).

### **2.2.1 Multimedia Fate and Transport Models**

Multimedia mass balance models are simplified mathematical descriptions of the natural environment designed to provide a qualitative understanding of the environmental behaviour of chemicals, which are likely to be found in more than one environmental phase or medium. The environment is divided into a number of compartments – well-mixed boxes assumed to have homogeneous environmental characteristics and chemical concentrations. The model then calculates how a chemical is distributed within that simplified system at equilibrium. The distribution and thus the concentration, which is established in each medium, is influenced by the chemical's intrinsic properties and emission patterns and the characteristic of the environment into which it is released. The models attempt to integrate information on multiple and interacting processes of partitioning, transport and transformation into a prediction of a chemical's fate in the environment.

These models can be used in two contexts: real and evaluative situations.

- The models can be used to simulate the observed behaviour of contaminants in a real situation.
- The models can be used to describe the fate of a chemical in a hypothetical or evaluative setting where the objective is to predict a likely picture of the chemical's fate in a generic environment for the purpose of assessment and evaluation.

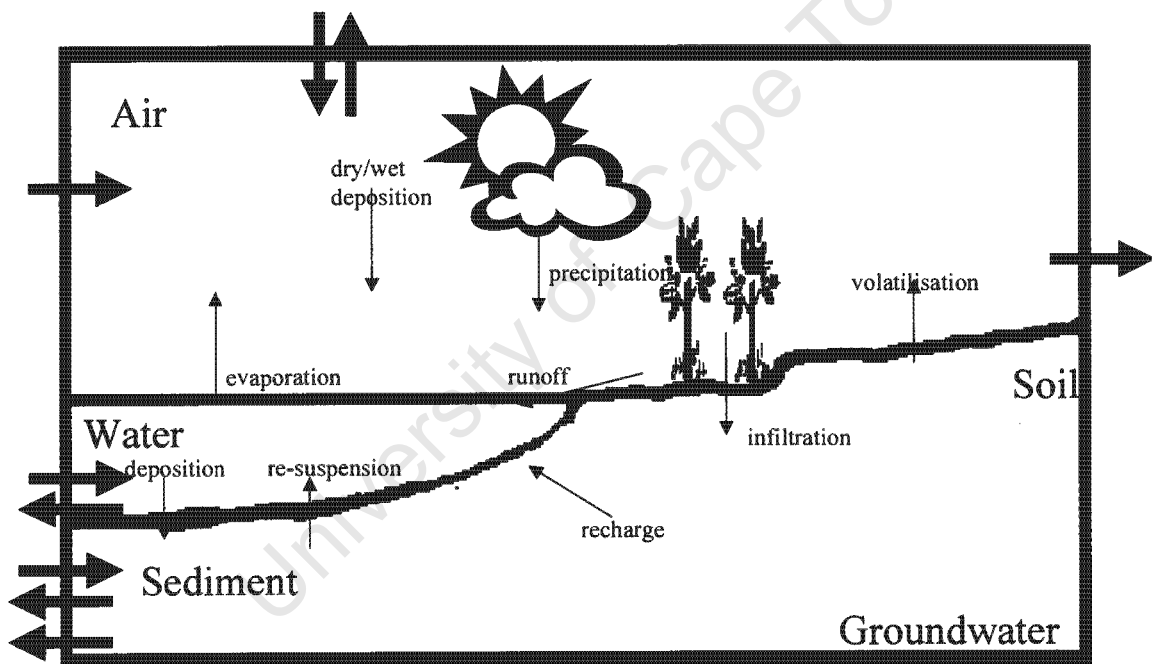
Environmental exposure models have been developed and used by scientists and regulators to estimate the level of contamination resulting from accidental or continuous releases of chemicals in a landscape. Many multimedia models have appeared; the most promising and popular of which is the MacKay's equilibrium model (Cowan *et al.*, 1995).

The MacKay equilibrium model is based on well-understood thermodynamic principles where a contaminant introduced into an environment will reach equilibrium among the different environmental compartments. For solid/liquid systems, an equilibrium partitioning between phases is a valid representation of the system. This principle can be applied to an evaluative environment consisting of many different phases between which the chemicals will move and reach equilibrium. The different phases can be represented by boxes or compartments, which are then linked together through the

equilibrium partitioning of the chemical and the transport parameters. Each box is described as a homogeneous and well-mixed compartment.

In order for multimedia models to be useful, accurate representation of the physical, chemical and biological transformations is necessary. The multimedia approach provides the necessary tools to determine the effect of every contribution to a given compartment, and thus allow assessment of the impact of the contaminant on the total environment. An illustration of the multimedia model, along with different compartments and processes controlling the fate of contaminants in the environment, is provided in Figure 2.2.

**Figure 2.2: Schematic Representation of a Catchment**



The figure includes five major compartments, subdivided as follows:

1. The air compartment consists of pure air phase and aerosols.
2. The soil compartments consist of soil and terrestrial plants.
3. The water compartment consists of pure water phase, suspended sediment, and aquatic biota including fish, plant and other aquatic populations.
4. The sediment compartment includes the deposited sediment layer.

The groundwater compartment includes solutes leached from the soil and those remaining from the initial emission, based on the level of complexity desired and on the goal of the modelling efforts, all these advective, reactive and diffusive processes can be accounted for in multimedia models. These considerations were the basis of distinguishing four different levels of equilibrium models. (see Mackay (1991), Cowan *et al.* (1995), Coulibaly (2000) and Heijungs (1999)). These and a generic description of an Equilibrium Model are presented in Appendix A.5.

In this work, a fate and transport model is developed for a river. The approach taken in developing this model follows the principles of an equilibrium model, in that each cell is considered to be fully mixed and at equilibrium, but differs from these models in that the compartment, the freshwater compartment, is not considered as the entire freshwater compartment, but rather cells of a linear system.

### ***2.2.2 Fate and Transport Component of the Model***

A contaminant may enter and leave an environmental unit by a number of mechanisms or processes.. The processes that drive the fate and transport of the contaminant are divided in three types, namely advection, reaction processes and inter-media transfers.

Advective processes account for gains and losses within the system-modelled experiences. Contaminant gains and losses take place in the environment due to the degradation of the compound because of reactions with species present in the environment or other forms of transformation reactions. Not all reactions are degradations since some reactions change a chemical from one compound to another without leading to degradation. The environmental processes that are classified as reactions include:

1. *Biodegradation*
2. *Hydrolysis*
3. *Oxidation*
4. *Photochemical Transformation Reactions*

Contaminant fate and transport are determined by not only advection and transformation, but by other inter-media transfers such as non-diffusive and diffusive transfers. Diffusion itself can be divided into two phenomena, diffusion within one medium (i.e. dilution) and diffusion between two adjacent media (i.e. volatilisation). In

which is a linear system from source to mouth, and convection transport processes are critical to species distribution. If the concentration within the river is represented by the average concentration over the whole river, this is a gross simplification and does not take into account local perturbations in concentration. A release to a riverine system is encompassed in a small volume of the whole which then passes down the river course to the mouth affecting the communities on the way. Further, the release will only affect biota downstream of the point of the release, as a river is a unidirectional system. The size of the compartment is thus an important consideration when attempting to model the fate and transport of contaminants through a river system.

Rather than modelling a river as a single compartment, the concept of a plug flow reactor without back mixing is proposed here as a more suitable system concept by which to model the fate and transport of metals in a river system. In a natural system, some degree of back mixing and diffusion of chemical species will occur. For simplicity, these have been ignored in this work. The plug flow reactor can be approximated by a linear series of continuous stirred reactors (CSTR), within each of which, conditions are uniform. Each CSTR represents a single compartment. Multimedia modelling concepts are applied to each compartment. This approach allows the model to predict the concentration of the contaminants down the water course. The movement of contaminants in the sediment compartment can also be approximated by the principles commonly used by chemical engineers in the design of reactors. These differentiate between the residence times of solids and liquids in compartments. Modelling a river in this manner offers the opportunity for it to be viewed as a continuum in accordance with the River Continuum Concept.

In order to present the results of an environmental model, environmental performance indicators are used to summarise the output in a manner that can be communicated. Indicators can be misinterpreted and it is thus important that the indicators used are understandable and communicable. We now discuss indicators that can be used during the design process to aid the decision making processes and clarify the possible environmental impact of choosing a specific option above an alternate option.

## 2.3 Freshwater Indicators

An indicator can be defined as a parameter, or values derived from parameters, which provide information about a phenomenon, having significance beyond the properties directly associated with the parameter value. Two major functions of indicators are (OECD, 1993):

- They reduce the number of measurements and parameters that normally would be required to give an exact representation of a situation.
- They simplify the communication process by which the information of results of measurement is provided to the user.

Indicators are used to depict the vast quantity of environmental data of a firm in a comprehensive and concise manner. They are mostly applied to set absolute material and energy data in relation to other variables in order to increase the informational value of the quantitative data. The purposes of environmental indicators are summarised by Jasch (2000). Data used for environmental performance indicators can be expressed as absolute or relative measurements, and, depending on their use and application, can be aggregated and/or weighted. The reference unit is usually production. If this proves impossible, alternative could be revenue, number of employees, or days of production. Jasch (2000) discusses the derivation of principles for environmental indicators

Indicators can measurable quantities that directly the objective being reported (natural), or based on combinations of information that pertains to the objective (constructed). Direct indicators immediately reflect the measured objective while proxy indicators indirectly reflect the objective by measuring and reporting a means objective (Hertwich and Hammit, 2001). This work focuses on using "proxy" environmental indicators, which can directly link design level information to environmental impacts. The proxy indicator indicating environmental impact could be based on changes to aquatic invertebrate assemblages, evaluating a measure of ecological toxicity or an impacted stream length.

Freshwater Indicators have been the subject of scientific research to define indicators against which ecological performance of a community, industrial installation, city, etc. can be measured. The acute awareness that useable freshwater resources are under greater pressure has resulted in a number of initiatives to provide a meaningful

indicator to which the current ecological status of a freshwater aquatic system can be measured.

### **2.3.1 Physiochemical Freshwater Indicators**

Owens (2002) reviews the current industrial physiochemical indicators and proposes a set of indicators for water resources based on the following characteristics:

- The quantity or volume of water removed from the environment and whether this volume withdrawn is returned or not, and
- The quality of the water returned to the environment, especially regarding impairment due to pollutants or other changes introduced during water use.

Owens (2002) explains that a water quantity indicator needs to address:

- The total quantity entering the system in inputs,
- Whether the water sources for these inputs are renewable and sustainable, and
- Whether the water outputs are returned to the original surface basins so that downstream human and ecological users are not deprived of adequate water volumes

The human and ecological water users downstream require adequate water quality, otherwise the ability to use the water is effectively denied to them. Water quality indicators need to address the issue of discharge water quality, or impairment, from other changes such as metal pollutants, or changes to the quality of an aquifer such as saltwater intrusion (Owens, 2002).

The Indicators of Water Quality proposed by Owens (2002) can be summarised as follows.

- Eutrophication – a measure of the nutrient load
- Acidification
- Dissolved Oxygen Demand
- Thermal
- Pathogenic micro-organisms
- Colour and turbidity
- Suspended solids
- Toxic hazard
  - Toxic hazard to humans

- Toxic hazards to Environmental Organisms

The measurement/estimation and reporting of these indicators is difficult during the design phases of a project. Water Quality Guidelines proposed by government agencies are useful in determining legal standards for release to natural environments, but these are generally presented as a threshold value.

### ***2.3.2 Biological Freshwater Indicators***

Biological monitoring, defined as the utilisation of biota to provide an indication of the quality of the riverine environment, utilises one or more components of the biota such as fish, macroinvertebrates, diatoms etc., to provide a time-and constituent-integrated assessment of the system under consideration (Dallas 2000). The fundamental principle of biomonitoring is that living organisms reflect the conditions in which they live, and so changes in some aspect of the biota implies a change in the environment from which the organism came. (Day 2000). An ecological reference condition is the condition that is representative of a group of least impacted sites organised by selected physical, chemical and biological characteristics. Reference conditions enable the degree of degradation or deviation from natural conditions to be ascertained, and thereby serve as a foundation for developing biological criteria for the protection of aquatic ecosystems. When using biotic communities to detect the impact of one or more environmental stresses on a site, it is necessary to know the fauna to be expected at the site in the absence of environmental stresses (Dallas 2000).

Biomonitoring has been claimed to be a more sensitive and reliable measure of environmental condition (e.g. in terms of water pollution) than either physical or chemical measurements, but the two, i.e. biomonitoring and physiochemical monitoring, should be viewed as complementary with the goal of biomonitoring being to evaluate the effect of human activities on biological resources. Of the potential biotic components available for biomonitoring, macroinvertebrates are most commonly used since they are relatively non-mobile, readily sampled, and amongst the most sensitive components of aquatic ecosystems, thus being useful for assessing biological integrity. The advantages of using macroinvertebrates are summarised by Dallas (2000). Macroinvertebrates act as a continuous monitor of the water they inhabit enabling long term analysis of both regular and intermittent discharges, variable concentrations of

pollutants, single and multiple pollutants, and synergistic and antagonistic effects (Dallas 2000).

#### Bioassessment of water availability

It is relatively easy to assess the amount of surface water in a river, either visually or by means of some measuring device. Monitoring of riparian trees can provide useful information about changes in patterns of flow in a river (Day 2000).

#### Bioassessment of water quality

The most common bioassessment techniques are those that use component of the biota to assess water quality in a river. Most techniques are based on the assumption that some species are much more tolerant of chemical pollutants than others are, and that the overall composition of a biological assemblage will reflect the kinds and concentrations of pollutants in the water. Taxa or assemblages that seem to lend themselves to techniques of this kind include periphyton, diatoms, protozoans and fish. The prime disadvantage to using most of these organisms in biomonitoring are that one needs to use a microscope to identify them or, in the case of fish, to use time-consuming electrofishing or destructive sampling methods (Day 2000).

#### SASS, the South African Scoring System

Riverine invertebrates are particularly suitable biomonitoring tools because they are usually present in large numbers, fairly diverse, have relatively short life-spans, and differ in their tolerance to pollutants and other aspects of water quality . The prime disadvantage of using invertebrates has largely been the fact that they are difficult to identify to species level (Day 2000). The British Monitoring Working Party developed a technique for the evaluation of water quality which uses invertebrates identified only to family level (Moss 1998), which has been modified for use in South Africa (Day 2000). A description of the SASS method is given in Davies and Day (1998) and in Dickens and Graham (2001).

Dickens and Graham (1998) evaluated a number of waste water works in KwaZulu-Natal and concluded that biomonitoring using SASS gave a clear indication of the impact of effluents on a number of downstream rivers. Despite the general compliance with standards, the impact of effluent on the biota was generally significant. Given the importance of effluent dilution on entering the river and the large discrepancy between

the standards for wastewater and acceptable concentrations for the protection of aquatic life, it is clear that this system of management does not and cannot successfully protect the downstream environment (Dickens and Graham 1998).

### **2.3.3 Integrated Freshwater Indicators**

Cairns (1995) states, "*the best indication of pollution is a mix of chemical and biological information. If either is done in isolation then the information provided by the results is only partial and will have serious limitations.*" Integrated, weight-of-evidence approaches combine multiple site characterisation components such as physiochemical data, water and sediment quality criteria, habitat, flow, biological communities and toxicological information. Pollutants loading into aquatic ecosystems from the point and non-point sources vary in magnitude, frequency, duration and type, depending on meteorological and hydrological conditions, terrestrial aquatic system processes and anthropological activities. A myriad of potential stressor combinations are possible in water that receive significant non-point source pollutant loadings. In the laboratory, it would be impossible to evaluate even a small number of all combinations of stressors, varying the magnitude, frequency and duration of each stressor. Traditional methods simply look at one exposure scenario (Burton, 1999).

Traditional toxicity testing is inappropriate for many environmental exposures such as time-scale studies of runoff effects because of the exposure design of constant toxic concentrations. There are a number of uncertainties associated with predicting bioavailability using chemical criteria, suggesting that toxicity testing is crucial to any site-specific assessment. A major factor complicating the process of evaluating ecological effects is the uncertainty associated with extrapolating single species effect levels from laboratory exposures to multiple species/population/communities in situ (Burton, 1999).

Most sites have multiple stressors (physical, chemical and biological). Is it therefore essential that the relative contributions of these stressors be defined to design corrective measures effectively. The integrated laboratory and field approach rigorously defines the exposure of organisms (media of exposure and contaminant concentration), separating it into overlying water, sediment, historical sediment and interstitial water. The degree of contaminant-associated toxicity can best be assessed using a combination of laboratory and field screening methods which separate stressors into

different major categories including: metals, non-polar organics, photo-induced toxicity from poly aromatic hydrocarbons, ammonia, suspended solids, predators, dissolved oxygen, and flow (Burton, 1999).

#### ***2.3.4 Freshwater Indicators for the Design of Metals Refineries***

Any set of freshwater indicators selected for use during the design stages of base metals refineries need to meet the Goodland and Daly (1996) definition of sustainable development in that the indicator set should account for both absorptive and regenerative capacities of the catchment. Further, the indicator set should predict the anticipated environmental impacts of the proposed refinery from the level of information available at the various stages of design. Aspects of the indicator should be calculable and confirmed by measurements made in the field after the refinery is operational.

Ashton et al (2002) identified five major effects of mining industry on aquatic ecosystems. These are acid mine drainage, metals in aquatic systems, sedimentation, cyanide and water use. As discussed in Chapter 1, only water use and metal in aquatic systems are considered to this work. Owens (2002) proposes that both water quantity and quality should be incorporated in an indicator set for freshwater systems. These should be reflected in an environmental impact that can be evaluated in relation to the regenerative and absorptive capacity of the receiving water body. Water abstraction from, or effluent release to, a river system can be viewed as a disturbance to the system. The indicator set should thus also provide a measure of the period of recovery of the system to conditions prior to the disturbance.

Biological indicators are an important consideration when considering the state of a riverine ecosystem and in identifying changes to the ecological functioning of a riverine system. These indicators provide an effective means for evaluating the ecological impact of releases from operating plants provided some reference condition has been established. The causative relationship between biological indicators of river environmental quality and typical design variables in minerals refining is very poorly understood, and therefore I have chosen to focus on an examination of proxy indicators, which are all physiochemical in nature.

During the design phases, physiochemical variables relating to metal releases can be calculated from mass balance information for the proposed process. Further, the total

water use in terms of consumptive use and non-consumptive use – water returned to the river system – can also be derived from the same mass balance information. These variables do not necessarily represent the final environmental impact but could possibly serve as proxy indicators for environmental impacts provided a clear relationship can be established between the variable and the environmental impact. Typically, an environmental concentration can be calculated for a metal release to a river system. This environmental concentration could be linked to an environmental impact provided the fate of the metal in the system can be predicted and the environmental concentration linked to an environmental impact. In order to predict these, an understanding of the behaviour of metals in freshwater systems is required.

## **2.4 Aquatic Toxicity and Persistence**

Before discussing metals in freshwater aquatic ecosystems, definition of the parameters relating to the toxicity and persistence of substances in aquatic systems is required.

### **2.4.1 Aquatic Toxicity**

The aquatic toxicity of a substance is the basis for the identification of hazard to the aquatic environment. Classification is predicated from toxicity test results for fish, crustaceans and algae/aquatic plants as representative of aquatic fauna and flora for hazard identification (OECD, 2001a, DWAF, 1996).

- Acute toxicity - intrinsic property of a substance to be injurious to an organism in a short term exposure to that substance.
- Chronic toxicity - the potential or actual properties of a substance to cause adverse effects to aquatic organisms during exposures that are determined in relation to the life cycle of the organism.

Acute toxicity is generally expressed in terms of a concentration which is lethal to 50% of the test organisms ( $LC_{50}$ ), causes a measurable adverse effect to 50% of the test organisms (e.g. immobilisation of daphnids), or leads to a 50% reduction in test (treated) organism responses from control (untreated) organism responses (e.g. growth rate in algae) (OECD, 2001a).

### **2.4.2 Persistence**

The persistence of substances is the length of time the substance remains in the environmental compartment. Persistence increases the possibility that the substance will accumulate over time. Further, exposure of organisms to the substance may increase with additional inputs. Persistence of organic substances is assessed using biodegradation (CO<sub>2</sub> evolution/loss of dissolved organic carbon), hydrolysis, chemical/biological transformations and photolysis measurements. Loss of parent compound and conversion to a less toxic and persistent break down product is viewed as desirable. Rapid degradation is interpreted as leading to a reduction in exposure. Complete degradation to carbon dioxide and water is desirable (OECD, 2001a, Adams *et al.*, 2000, di Toro *et al.*, 2001a, Parametrix, 1995, Chapman, 1996, Chapman and Wang, 2000).

While this is an appropriate approach for organic compounds, the degradation tests used do not apply to metals. The inability of metal elements to undergo degradation is often translated to mean that metals are persistent (OECD, 2001a, Adams *et al.*, 2000, di Toro *et al.*, 2001a, Parametrix, 1995, Chapman, 1996, Chapman and Wang, 2000). This concept is discussed further in Chapter 2.5.3.

### **2.4.3 Bioaccumulation**

Bioaccumulation is '*the net result of uptake, transformation, and elimination of a substance in an organism due to waterborne exposure*'. The ratio of tissue concentration to the water concentration is termed the bioaccumulation factor (BAF) (OECD, 2001a). BAF estimates assumed exposure from water or diet or both and are derived from field data (Adams *et al.*, 2000). Bioconcentration is '*the accumulation and transfer of substances via food chain, resulting in an increase of internal concentrations in organisms on higher levels of the trophic chain*'.

For most organic chemicals uptake from water (bioconcentration) is believed to be the predominant route of uptake (OECD, 2001a). The degree of bioconcentration also depends on factors such as the degree of bioavailability, the physiology of test organism, maintenance of constant exposure concentration, exposure duration, metabolism inside the body of the target organism and excretion from the body (Adams *et al.*, 2000). For non-polar organic substances, bioconcentration factors can be

estimated by a measure of the octanol/water partition coefficient ( $K_{ow}$ ) (OECD, 2001a, Parametrix, 1995, Adams *et al.*, 2000, di Toro *et al.*, 2001a). There are important differences between organic substances and metals (defined as soluble metals in the water phase and total metal in the diet or tissue). These are discussed further in Chapter 2.5.3.

## **2.5 Metals in Aquatic Ecosystems**

The form of a metal has a direct bearing on its availability to aquatic life. Depending on the level of exposure, such availability may result in either beneficial or adverse environmental effects. Hazard identification and risk assessment procedures evaluate both metal elements and metal compounds and both are evaluated based on the available metal ions and available/soluble metal complexes that exist in the solution phase. When assessing the potential for ecological effects from the release of metals to an aquatic system, it is as important to consider the duration of exposure, as well as the form and concentration of the metal in the environment. The longer a substance remains in an environmental compartment in an available form, the greater the possibility that the substance will increase in environmental concentration over time, and that exposure levels will increase with the addition of new inputs to the system (di Toro *et al.*, 2001a, Chapman and Wang, 2000, Adams *et al.*, 2000).

### **2.5.1 Biological Effects of Metals**

Metals can be divided into two groups:

- Those which occur naturally in trace amounts in most waters, most of which are plant nutrients (including cobalt, copper, manganese, molybdenum, and zinc); and
- Those which usually do not occur in measurable amounts in natural waters, are potentially toxic in low concentrations, and have been widely distributed as a result of human activities (including cadmium, lead, mercury) (Dallas and Day, 1993, Dallas *et al.*, 1994, Davies and Day, 1998).

The US EPA considers only beryllium and mercury as hazardous, and barium, cadmium, lead, nickel, tin, vanadium, and zinc as potentially hazardous (Dallas and Day, 1993, Dallas *et al.*, 1994, Davies and Day, 1998).

**Table 2.3: Metals Classified according to their Toxicity and Availability in Natural Aquatic Systems (Dallas and Day, 1993)**

Non-critical	Toxic but insoluble or very rare	Very toxic and relatively accessible
<i>Na*</i> , <i>K*</i> , <i>Mg*</i> , <i>Al*</i> , <i>Li</i> , <i>Ca*</i> , <i>Fe*</i> , <i>Rb</i> , <i>Sr</i>	<i>Ti*</i> , <i>Hf</i> , <i>Zr</i> , <i>W</i> , <i>Nb</i> , <i>Ta</i> , <i>Re</i> , <i>Ga</i> , <i>La</i> , <i>Os</i> , <i>Rh</i> , <i>Ir</i> , <i>Ba</i>	<i>Be</i> , <i>Co</i> , <i>Ni</i> , <i>Cu</i> , <i>Zn</i> , <i>Sn</i> , <i>As</i> , <i>Se</i> , <i>Te</i> , <i>Pd</i> , <i>Ag</i> , <i>Cd</i> , <i>Pt</i> , <i>Au</i> , <i>Hg</i> , <i>Tl</i> , <i>Pb</i> , <i>Sb</i> , <i>Bi</i>

Italics atomic mass < 40.078 (i.e. not a heavy metal)

\* abundant in the earth's crust (i.e. not defined as trace metal)

Although many metals exhibit toxic properties at high doses, certain metals are essential for life and are required in animal nutrition. Essential metals are involved in many of the enzymatic and metabolic reactions that take place in an organism, either as a component or an activator of enzymes (Parametrix, 1995, Chapman and Wang, 2000). Examples of metals and their biological functions are presented in Table 2.4.

**Table 2.4: Examples of the Biological Functions of some Essential Metals (Parametrix, 1995, Dallas and Day, 1993, Chapman and Wang, 2000)**

Metal	Example of Biological Function
Cadmium	Cofactor of carbonic anhydrase when Zn is depleted
Cobalt	Component of vitamin B <sub>12</sub>
Chromium	Cofactor for insulin action
Copper	Prosthetic group for cytochrome, ascorbate peroxidase, chelatase and haemocyanin
Iron	Prosthetic group for haem enzymes (cytochrome oxidase, and haemoglobin)
Manganese	Cofactor in arginase, superoxide dismutase and O <sub>2</sub> evolving enzyme
Molybdenum	Cofactor in xanthine oxidase and nitrogenase
Nickel	Cofactor in urease
Selenium	Cofactor in glutathione peroxidase
Vanadium	Cofactor in nitrate reductase
Zinc	Cofactor in carbonic anhydrase, DNA and RNA polymerase and alkaline phosphatase

Metals usually exert their biological effects (either as essential micronutrients or as toxins) forming stable co-ordinate bonds in proteins where they function as catalysts in Redox reactions (e.g. Fe, Cu, Mo) or form part of the active centre of enzymes (e.g. Co, Zn) (Dallas and Day, 1993). The metals known to be essential in one or more biological systems are Mn (in enzymes), Fe (most important in haeme-containing pigments), Co

(in vitamin B12), Cu (in enzymes involved in Redox reactions), Zn (in enzymes) and Mo (proteins involving electron transfer and photosynthesis) (Dallas and Day, 1993, Parametrix, 1995). The particularly toxic metals tend to form more stable bonds with the SH group than with anions such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{OH}^-$  and  $\text{Cl}^-$  and thus affect proteins by combining with their thiol groups and thus altering their functioning (Dallas and Day, 1993). The utilisation of essential metals requires that a concentration of metabolically available metal must reach a minimal concentration in an organism (Parametrix, 1995).

### **2.5.2 Factors Affecting the Fate of Metals in Aquatic Systems**

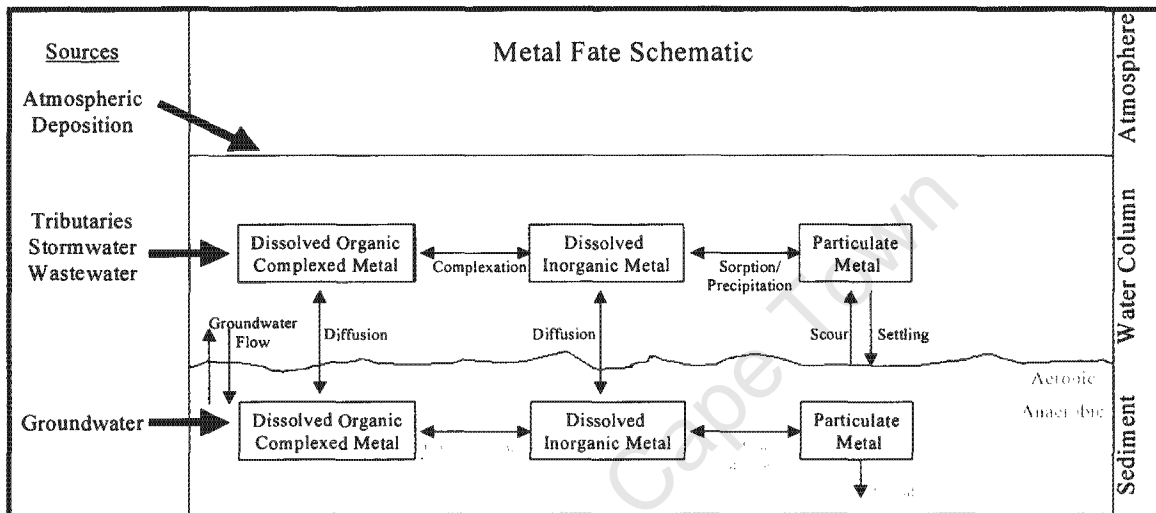
An evaluation of the toxicity of these substances to aquatic life requires that the form of the metal that is present and that the alternative routes of exposure of the organism to the metal be considered. Figure 2.3 below provides a very simple conceptual representation of an aquatic system, including both the water column and the underlying benthic sediment. The metal in the water column will be present in one of the following three forms:

- Dissolved Inorganic Metal, including both the ionic form and the inorganic complexes of the metal
- Dissolved Organically Complexed Metal and,
- Particulate Metal including both the absorbed and precipitated forms of the metals as well as any mineral phases that may be present.

The water column and sediment layer are in direct contact in aquatic systems. This leads to an exchange of constituents, including metals, between these compartments. The metal that ends up in the benthic sediment is distributed among the same three forms as in the water column. The percentage of the total metal associated with each form, as well as the detailed chemical speciation, will probably differ considerably from the distribution in the water column. The Redox conditions in the sediment will control the forms of the metals present in the sediment. Understanding the distribution of the metal among the various forms in both the water column and sediments is of critical importance for assessing the potential for toxicity, because the form of the metal will generally control its availability to the organism (di Toro *et al.*, 2001a). Distribution of the metals at a location is dependent upon the physics of the system: movement of water (i.e. fluid transport) and movement of particulate matter (i.e. sediment transport).

It is also dependent upon the chemistry of the system, as this controls the detailed speciation of the metal and its sorption to particulate matter in both the water column and the sediment compartments (di Toro *et al.*, 2001a, Adams *et al.*, 2000, Chapman and Wang, 2000).

**Figure 2.3: Fate of Metals in the Aquatic Environment (di Toro *et al.*, 2001a).**



The process of metal discharge to a water body and transport to the sediment can be summarised as follows (di Toro *et al.*, 2001a, Adams *et al.*, 2000):

- Dissolved metal partitions to particles
- Particles settle to the sediment
- New clean particles are:
  - Created (e.g. algae)
  - Introduced (e.g. runoff)
  - Resuspended (e.g. scour)

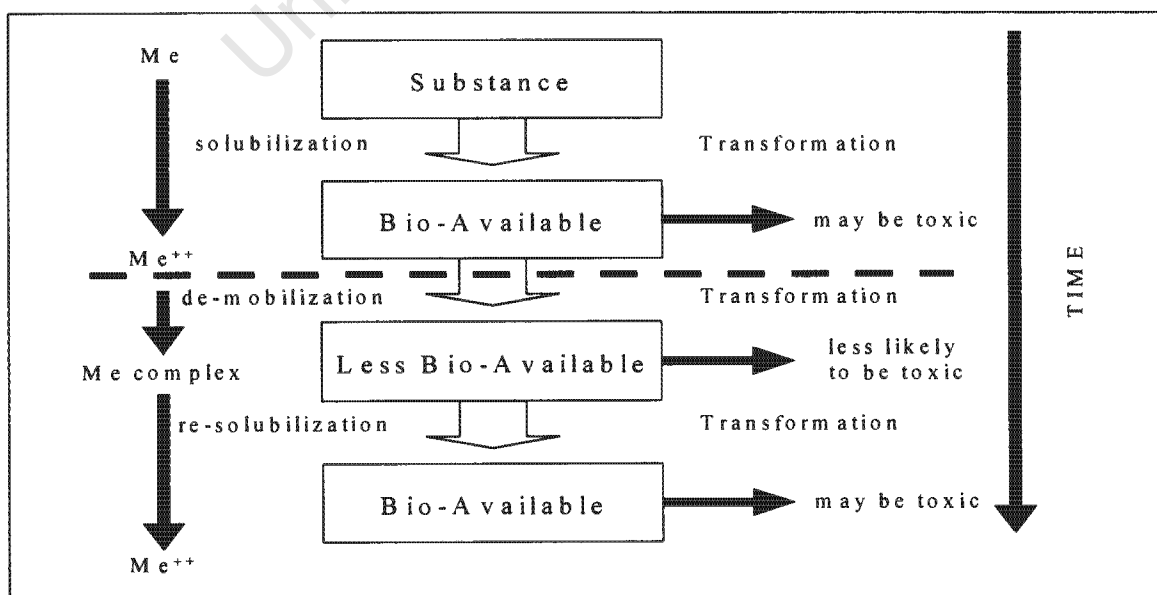
Re-suspension or scour of particulate material from the benthic sediments may occur through extreme flow or wind mixing events. Short term increases in total metal concentration in the water column may result from such events. The pH, Redox potential, solids sorption partition coefficient, hardness, salinity/total dissolved solids, dissolved oxygen concentration, and the presence of sulphides all have an impact on the complexation reactions taking place in the water column and the sediment (di Toro *et al.*, 2001a). Differences in metal specific characteristics result in dramatic differences in metal availability in surface waters and sediments.

### 2.5.3 Metals Persistence

The inability of metal elements to undergo degradation (especially biodegradation) is often translated to mean that metals are persistent. For organic substances, biodegradation is a primary, but not only, route of degradation of a substance in water. For metals and metal compounds, fate mechanisms other than biodegradation act to transform, bind, or transport forms of the metal or metal compounds such that the concentration of the bioavailable forms may decrease over time. Mechanisms such as oxidation have the potential to increase the concentrations of the oxidised metals. It is the net result of these processes together and the rate of input to the system that controls the amount of metal in solution (Chapman, 1996).

Persistence should reflect a measure of the bioavailable species. Measurements such as complexation, precipitation, and remineralisation are often more appropriate measures of persistence for metals than degradation. Complexation with dissolved organic carbon and suspended solids in the surface waters and binding with iron and manganese oxides and sulphides in sediments are key processes controlling metal exposure in aquatic ecosystems (OECD, 2001a, di Toro *et al.*, 2001a, Adams *et al.*, 2000, Chapman and Wang, 2000, Parametrix, 1995, Chapman, 1996).

**Figure 2.4: Transformation of Metals in Aquatic Environments (Chapman, 1996)**



Both total and soluble fractions of most metal ions decline fairly rapidly following release in typical surface waters and propose that an appropriate assessment of the metal persistence in surface waters should include an assessment of the bioavailable form of the metal species (di Toro *et al.*, 2001a, Adams *et al.*, 2000).

#### ***2.5.4 Bioavailability of Metals in Aquatic Ecosystems***

Because the toxicity of a metal depends on its fate in the environment, it is of paramount importance to understand all factors that might influence such fate. This fate depends upon the properties of the substance and the surrounding medium, whether it be water or sediment. Toxicity and bioaccumulation cannot be quantified if bioavailability is ignored. Bioavailability refers to the amount or concentration of a chemical that can be absorbed by an organism, thereby creating the potential for toxicity or the necessary concentration for survival. Concentration of metals in sediments usually exceeds those of overlying water by three to five orders of magnitude. With such high concentrations, the bioavailability of even minute fractions of total sediment associated metal assumes considerable importance. The composition of sediments is so complex and variable that it is often difficult to assess the bioavailability of sediment bound metals. In water and sediments, the most important factors in determining the bioavailability of metals are hardness, alkalinity, pH, Redox potential, and the composition and concentration of ions, particulate matter and organic carbon (Parametrix, 1995).

The flow rate and volume of the receiving water body influence metal toxicity via dilution within the system. Flow rate and water volume will vary with rainfall, season, groundwater, flow, etc. Substratum type influences the accumulation and remobilisation of metals in the sediments. At high temperatures an organism's respiratory activity is elevated, as is trace metal availability (faster rates of adsorption and releases), leading to increased toxicity. Linked to increase in temperature is a decrease in the oxygen content of the water that normally results in an increase in metal toxicity (Dallas and Day, 1993).

#### **Measuring Metals in the Environment**

While it is possible to model the behaviour of metals in a controlled laboratory experiment, it is difficult to predict or model the behaviour of metals in natural waters

and sediments. It has been shown that metal cation concentration correlates best with toxicity (Allen, 2000). Because there is no direct way to determine actual metal species in natural waters, indirect methods – such as characterising the water medium with respect to pH, Redox, particulate concentration and complexing agents - are used along with equilibrium models (e.g. MINTEQA2), to predict the metals speciation. Because bioavailability of metals depends on chemical form or speciation, it is necessary that analytical methods become available to determine or predict the bioavailable fraction of metal. Speciation of trace metals involves determination of the physical and chemical forms of the metal in solution. This includes the evaluation of free metal ions, inorganic and organic complexes, and organometallic compounds (Allen, 2000). The most common physical and chemical forms of metals in aquatic environments is presented in Table 2.5.

**Table 2.5: Physical and Chemical forms of Metals in Aquatic Systems (Allen, 2000)**

Description	Examples
Free metal ion – hydrated	$M(H_2O)$ or $M^{2+}$
Inorganic ion pairs and complexes	$MOH^+$ , $M(OH)_2$ , $MHCO_3$ , $MCO_3$
Organic complexes and chelates	M-SR (Metal cysteinate), M-OOCR (Metal Glycinate), M-EDTA
Metals bound to high molecular weight organic matter	M-humates
Metals present as highly dispersed inorganic colloids	FeOOH (goethite), $Fe(OH)_3$ , MS
Metals adsorbed on, or occluded in, inorganic colloids	$\square S-O-M+$ ( $\square S-O-H$ is iron oxide, manganese oxide, silica, clay, etc.)
Precipitates, minerals, organic detritus	

The physiochemical factors affecting metal bioavailability in aquatic systems are:

- Water Hardness and Alkalinity
- Ionic Strength
- Redox Potential and pH
- Ligands
- Suspended Particulate Matter and Organic Carbon
- Interactions at the Sediment/Water Interface

These are discussed further in Appendix A.3 with a view to provide an understanding of how these parameter affect the bioavailability of metals in aquatic systems.

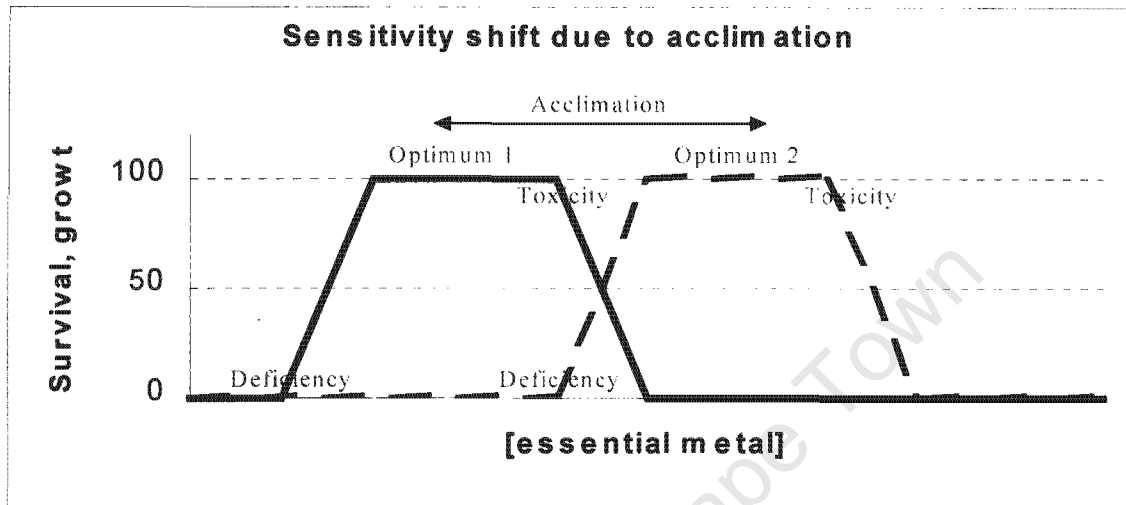
### **2.5.5 Deficiency, Tolerance and Acclimation**

The biological factors responsible for determining the response of an organism to a toxic trace metal include its life history stage, age and sex, levels of starvation and activity, the degree of physical protection, tolerance levels and acclimation, all of which may also affect susceptibility of organisms to pollutants other than trace metals (Dallas and Day, 1993). Recent research efforts have led to an enhanced understanding of the physiological basis of metal toxicity effects on aquatic organisms. These studies have, in combination with metal speciation work, led to an improved understanding of how water chemistry affects bioavailability, how metals interact with aquatic organisms to exert toxic effects at the organism site of action, and how toxic effect levels can be predicted (Janssen *et al.*, 2000).

Since organisms are dependent on essential metals for optimal growth and development, all species are acclimated to a range of bioavailable metal background concentrations occurring in their habitat (Janssen *et al.*, 2000). For essential metals, each species has an optimal range of concentration that is required for normal metabolic functioning. The essentiality of metals and metalloids to organisms is expressed in a bell-shaped dose-response curve. Deficiency symptoms occur at low concentrations and toxic effects at high concentrations. Between the two extremes, there is an optimal concentration range within which an organism experiences optimal growth, development and reproduction (Chapman and Wang, 2000). An organism's homeostatic capacity has limits and when the external concentration of an essential metal gets too high or too low, regulation will fail and toxicity or deficiency will occur (Janssen *et al.*, 2000). When the environmental concentration of an essential element is within the optimal concentration range, organisms can regulate their internal concentrations of the element. Non-essential metals and metalloids, such as lead, mercury and antimony, do not have explicit positive effects to organisms, because they do not have direct nutritional or biochemical effects, but adverse effects are not observed at low metal concentrations due to detoxification and adaptation. Adaptation is genetic, beyond the life span of the individual and it may occur without appreciable metabolic cost, acclimation is a physiological/structural mechanism of gaining increased

tolerance within a lifespan of the individual, and may have an appreciable metabolic cost (Chapman and Wang, 2000).

**Figure 2.5: Dose Response Curve (Janssen *et al.*, 2000, Chapman and Wang, 2000)**



The occurrence of deficiency effects and shifts in tolerance caused by metal acclimation has not, or has inadequately, been considered in most environmental risk assessments of essential metals. Acclimation, adaptation and deficiency effects induced by essential metals in naturally occurring plant and animal communities have been reported. Deficiency effects and metal acclimation can also be induced in a laboratory environment during long term culturing. It is possible that as certain test species are cultured in standard artificial culture media, which contain few or no essential metals, these organisms acclimate to the low metal concentrations and subsequently exhibit an increased (or decreased) susceptibility to these metals. Conversely, organisms cultured in media with elevated metal concentrations may become less (or more) sensitive. Considering that laboratory toxicity data are used for Water Quality Criteria and Predicted No Effect Concentration derivation, these acclimation induced sensitivity shifts may effect the ecological relevance and effectiveness of these environmental quality criteria (Janssen *et al.*, 2000, Chapman and Wang, 2000).

### **2.5.6 Bioaccumulation**

The ecological effect of metals on aquatic biota is discussed in Chapter 2.5.1 above. In this chapter the mechanisms of the uptake of metals in aquatic organisms is discussed.

Aquatic organisms can take up metals from the water and/or diet and store in their tissues. The process of bioaccumulation occurs for both essential and non-essential metals. Metal bioaccumulation is an important process whereby aquatic organisms obtain the metals essential for various biological functions. Aquatic biota regulate their internal concentration of essential metals by active regulation, storage, or a combination of both. Active regulators are organisms that maintain stable tissue concentrations by excreting metals at rates comparable to the intake rate (e.g. fish and crustaceans). Other biota store metals in detoxified forms such as in inorganic granules or bound to metallothioneins. Non-essential metals are also regulated to varying degrees because the mechanisms for regulating essential metals are not metal specific (Adams *et al.*, 2000).

As a result of these metal regulatory processes, an inverse relationship exists between water concentrations of metals and corresponding BCFs – at low water concentrations of metals, organisms are actively accumulating essential metals to meet their metabolic requirements while at high water concentrations, organisms with active regulatory mechanisms are able to excrete excess metals or limit uptake (Adams *et al.*, 2000).

### **2.5.7 Toxicity**

It is widely recognised that the toxicity of mono- and divalent metals is due predominantly to the free metal ions in solution (estimated by soluble metal measurements). Most of the toxicity data available to date have been derived using soluble metal salts and these data are used to characterise the toxicity of the metal itself. The assumption is that the dissolved metal ions in laboratory tests are completely bioavailable. Recent advances in estimating the bioavailable fraction of metal in solution using the Biotic Ligand Model (Paquin *et al.*, 2000, di Toro, Allen *et al.*, 2001b, Santore *et al.*, 2001) allows for more accurate prediction of toxicity under relevant environmental conditions. Differences in pH, dissolved organic carbon, hardness, and other water quality parameters can be accounted for in the model allowing predictions of bioavailability and toxicity in the field using laboratory data.

The presence of other metals and/or compounds may result in either synergistic or antagonistic interaction. Nickel and zinc and copper and zinc cause synergistic effects and are five times more toxic together than either on its own. While cadmium and

mercury have an antagonistic detoxifying effect (Dallas and Day, 1993, Dallas *et al.*, 1994, Davies and Day, 1998).

Janssen *et al.*, (2000) suggest that if standard test organisms are used, they should be cultured at a bioavailable metal background concentration that is representative of the environmental system under consideration. The dilution medium should be a natural medium representative of the system and that test organisms may be collected in a representative natural environmental, cultured on the natural medium and used in the toxicity tests.

## **2.6 Criteria to Evaluate Ecotoxicity Indicators**

The criteria to evaluate ecotoxicity effect indicators for their applicability include the following aspects (Hauschild and Pennington, 2000):

- Scientific validity
- Environmental relevance
- Reproducibility
- Transparency
- Quantification of uncertainty
- Complexity
- Feasibility
- Data availability

These criteria could be used to evaluate the models proposed once the models have been verified. A brief review of the models in terms of these criteria is presented in Section 5.4.3 of this thesis.

## **2.7 Modelling Metal Toxicity and Persistence**

Models have been proposed to describe the toxicity of metals in aquatic environments. The models try to describe the effects of water variables such as hardness, pH, TDS, dissolved organic carbon, on the toxicity of metals. The most successful of these models is the Biotic Ligand Model (di Toro, Allen *et al.*, 2001b, Santore *et al.*, 2001, Paquin *et al.*, 2000), which has been successful at describing the toxicity of copper and silver.

### Biotic Ligand Model

The Biotic Ligand Model (BLM) provides a direct and quantitative method for the evaluation of metal bioavailability as a function of water chemistry and organism sensitivity, thereby providing a means for estimating the effect of site-specific factors on metal toxicity (Paquin *et al.*, 2000). Paquin *et al.* (2000) describe the BLM as follows: *The BLM incorporates chemical equilibrium models used to calculate the distribution of metal among the free ion, inorganic complexes and organic complexes. The level of metal accumulation is calculated for the site of metal accumulation (biotic ligand), the gill in the case of fish. The metal concentration of metal that is associated with the biotic ligand is calculated in the same way as the concentration of metal that exists in association with any other organic or inorganic complexing ligands in the water. The biotic ligand competes with other complexing ligands (e.g. natural organic matter or the carbonate ion) for binding on the available metal. The BLM framework provides a direct basis for predicting the reduction in copper bioavailability due to increasing levels of natural organic matter, carbonate, alkalinity, or pH.*

Detailed description of the BLM are presented in di Toro, Allen *et al.* (2001b), Santore *et al.* (2001), Paquin *et al.* (2000). The reader is referred to this work as it represents the most recent development in relating the toxicity of metals to environmental factors. The model has not been used in this work as it has only been developed for two metals, copper and silver, and requires extensive parameterisation. It has been included for completeness.

### Modelling the Environmental Concentration of Metals in Aquatic Environments

Diamond *et al.* (1990) cited by di Toro *et al.* (2001a) and Adams *et al.* (2000) conducted mesocosm experiments in the great lakes region of the USA. The results indicated that the half-life for metals in the water column is directly related to the fraction of the metal that is absorbed to particles. The researchers found that for the case where there is an instantaneous release of metal with no inflow or outflow, the concentration profile for the dissolved metal in solution can be described by the following formula :

$$C_T = C_0 e^{-K_s f_p t} \quad (2-1)$$

where  $C_t$  is the concentration of dissolved metal (g/L) at time (t) in a completely mixed volume,  $C_0$  is the initial concentration of the metal in the water column (g/L),  $f_p$  is the particulate fraction,  $K_s$  is the first order removal rate coefficient ( $\text{day}^{-1}$ ).

The experimental procedure used by Diamond and co-workers is similar to the common practice of batch evaluation of chemical processes practices by Chemical Engineers. These batch results are converted to plug flow applications for the design of many Chemical and Metallurgical Processes. As discussed in Chapter 2.2 above, a model of a plug flow reactor was proposed to describe a river system. Admittedly, the description of the testwork results does not describe all the variables of the system. The sediment concentration and composition is not discussed. The prevalent water chemistry and physiochemical variables are not recoded. The stated equation assumes a first order reaction for all the metals considered in the lake system. The applicability of this relationship in a riverine system needs to be confirmed. Having considered these comments, it is believed that the relationship can be used to describe the behaviour of metals in river systems with the knowledge that the applicability needs to be confirmed. Southern African rivers carry high sediment loads naturally (Davies and Day, 1998) and it can be assumed that the sediment load of the Southern African rivers is sufficient sediment with the required characteristics to result in a first order reaction rate for metal removal from the water column. Using the above equation 2-1 allows for the prediction of the attenuation of the environmental concentration of metals down the length of a river.

This relationship between the environmental metal concentration and the initial release concentration is developed further in Chapter 4, during the development of a model for the removal of metal from the water column in a stream.

### **2.7.1 Ecotoxicity**

Having established that Ecotoxicological impacts depend on exposures to chemical and biological substances in Chapter 2.5.7 and that the environmental concentration of a metal released to a river can be described by equation 2-1, the link between the environmental concentration and the ecotoxicological impact of a metal in an aquatic system is explored here. The potential effects on ecosystems depend on the actual emission (exposure of the organism to the specific substance) and fate of the specific

substances emitted to the environment. The toxic effect of substances released to an environment can be described by the following equation (Schultze *et al.*, 2001)

$$S^m = \sum_i F_i^m E_i^m M_i^m \quad (2-2)$$

where  $m$  is the medium in which an effect occurs,  $i$  is the substance,  $S$  is the category indicator (of toxic effect score),  $F$  is the Fate and exposure factor and is based on the persistence of the substance in the medium,  $E$  is the effect factor which is usually represented as the reciprocal of the no observed effect concentration, and  $M$  is the mass emitted, which could be expressed as an environmental concentration. This equation can be related to the concentration of the substance in the environment after an effluent emission. The fate of chemical substances depends on:

- degradation rate (aerobic/anaerobic, hydrolytic/photolytic)
- bioaccumulation
- evaporation
- deposition

The degradation rate will affect both the possibility of the substance to reacting the target organism and the kind of toxic effect. Readily degradable substances can show acute toxic effects depending on the degradation type and rate in the actual medium, whereas substances that are not readily degradable can bioaccumulate in the environment and/or show chronic toxic effects. The rates of evaporation/deposition will affect the transfer of substances between the different mediums e.g. air, water, soil or food chains). For example, aeration leads to evaporation of volatile substances from the water, and thereby protecting the biological processes in the wastewater treatment plant against potential toxic or inhibitory effects but also burdening the surroundings (Schultze *et al.*, 2001).

The model proposed for the environmental concentration of metals in river (equation 2-1) accounts for these fate processes, but not for the exposure aspect of toxicity to organisms.

A number of methods have been proposed for the evaluation of the eco toxicological impacts of emissions to the environment. There is currently no internationally accepted method of evaluating the ecotoxicological impacts. Boustead *et al.* (2000), Schultze *et al.* (2001) and Guinee *et al.* (2001) provide discussion on a selection of current

methods. Schultze *et al.* (2001) compared four methods of determining the toxic effect of a substance. These are discussed further in Appendix A.4. This has been included to allow the reader to become further acquainted with the calculation of ecological toxicity. Since the link between environmental concentration and ecological toxicity has not been internationally accepted, this work reports the ecological concentration as a final output to allow the reader to use their preferred methodology for evaluating the ecological toxicity of metals.

### **2.7.2 Multi-species Toxicity**

The methods discussed above concentrate on assessing ecotoxicological effects based on a threshold value, expressed in the effect factor as the reciprocal of a No Observed Effect Concentration (NOEC) or something similar. For such methods, the prevailing background concentration is unimportant. There is, however, a trend towards incorporating concentration effect curves, or the slopes of such curves, in which the effect factor is dependent upon the background concentration. This is the approach used in the Eco-Indicator 99 proposed by Goedkoop and Spriensma (1999). The approach is based on the notion of PAFs (Potentially Affected Fraction), the fraction of species that, given an environmental concentration, is exposed above the NOEC. The higher the concentration, the greater the percentage of species considered to be affected. PAFs are based on substance specific species sensitivity, which, in turn based on the NOECs for these substances for different species. Huijbregts *et al.* (2001) discuss the PAF concept further.

The concept of multi-substance Potentially Affected Fraction (msPAF) accounting for the cumulative effect of a suite of chemical species has been proposed (Huijbregts *et al.*, 2001). The method by which the toxicity of the individual chemicals is aggregated has not been formally established. As discussed above, some metals exhibit synergistic or antagonistic toxicity effects. The following have been proposed as methodologies for aggregating the toxic effect of a multi-substance effluent:

1. Concentration addition for hydrophobic, chemically inert organic substances (i.e. narcotics)
2. Response addition for all other compounds
3. No correlation in sensitivities or interaction of effects between substances exists.

Huijbregts *et al.* (2001) propose an alternative approach of a damage function where the results of the analysis are presented in terms of the Potentially Disappeared Fraction of species (PDF) as a preferred indicator. The PDF can be interpreted as the fraction of species that has a high probability of no occurrence in a region due to unfavourable conditions.

The concept of multi-species toxicity has been investigated to allow the description of whole effluent toxicity, where the toxic effect of the whole effluent is considered rather than the individual effect of the substances contained in the effluent. Whole effluent toxicity has been the subject of discussion presented by Grothe *et al.* (eds)(1995), Chapman (2000), Diamond and Daley (2000), and Markle *et al.* (2000) but will not be covered in this thesis.

## **2.8 Closure**

In this section, water variables have been discussed from a riverine ecosystem perspective. Environmental Modelling is briefly reviewed with the fate and transport aspects of these models and their application to the modelling of riverine systems. A methodology for the modelling of a riverine ecosystem, by means of a series of continuous stirred tank reactors, is proposed. This concept is developed further in Chapter 3 when a River Compartment Model is proposed to represent a riverine system.

Freshwater Indicators covering both physiochemical and biological indicator systems have been discussed and indicators for the monitoring of industrial performance are discussed. Indicators are grouped into two general categories of water quantity and water quality. Water abstraction from, or effluent release to, a catchment, and the resultant environmental effects of changes to the flow patterns of riverine systems are reflected in water quantity indicators. The change in the physiochemical constitution of a river system by the introduction of an agricultural, industrial or domestic effluent is reflected in water quality indicators.

Finally, the persistence and toxicity of metals in aquatic ecosystems has been discussed considering factors which affect the fate of metals in aquatic systems. The discussion focused on freshwater rather than incorporating all aquatic habitats. The modelling of metals in aquatic ecosystems has been introduced with considerations of how indicators

can be represented in the design phase of process design projects. The relationship between environmental concentration of a substance and the resultant toxic effect is discussed.

University of Cape Town

## **CHAPTER 3 – DESIGN OF BASE METALS REFINERIES**

Having reviewed the literature discussing the prediction of environmental impact of metals in river systems, this chapter turns to the design of process plant, and the incorporation of environmental considerations into the design process. Given the overall focus on minerals and metals, the design of base metals refineries is discussed briefly in order to establish the requisite level of information available at the various design stages. The current environmental initiatives of the mining and metallurgical industry are briefly highlighted and the use of water in base metals refineries is discussed. Life Cycle Assessment is introduced as a systems tool suitable for the evaluation of environmental impacts of releases from these plants. The shortcomings of Life Cycle Assessment regarding metals and river systems are briefly discussed. Finally, the stated hypothesis is evaluated in terms of the literature reviewed.

### **3.1 Design of Chemical Plants**

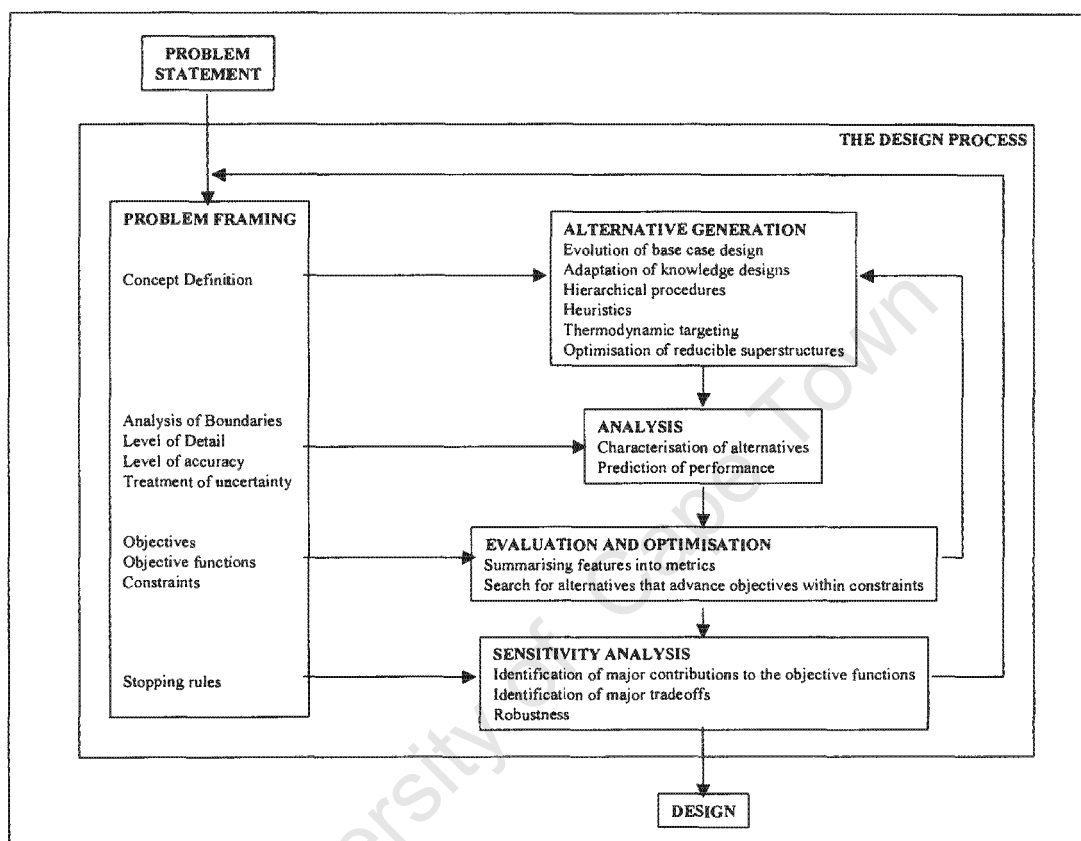
Process design follows a general procedure, which begins with initial, low-accuracy, evaluations of the proposed project. The level of detail included in each step of the process increases as the process concept evolves to a mature fully commissioned and operating plant. Further evolutions of the plant continue through the operating life of the plant in the addition of new technologies, process modifications, pollution abatement etc. As the level of detail increases, so does the level of accuracy of process information that is available to determine the environmental impact of the proposed process facility. To appreciate how environmental objectives can be incorporated into the design of metallurgical plants, an understanding of the design process is required. For this purpose, the work of Cano-Ruiz and McRae (1999) is used as a major reference since this work constitutes a review of environmental considerations during the design of chemical plants. There are other representations of the design process, but these are not considered here since this thesis focuses on consideration of freshwater issues in the design of base metals refineries, rather than the design process itself.

#### ***3.1.1 Design of Chemical Plants***

Cano-Ruiz and McRae (1999) summarise the design process in the diagram presented in Figure 3.1. The Problem Statement describes the requirement established by the owner. Once the problem has been stated, it is framed to set the context for the

ensuing work. Problem framing is essential as it establishes the battery limits of the design, the level of accuracy, the feedstocks and the expected products. This has also been referred to as the basis of design.

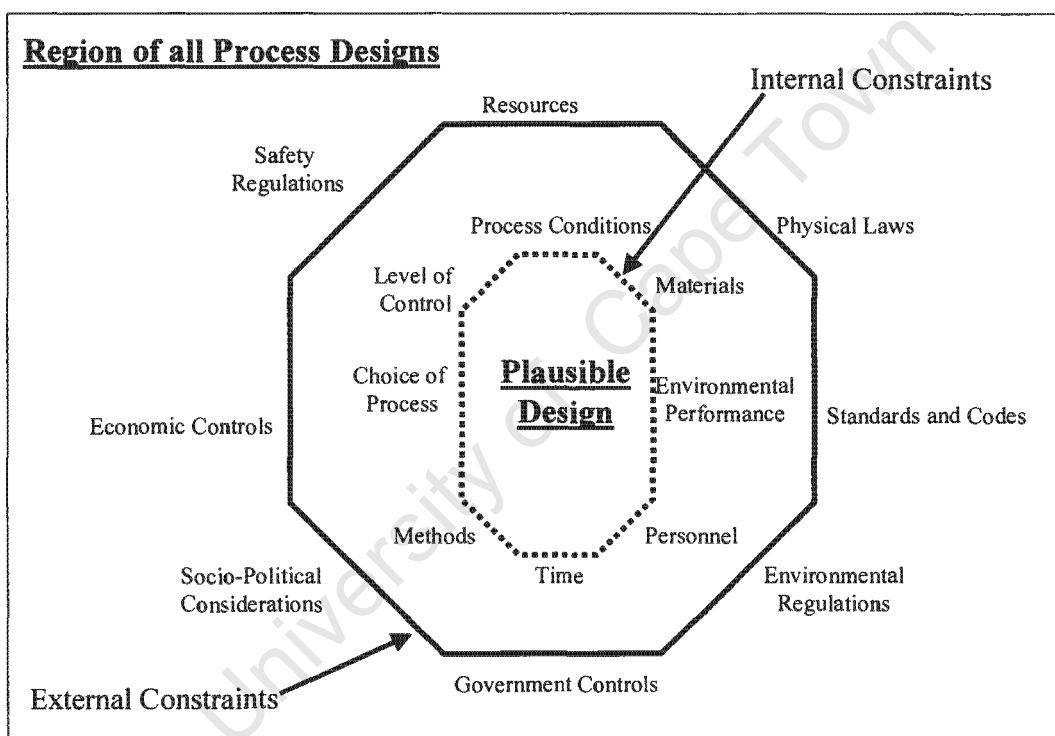
**Figure 3.1: The Design Process (Cano-Ruiz and McRae, 1999)**



Cano-Ruiz and McRae (1999) highlight the importance of the problem framing exercise and state that design problems are rarely fully specified. On the path from receiving a problem statement to delivering a completed design, design teams make decisions regarding the concept definition, scope of analysis, design objectives, constraints, evaluation criteria and stopping rules. Framing is often conducted implicitly by following available precedents. The constraints placed on a design project limit the alternatives available in the design space. Including environmental considerations in the problem framing exercise increases the number of constraints on the design process. This has the obvious effect of reducing the possible design space. Figure 3.2 details the plausible design space that constrained by the internal constraints placed on it by the owner and the external constraints exerted by economic climate, socio-political and legislative constraints.

Once the design problem has been adequately specified, alternatives to meet the requirements are generated. There are many different methods available for generating process design alternatives including the application of existing design concepts and the generation of new ones from first principles. Time is often limited in design projects. This limits the number of alternatives that can be generated and the level of detail to which these alternatives can be analysed. Trade-offs between comprehensiveness and economy are generally required in the number of alternatives that can be analysed.

**Figure 3.2: Process Design Constraints (adapted from Sinnott *et al.*, 1983)**



Once a set of alternatives has been generated, these are analysed in accordance to the criteria established in the framing exercise. Engineering analysis usually begins with evaluation of mass and energy balances for each of the candidate process flowsheets. This information is used to determine the flow rates, compositions, pressure, temperature, and physical state of all material streams, as well as the energy consumption rates from various sources. From this information, basic units can be sized and specifications drawn up.

The analysis evaluates the design alternatives against a predetermined set of performance indicators or objectives. These indicators are typically economic in nature, but increasingly take explicit account of other objectives, including environmental impacts. The analysis compiles a ranking of the alternatives according to the overall attractiveness of the specific alternatives.

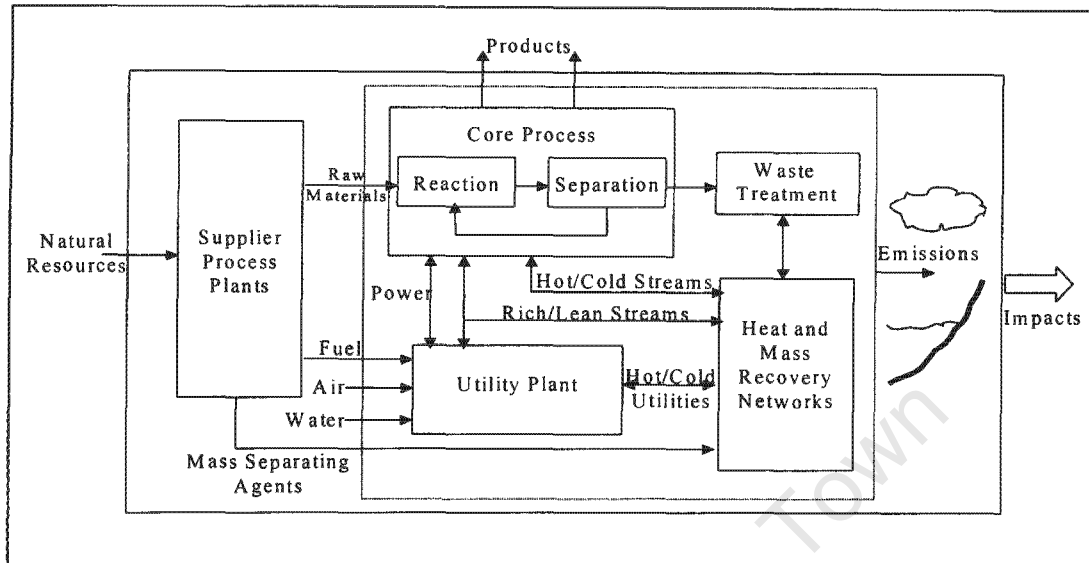
Process design is iterative, guided by opportunities for improvement. This can be done in a sensitivity analysis. Should opportunities be identified, these can be incorporated in the design framing exercise of the next iteration of the design process. Subsequent iterations usually incorporate an increase in the level of detail and accuracy of the design, which is commonly expressed in economic terms (Table 3.1), representing increased levels of detail of the process flows and resultant information available to evaluate environmental impacts

**Table 3.1: Types of Design Estimates (Douglas, 1988)**

Level of Design	
Order of magnitude estimate	(ratio estimate) based on similar previous cost data; probable accuracy exceeds $\pm 40\%$
Study estimate	(factored estimate) based on knowledge of major items of equipment; probable accuracy exceeds $\pm 25\%$
Preliminary estimate	(budget authorisation estimate, scope estimate) based on sufficient data to permit the estimate to be budgeted; probable accuracy exceeds $\pm 12\%$
Definitive estimate	(project control estimate) based on almost complete data, but before completion of drawings and specifications; probable accuracy exceeds $\pm 6\%$
Detailed estimate	(contractor's estimate) based on complete engineering drawings, specifications and site surveys; probable accuracy exceeds $\pm 3\%$

Cano-Ruiz and McRae (1999) discuss the evolution of the Design Framing over the last 40 years. Beginning in the 1960s' the authors suggest that process design only considered the core reaction and separation processes. In the 1980's, the chemical process design incorporated heat and power integration revealing opportunities to decrease energy consumption with significant cost savings because of the energy crisis of the 1970's. The authors propose that in the 21<sup>st</sup> century further incorporation of integration principles will reveal opportunities to decrease raw material consumption, realising increased cost savings, in the chemical design process (Figure 3.3).

**Figure 3.3: Framing of Chemical Process Design (Cano-Ruiz and McRae, 1999)**



Though the above discussion is generic, the arguments and structures apply to minerals as well as to chemical process design. That said, there are some important differences between the two. Base Metals Refineries have a number of constraints posed on them, which constrain the design space. These include, amongst others, the ore type being processed, the impurities present in the ore body, the variability in the metal content and mineralogy of the ore body, the location of the ore body, etc.

### **3.1.2 Design of Base Metals Refineries**

The design of base metals refineries is influenced greatly by the complexity and variability of the feed. For example, Stewart (2002) stated that a feed to a copper refinery can contain more than 60 elements in thousands of combinations as minerals. The deportment of these minerals through the process steps and finally to the end products or the environment is challenging to quantify. Designers in the minerals industry rely heavily on existing process plants and testwork to design base metals refineries. The level of information available through the design process increases in accuracy as testwork and design teams work through a flow sheet template. For a hydrometallurgical flowsheet, the template would follow a generalised programme of preparing the ore and concentrating value metal minerals, solubilising the valued metals, purifying the solutions by removal of bulk impurity elements e.g. iron, separating major metal streams, purifying the major streams, and finally recovering

value metals from solution. The level of information available for the evaluation of the environmental impact of a process facility increases through the design process. Table 3.2 summarises the level of information available for environmental impact evaluation as a function of the level of design accuracy.

**Table 3.2: Level of Information for Design Estimates**

Level of Design	Level of Information for Environmental Impact Evaluation
Order of magnitude estimate	Mass balance for core process covering major metals. Process based on existing plants treating similar ore body. Site not selected.
Study estimate	Mass balance for major and selected minor metals. Process based on scoping testwork performed on proposed ore body. Existing plants treating similar ore body used as a template for testwork. Site not selected.
Preliminary estimate	Mass balance for major metals and most minor metals. Process variables determined from testwork. Utility requirements determined from testwork and process simulations. Site selection considered but possibly not finalised.
Definitive estimate	Mass balance for all elements. Process variables determined by locked cycle testwork. Utility requirements defined, waste treatment requirements proposed. Site selected. Information used for Environmental Impact Assessment.
Detailed estimate	Complete Mass and energy balance. Process and utilities plant completely defined. Environmental Impact Assessment completed.

The early stages of the design process offer the greatest flexibility in selecting the process routes for a process facility. The ore type (sulphide or oxide) plays a great role in limiting the options available to the design team. The ore type and valued metal concentration in the ore have the greatest influence in determining the possible process routes available to the design team. For example, oxide ores are not well known for their floatation characteristics and are thus treated as whole ores in hydrometallurgical facilities by heap, vat or high-pressure acid leach, or reductive pyrometallurgical processes. Sulphide ores can be treated in concentrators to separate a concentrate from the tailings material. The concentrate could be further processed in a roaster or smelter followed by a hydrometallurgical facility, or directly by a hydrometallurgical facility.

Environmental Impact Assessments are generally conducted between the Definitive Estimate and Detailed Estimate stages of the design process, or concurrently with the

Detailed Estimate. This does not readily allow scope for environmental impact information to be incorporated in the design process in order to reduce the environmental impact of metallurgical process facilities. The net result is that waste treatment facilities are added on to the core process to meet the legislative guidelines.

### ***3.1.3 Environmental Initiatives in the Minerals Industry***

The minerals industry has taken initiatives to reduce the long-term environmental impact of mining and minerals refining operations. A charter has been proposed for the mining and minerals industry and significant advances in understanding the environmental impacts related to mining and the minerals industry were made during the Mining Minerals and Sustainable Development (MMSD) project undertaken by the International Institute for Environment and Development (IIED). The sections of the charter relevant to the design of minerals operations are presented below.

The International Council on Mining and Metals (ICMM) has adopted a Sustainable Development Charter, which details management principles in four key areas: Environmental Stewardship, Product Stewardship; Community Responsibility and General Corporate Responsibilities. The ICMM Charter recognises that sustainable development is a corporate priority and expresses the commitment of ICMM members to high quality in their economic, environmental and social performance and in the following of sustainable development. A copy of the charter is available on the ICMM website ([www.icmm.org](http://www.icmm.org)). The sections of the charter relevant to this thesis are presented below:

- Review and take account of the environmental impacts of exploration, infrastructure development, mining or processing activities, and plan and conduct the design, development, operation, remediation and closure of all facilities in a manner that optimises the economic use of resources while reducing adverse environmental impacts to acceptable levels.
- Employ risk management strategies in design, operation and decommissioning, including the handling and disposal of hazardous materials and waste. If a preliminary risk assessment indicates unacceptable risks for human health or the environment, the lack of full scientific certainty will not be used as a reason to delay the introduction of cost-effective measures to reduce environmental and human health risks to acceptable levels.

- Develop approaches in the early stages of exploration projects that take into consideration related environmental and community impacts.
- Develop, design and operate facilities and conduct activities taking into consideration the efficient use of energy, water and other natural resources and materials, including their recycling and reuse, the minimization of waste and the responsible management of residual materials.

The challenge to the minerals industry is to translate the intent of this charter into action plans “on the ground”, including the design of new processing plants. The need for such concrete action is nowhere more apparent than around the issue of water consumption and water quality. This is discussed below, with specific reference to base metals’ refining.

#### ***3.1.4 Water Use in Base Metals Refineries***

Base Metals Refining is a significant contributor to metal releases to the environment. As such, the refining of base metals has been used as a case study for this thesis. However, the concepts discussed here are applicable to other process industries in which metal-containing effluent streams are generated.

The base metal refining process can be considered as three processes, each with different water requirements and pollution characteristics. Base Metal Refineries can be grouped into three basic categories:

- Minerals Processing Facilities,
- Pyrometallurgical Facilities, and
- Hydrometallurgical Facilities

The water use in each of these types of facilities varies. In minerals processing, water is used primarily as a transport medium for generally (but not always) inert materials. Reagents are added to the water such as frothing agents, depressants, surfactants etc., and these tend to persist in dilute concentrations in the water. Large volumes of water are used, but the water can often be re-used. Losses from the system include water retained in both the tailings (although this can usually be recycled into the process) and concentrate, and evaporation from the large inventory. The long-term environmental impact of tailings are not considered here e.g. acid mine drainage and groundwater pollution from tailings dams, which are important considerations for closure. Suspended

solids in natural water systems are a major problem too, but this often constitutes inert materials (or at least those thought to be so!).

Water use in Pyrometallurgical facilities is largely as a utility for cooling or slag and/or matte granulation. Water is used for pollution abatement, especially in the capture of sulphur dioxide in acid plants. Pyrometallurgical plants have an indirect impact on natural water via atmospheric emissions of SO<sub>x</sub> and NO<sub>x</sub> causing acidification.

**Table 3.3: Water Use in Base Metals Refining**

Facility	Minerals Processing	Pyrometallurgical	Hydrometallurgical
<b>Water Use</b>	Transport	Utilities (Cooling) Pollution Abatement Granulation	Reaction Medium Transport Utilities Pollution Abatement
<b>Inventory</b>	Very Large	Small	Large
<b>Re-use</b>	Very High	High	Moderate to High
<b>Water quality</b>	Raw to Potable	Raw to Potable	Potable to Demineralised
<b>Losses</b>	Entrainment Evaporation	Evaporation	Inventory Evaporation Spills/Releases Products
<b>Environmental Impact</b>	Consumption Suspended Solids	Consumption Thermal Acidification (via atmospheric transport)	Consumption Ecotoxicity Eutrophication Acidification Chemical Oxygen Demand Suspended Solids

Hydrometallurgical facilities pose the greatest direct environmental impact on aquatic systems. These facilities use water as a reaction medium and have a considerable inventory. Water input to the facility is also not necessarily converted to water output, with large quantities of water being allowed to evaporate in impoundments. Environmental impact is through metals toxicity, acidification, suspended solids, COD, Redox pH, eutrophication, organic compounds, losses to evaporation. Water consumption and inventory holding in evaporation dams increases the environmental consequences of hydrometallurgical facilities.

## **3.2 Environmental Considerations in the Design of Process Plant**

It is widely recognised that early consideration of environmental matters during the design is needed to obtain good environmental performance at least cost. The early stages of chemical process design – chemical route selection and conceptual design – provide the greatest opportunities for identification of potential environmental impacts and to take remedial action. The flexibility existing during flowsheet development still allows some creativity to be focussed on environmental performance. The later stages of design (detailed design layout etc.) tend to have limited scope to influence the environmental performance of the proposed facility as most of the process steps have been defined and the resultant environmental impact largely determined. At these stages, processes have been finalised and it is only through equipment selection or the addition of specific waste treatment units that the environmental impact can be reduced. Both of these options usually increase the projected cost of the completed plant. To manage the profit in a life cycle basis, process planning at the conceptual phase is important because 85% of the life cycle cost is determined by decisions made in planning and design phases (Blanchard 1991)

### ***3.2.1 Including Environmental Impacts as Design Objectives***

Cano-Ruiz and McRae (1999) propose a number of mechanisms by which environmental impacts can be included as design objectives. These include:

- Setting environmental concerns as constraints on economic optimisation
- Setting environmental concerns as objectives by:
  - Minimisation of emissions of pollutants of concern.
  - Minimisation of mass of waste generated.
  - Minimisation of contribution to specific environmental problem.
  - Minimisation of the overall indicator of environmental impact.
- Trading off environmental objectives against other design objectives.

Placing water and other environmental considerations high on the priority list in the design process constitutes an important step in establishing an ethic of environmentally conscious design. Water and environmental considerations can be incorporated within the design framing exercise thus posing a top-down constraint of the design process. This can be achieved by adopting a systems engineering view of a top down approach to engineering design, requiring a fundamental shift in the approach of engineering

houses and owners during the design process. Decision criteria can be set as a design criteria document such as those adopted by Rio Tinto, summarised in Table 3.4.

**Table 3.4: Rio Tinto Guidelines for Water Management (Leiner *et al.*, 1998)**

1	Water use and discharge planning conforms to the water requirements of other users within the catchment
2	Senior management through formalised objectives and targets communicates policy for water management
3	Water use, storage and discharge are defined in a site water balance that is updated to reflect changes to operational requirements
4	Water management practices include the monitoring of supply and discharge
5	Freshwater use is to be reduced through process improvement, recycling of waste-water and, where applicable, by the use of poorer quality water
6	Water abstraction, storage or discharge does not irreversibly reduce the health of wildlife or habitats
7	Water storage, treatment and discharge facilities are designed, constructed and managed based on best available applicable to local operating conditions

Rio Tinto used these principles on an existing plant and a conceptual design, reducing the water consumption at both facilities. At Rossing Uranium in Namibia, water consumption was reduced by more than 50%, and at Hamersley Iron Yandi Project in Australia, the long-term water usage was considered in selecting mining and operational strategies ensuring that water quality for the surrounding ecosystems was not compromised (Leiner *et al.*, 1998).

### **3.2.2 Predicting Environmental Impacts during Design**

Cano-Ruiz and McRae (1999) summarise the various methods of evaluating the impact of the toxic effect of substance release to the environment. These are summarised as follows:

- Sum of mass flows of substance divided by 50% lethal dose concentration of substance.
- Sum of mass flows of substance divided by the threshold limit value of substance.
- Scoring systems to evaluate chemicals based on measure of toxicity or measures of toxicity and exposure.

- Indexes based on the ratio of the predicted environmental concentration to the predicted no effect concentration.
- Systems which include toxicity, persistence, environmental mobility and taking into account the relationship between environmental concentrations and chemical doses received through different exposure routes.
- Aggregation of all impacts into a single index for environmental impact.

These impacts relating to environmental toxicity have been discussed in Chapter 2.7. These methodologies of predicting environmental impacts need to be related to the information available at the design stages of process plants to be of any use during the design process. These metrics can be used to formulate environmental objectives during the design process, although there are challenges associated in reconciling process level information used during the design of process plants and the eco-system scale impacts.

### ***3.2.3 Importance of Site- and Catchment-Wide Considerations***

Cano-Ruiz and McRae (1999) recommend that there should be a shift from considering boundary effluent concentrations to the consideration of overall environmental impacts. This suggests a need to move from a "process boundary" consideration, to one in which all ecological system-wide impacts are considered. This is particularly relevant to riverine ecosystems. Environmental impacts on riverine systems manifest themselves downstream of the point of interaction. Moving the focus from site boundary conditions to catchment level impacts places a broader focus on the consequences of releasing materials to surrounding ecosystems.

### **3.3 Life Cycle Assessment**

Life Cycle Assessment (LCA) is an increasingly common method of predicting and evaluating the potential environmental impact of process plants. As such, it fits well with process design, being based on common chemical engineering practice of mass and energy balances, but with the specific intention of addressing all material and energy transformations over "cradle to grave". An LCA tabulates the emissions and the consumption of resources at every stage in a product's life cycle, from its cradle to its grave (raw material extractions, energy acquisition, manufacturing, use and waste disposal). Indicators of the likely impacts and the potential consequences of associated impacts are calculated in the context of, e.g. climate change, stratospheric ozone

depletion, tropospheric ozone (smog) creation, eutrophication, acidification, toxicological impacts on human health and ecosystems, fossil fuel depletion, water consumption, land use (Guinee *et al.*, 2001).

LCA is well documented and standards are available from the International Standards Organisation for the execution of an LCA. LCA is a decision support tool and as such lends itself to providing information upon which informed decisions can be made – including those pertinent to process design (Hertwich and Hammitt, 2001).

A LCA consists of four phases (Guinee *et al.*, 2001):

- **The goal and scope** definition of an LCA provides a description of the product system in terms of the system boundaries and a functional unit. The functional unit is the important basis on which alternative goods, or processes or services, are comparable.
- **Life Cycle Inventory** (LCI) is a methodology for identifying and evaluating resource consumption and emissions at all the stages in a product's life cycle.
- **Impact Assessment** - evaluates the potential impact of the life cycle of the operation; some consideration of valuation is often attempted here.
- **Interpretation/Improvement** - evaluation of the results, choices and assumptions of the LCA in terms of soundness and robustness and the overall conclusion drawn

A large number of indicator methodologies are proposed in the literature for characterising impacts in different impact categories in LCA. Not all these methodologies are suitable, or scientifically defensible, in the context of risks and potential consequences. Methods in LCA software are often outdated, providing conflicting and sometimes misleading results (Pennington and Yue, 2000, Boustead *et al.*, 2000). Guinee *et al.* (2001) provides a summary of the practices used in evaluating the various impact categories currently used in LCA. This presents a challenge to users of the methodology in process design, and is particularly apparent in consideration of impacts related to minerals and metals. Of importance here are issues relating to the spatial and temporal dimensions of impacts. Typically, within Life Cycle Assessment (LCA), all impacts are assumed to occur instantaneously, and to occupy a global footprint. This is a significant limitation of the approach, and there is significant current research effort underway to address these limitations (see UNEP/SETAC Life Cycle

Initiative, 2003). What is apparent is that there is a need to identify, at the very least, “proxy” indicators of environmental impact, which are more meaningful than the global-averaged values. This is particularly important for minerals and metals, which to date, have been poorly studied in terms of their environmental impacts. This clearly has consequences for designers of minerals and metals refining technologies intent on bringing on board more representative metrics of environmental impact. This is discussed below with reference to river systems.

### **3.3.1 Life Cycle Assessment in the Design Process**

A number of authors have addressed the use of Life Cycle Assessment in the design process. These include Azapagic (1999), Sharrat (1999), Ishii et al. (1997), Stephanis et al. (1995), Kahn et al. (2001) and Kahn et al. (2002). A full Life Cycle Assessment is a time-consuming and difficult process that requires a combination of high quality information and environmental expertise. A full Life Cycle Assessment takes too long to be applied to each conceptual design alternative proposed (Borland et al., 1998).

In Life Cycle Process Design, environmental considerations are incorporated at an early stage in the design, alongside the more traditional technical and economic criteria. LCA is used throughout the design process, initially on a reference process. The conventional system boundary is extended to include the life cycles of the different technologies and raw materials, all the way from extraction of primary resources through to production. This enables a quantitative comparison of different technological routes for production of the same set of raw materials (Azapagic, 1999).

Two attractive features of LCA techniques in this regard are (Stephanis *et al.*, 1995)

1. The inclusion in the analysis of input wastes associated with a process, and
2. The emphasis on environmental impact rather than the actual emission as a means of comparing different types of waste emissions.

Stephanis *et al.* (1995) present a method for minimising the environmental impact (MEIM) of process systems by embedding LCA principles within a formal process optimisation framework. The proposed waste minimisation technique extends the existing waste minimisation techniques by providing a considerably more complete description of the environmental impact of a process, it also adds to conventional LCA

tools by employing process modelling and optimisation techniques to yield optimal design/operating conditions in order to achieve minimum environmental impact.

While on the surface it appears easy to set environmental constraints for process design problems, there are many pitfalls. Incorrect and incomplete appreciation of the relationship between environmental concerns and the process and inappropriate definition of impact measures can all lead to difficulties (Sharrat, 1997).

The above discussion shows that LCA can be used in the design process to evaluate the environmental impact of process plants. LCA is one of the tools available to evaluate the environmental impact during the design process. The shortcomings of LCA are in the area of the freshwater compartment and in evaluating the effect of metals in the environment.

### ***3.3.2 River Systems in Life Cycle Assessment***

In LCA, the freshwater "compartment" into which emissions are discharged is the entire freshwater in the area. Releases to freshwater are evaluated on the basis of ecological toxicity, which in turn is based on the "No Observed Effect Concentration" or NOEC.. The applicability of the NOEC is discussed in Chapter 2.5. There is currently no impact category in LCA that considers water consumption. This has been identified as an area that requires further investigation (Graedel, 1998, Stewart, 2002).

USES, a multi-compartment fate and transport model containing fate and toxicity parameters for about 700 chemical species (Huijbregts et al, 2001), has been accepted in many European countries as a protocol for Life Cycle Impact Assessment and is currently the most commonly used LCIA package (Schultze et al, 2001). USES evaluates the environmental impact of a release to a freshwater body by calculating the quantity of water required to dilute the release to the NOEC level (Huijbregts et al, 2001). For a riverine system, this methodology does not account for the environmental impact along the length of the river from the point of release to the point where the NOEC level is reached. The methodology of USES is more suitable to evaluating the environmental impact on a lake system, rather than a river system.

Owens (2002) proposed a set of environmental impact categories for freshwater. These are presented in Chapter 2.3.1. It is unclear whether these have been incorporated in LCA at present.

### ***3.3.3 Metals in Life Cycle Assessment***

The difficulties of modelling metals in the environment are discussed in Chapter 2.5. Stewart (2002) reviewed the complexities in applying LCA to Mining, Minerals Processing and Metals. Stewart identified ecological toxicity and resource depletion as two impact categories of LCA that caused problems in their articulation. Persistence, bioaccumulation and toxicity were identified as concepts more applicable to pesticides and similar organic compounds than to metals. As discussed in Chapter 2.5, metals do not degrade in the environment and are by definition persistent. Stewart states that bioavailability is more suitable for describing the toxicity of metals.

Further, base metals refinery streams contain numerous metal species in a myriad of combinations. Understanding of exposure pathways of mineral containing compounds within an environment is required when evaluating ecological toxicity. There is limited information available for exposure or uptake mechanisms for the majority of metals processed by the minerals industry. This detail is not available for most minerals.

Stewart (2002) concludes that the metals ecological toxicity impact category requires significant work with respect to definition and information available.

## **3.4 Review of the Hypothesis**

Having reviewed the literature, we are in a position to evaluate the hypothesis proposed for this work. As stated in Chapter 1, this thesis attempts to evaluate the following hypothesis:

***The design of base metals operations for effective and efficient water usage and management requires consideration of both site- and catchment-wide effects of metal releases to freshwater aquatic systems, and their incorporation into the design process through suitable performance measures.***

The hypothesis is reviewed with respect to the literature reviewed discussing environmentally conscious design and riverine ecosystems representing freshwater aquatic ecosystems.

#### ***3.4.1 Environmental Considerations in Design***

There is a need for engineers involved in the design of base metals refineries to understand the impacts of their designs on the environment. Cano-Ruiz and McRae (1999) identified that design engineers should move their focus away from meeting effluent release concentration limits to identifying environmental impacts. Cano-Ruiz and McRae further identified that including waste treatment facilities within the site boundary and producing information suitable for inclusion in a Life Cycle evaluation were required for environmentally conscious design. Blanchard (1991) identified that 85% of the life cycle costs of a chemical plant are determined during the design phases. Cano-Ruiz and McRae (1999) added that an estimated 50% of capital expenditure on new process plants is associated with environmental issues. Formal environmental assessments such as Environmental Impact Assessments are only performed between the Definitive Estimate and the Detailed Engineering phases of the project, or concurrently with the Detailed Engineering Phase. This is often too late to significantly incorporate environmental constraints in the core process and remedial waste treatment processes are added onto the core process to meet legislative requirements. Early assessment of environmental impacts is required from the information available at the specific stage of the design process. Tools such as Life Cycle Assessment are currently available to evaluate the impact of releases, but these are deficient when considering the impact of releases to riverine ecosystems, specifically metal releases.

#### ***3.4.2 Riverine Ecosystems***

Rivers are linear systems and releases to river systems affect the entire river system downstream of the release. King and Schael (2001) identified that every catchment was unique and that any changes to the water quality (physiochemical and flow) has detrimental effect on the catchment downstream of the disturbance. Factors important in maintaining the functioning of a riverine ecosystem include maintaining flow regimes and preventing elevated (or out of natural range) physiochemical stressors in the system (King and Schael, 2001). Biomonitoring provides a comprehensive means for evaluating the state of a riverine ecosystem and establishing a benchmark state of a

river (Day, 2000), but does not prove to be useful during the design stages since the information used in biomonitoring cannot be linked to the information available during the design process. Biomonitoring should be employed during the evaluation of the operational performance of the base metals refinery and to evaluate the impact of the refinery during its operation. In the design context, minimising the environmental impact of the proposed process by maintaining the natural flow regimes and minimising the effect of physiochemical stressors should be set as objectives.

The modelling environmental impacts in rivers requires a linear model of the river system. This approach allows the environmental concentration to be evaluated along the length of the river system.

#### ***3.4.3 Result of Hypothesis Testing***

The literature indicates that there is a requirement to consider environmental impact of a proposed base metals refinery during the design process. This requires a link between the level of information available at the various stages of the design process and predicted environmental impacts. Ashton et al (2002) identified five major impacts of mining and minerals operations on freshwater systems. These are acid mine drainage, metals in the environment, cyanide, sedimentation and water use. These five impacts constitute environmental impacts outside the site boundary and thus classify as catchment environmental impacts.

The review of the literature thus supports the hypothesis and thus the hypothesis is not rejected.

#### ***3.4.4 Restating of the Hypothesis***

Having accepted the hypothesis from a literature review, the hypothesis is restated to hone into one specific aspect of the original hypothesis, the fate of metals in riverine systems. Riverine systems are important in areas such as Southern Africa and thus the restated hypothesis focuses on the environmental impact of metals in riverine systems during the design of Base Metals Refineries.

***The environmental impact of metal releases to riverine systems can be modelled and incorporated into the design of Base Metals Refineries***

***through the development of a suitable proxy indicator, or set of proxy indicators.***

This re-stated hypothesis is evaluated by:

- Proposing a model to link design level information to releases to riverine systems.
- Proposing a model to link metal releases to riverine systems to environmental metal concentrations.
- Proposing a proxy indicator to represent the environmental impact of metal releases to river systems.
- Evaluating the proposed model linking metal releases to riverine systems to environmental metal concentrations and the proposed proxy indicator in a Case Study.

### **3.5 Closure**

This Chapter discussed the design of chemical process plants and base metals refineries in order to establish the level of information available at the design stages. The inclusion of environmental impacts in the design process requires that environmental considerations be included in the problem framing exercise. Life Cycle Assessment was introduced as one of the tools available to evaluate process level information available at the design stages of metallurgical plant and predict environmental impacts of releases from these plants. The shortcomings of Life Cycle Assessment regarding metals and river systems are briefly highlighted.

The stated hypothesis was evaluated against the literature reviewed. The hypothesis was found to be correct and thus not rejected. For the remainder of the thesis, the hypothesis was restated focussing on the fate of metals in riverine ecosystems.

Having established the background for the development of a model for use in the design process to link design level information to environmental impacts, the development of two models is described in Chapter 4. The first, the Water Flow Model, provides a framework within which all the information available during the design process can be summarised such that water consumption and effluent flow and composition for the base metals refinery can be detailed. The second model, the River Compartment Model, describes the fate and transport of metals in a river system using the information presented in Chapter 2. An environmental impact metric of the

"Affected Stream Length" is proposed as an appropriate proxy indicator for use during the design process. The use of the River Compartment Model and the Affected Stream Length estimate are demonstrated in a case study in Chapter 5.

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## **CHAPTER 4 – MODEL DEVELOPMENT**

To this point in this thesis, the behaviour of metals in aquatic riverine environments and the difficulties in modelling the environmental effects of metals in river systems have been discussed. It has been established that the environmental concentration of substances is required before an ecological effect, e.g. toxicological effect, can be estimated. In Chapter 2, a first order kinetics scheme was proposed for modelling the persistence of bio-available metal species in riverine systems. This Chapter builds on this foundation to propose a methodology by which downstream effects of metal releases to riverine systems can be predicted, and this information used during the design process.

To enable process engineers involved in design to take stock of the various process flows and site-wide surface flows, and identify possible effluent emissions, a generic "stocks and flows model" is proposed, within which all sources and sinks of water within a process boundary are considered. This model allows the nature of the effluents to be determined and a summary of water consumption to be detailed. This model has the advantage of forcing the process engineers to account for all flows, including those due to infrastructural needs. Using this model, the water load on the local catchment can be determined, and the capacity of the local catchment to deliver the required water load can be established.

This model summarises the effluent releases from the process facility. This information is used by the River Compartment Model (developed in the second part of this chapter) to determine the ecological concentration, and thus ecological impact of the effluent release to the river system.

### **4.1 Water Flow Model for Design Applications**

The Water Flow Model is a methodology for following stocks and flows of water at process and site levels. It provides a basis for identifying areas of high consumption, which need to be addressed in a water minimisation exercise. Further, the nature of the effluents can be detailed and the legislative requirements can be checked for compliance. The model proposed in this section has not been expanded to a software version or tested in a Case Study. Its development is included here for completeness, to demonstrate an argument of inter-dependence between process-level, site-level, and

catchment scale water considerations. Before the Water Flow Model can be described, the system needs to be defined and the boundaries of the system delineated.

The Water Flow Model provides a basis from which the environmental impacts of a particular metallurgical plant can be evaluated. The model links process level information that is available during the design stages, to emissions to the surrounding environment, which, in turn, can be linked to an environmental impact through a fate and transport model, discussed in Chapter 4.2.

#### **4.1.1 Systems Boundary**

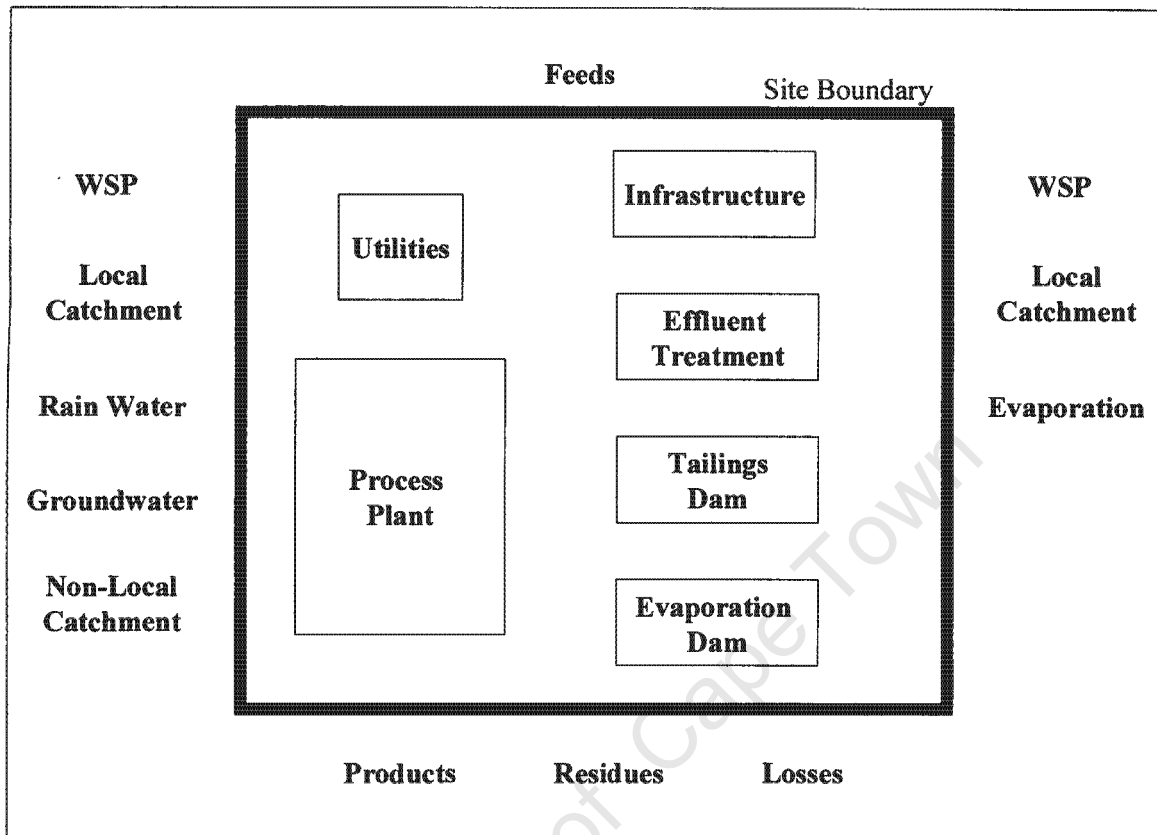
In order to establish a water stocks and flow model, a system boundary needs to be set against which cross boundary transactions can be evaluated. Three levels of system boundaries are defined in the current context at environment, site and process levels. The system boundaries are defined as follows:

- The environment is the entire area outside of the site boundary with which the site interacts. In terms of considering a riverine system, the river catchment in which the process facility is situated is defined as the environment.
- The site boundary of the process facility including all land covered by activities related to the process i.e. including tailings dams and evaporation dams.
- Process area boundaries for process units - These have been grouped into Process, Utilities, Effluent Treatment, Site Infrastructure, Tailings and effluent (re-usable) Dams and Evaporation (non re-usable) Dams. Areas may be divided into sub-areas e.g. Process 1, Process 2, Process 3, etc.

The site is detailed to provide information that could be used in a mass integration programme. The Water Flow Model collates all the site flows at a Process level, showing every stream on the plant representing inter-process flows. These are summarised at a site level as interactions between the major processes. Opportunities for mass integration may become visible using the process level information while these opportunities may be lost when using information at a site level. Site level information is used to evaluate the interaction of the site with the surrounding environment.

The system within the site boundary that the Water Flows Model represents is presented in Figure 4.1.

**Figure 4.1: Representation of Site and Process System Boundaries for the Water Flow Model**



**4.1.2 Inputs and Outputs**

Water input to the system could be sourced from Water Service Providers (WSP), the local catchment (or neighbouring catchment), captured rainwater, or imported with the raw materials. Taking stock of all the imports to the system is required to allow the complete environmental impact of water consumption to be evaluated. The environmental impact could be manifest in a different catchment, but this needs to be considered as it represents an environmental impact of the metallurgical process facility. Environmental impacts in different catchments as a result of the activities of Water Service Providers is outside of the management of the metallurgical facilities management, but these too need to be included in the analysis of environmental impacts. A full discussion of 'foreground' and 'background' system impacts is beyond the scope of this thesis. Suffice it to say that, in terms of design-related decision making, consideration is given primarily to 'foreground' impacts i.e. those over which the decision maker can exercise some degree of influence or control.

Water outputs from the system include sewage or municipal water returns to the WSP, discharge to the local catchments, storage in dams (tailings dams where a portion of the water is recovered or evaporation dams where there is no intention to re-use the water), losses to the atmosphere (process losses, intentional evaporative losses) and through products and waste products.

#### **4.1.3 Water Stocks and Balances**

A water balance is set up for the each of the process areas and these are aggregated to provide a site-level water balance. Hall (1997) provides guidelines for establishing the water balance for an operating site that considers the following:

- Establish the boundary of the water balance,
- Establish Fresh water sources,
- Establish Fresh water sinks,
- Establish Waste water sources,
- Establish Waste water sinks,
- Compile Water Balance,
- Determine Contaminants,
- Evaluate Existing Equipment.

The water balance details the flow between nodes in the water network and losses from the nodes in the network. The stocks need to be determined from an inventory analysis. There are two types of inventories constant inventories e.g. the processes, utilities, effluent treatment and infrastructure, and the variable inventories e.g. the tailings dams and evaporation dams.

For simplicity, the following assumptions are made:

- The only inputs to the system are to the Utilities and Process plants – this assumption is necessary to limit the number of inputs of water to the system. The inputs to the process plants are included to allow for water containing streams as feed to the process plant. This is common for metallurgical plants where the input to a process plant could be a wet concentrate. Limiting the other input to the Utilities plant is acceptable as this is the usual point of entry of water to the plant. Where water is drawn from the environment, the water would be treated in the Utilities section before being distributed through the plant and site.

- Only the input to Utilities originates from the local catchment (or WSP) – as stated for the first assumption, the feed to the process plant may contain water. To allow for tracking of the inputs from the environment or WSP, the input of water is limited to the utilities.
- All water, regardless of form, is distributed from Utilities – this assumption allows the network to track the water distribution through the site
- All water recycles are returned through the Utilities
- The only outputs are from Process, Effluent Treatment and Infrastructure – the products from the plant would originate from the process plant. Waste streams that are treated internally are treated in the Effluent Treatment plant. The infrastructure may produce sewage effluent that is not treated on site. This is an output from the system.
- Only the output from the Effluent Treatment section is returned to the local catchment – this assumption recognises that any effluent that is released to the environment may need to be treated before release to the environment.
- The Evaporation Dams are a total sink and nothing is recovered from that node – evaporation dams are defined as dams from which no solution is recovered for site use. These differ from tailings dams that are designed to recover water from the tailings, or other storage dams, and return it to the site for consumption.

The stocks and flow balance considers more than the flow of water through the process facility. The metal composition of each flow stream is considered and each stream is represented as a vector including flow, temperature, pH, and metal concentrations. The inter-nodal flows are summarised as an overall flow, but can be expanded to show all individual flows in the inter-nodal flow.

#### **4.1.4 Network Analysis for Water flows**

It is useful to conceive of the stocks and flows model as an interconnected network of nodes of different functionality and stability. This allows the use of formal network analysis tools, as discussed by Fleischmann *et al.* (2000), Gjerdrum *et al.* (2001) and Guide *et al.* (2000) cited in Treitz *et al.* (2002). For the nodes, a stock is calculated. The flows between the nodes represent movements of the stocks between the nodes. The network analysis summarises the stocks at the nodes and the flows between them. The inputs and outputs from the system can be calculated and evaluated. In the

current application, the input to the system represents the consumption of water by the site while the output from the effluent treatment plant represents the emission of and effluent to the environment, in this case a riverine system. The Water Flow model summarises the consumption and distribution of water through the site and the environmental discharges from the site. This provides a compact summary that can be produced from a design level steady state mass balance of a metallurgical facility that can be used to provide an input to an assessment of the environmental impacts of a metallurgical plant.

The Water Model network can be summarised in a network diagram that depicts relevant interactions between the network nodes and the inputs, outputs and losses from the network. The interactions are presented in Figure 4.4. Recycle streams to the Utilities are depicted as broken lines while other flows are shown as solid lines. The network represents a steady state model for the process operation. This is consistent with the steady state mass balance used as a basis for the design of the base metals refinery as discussed in Chapter 3. The nodes on the network are capable of having variable stocks, but under steady state conditions, most of these nodes do not display any variability. These constant stocks are displayed in Figure 4.2. The Process, Utilities, Infrastructure and Effluent Treatment nodes are constant under steady state conditions. The Tailings Dam and Evaporation Dams have variable stocks.

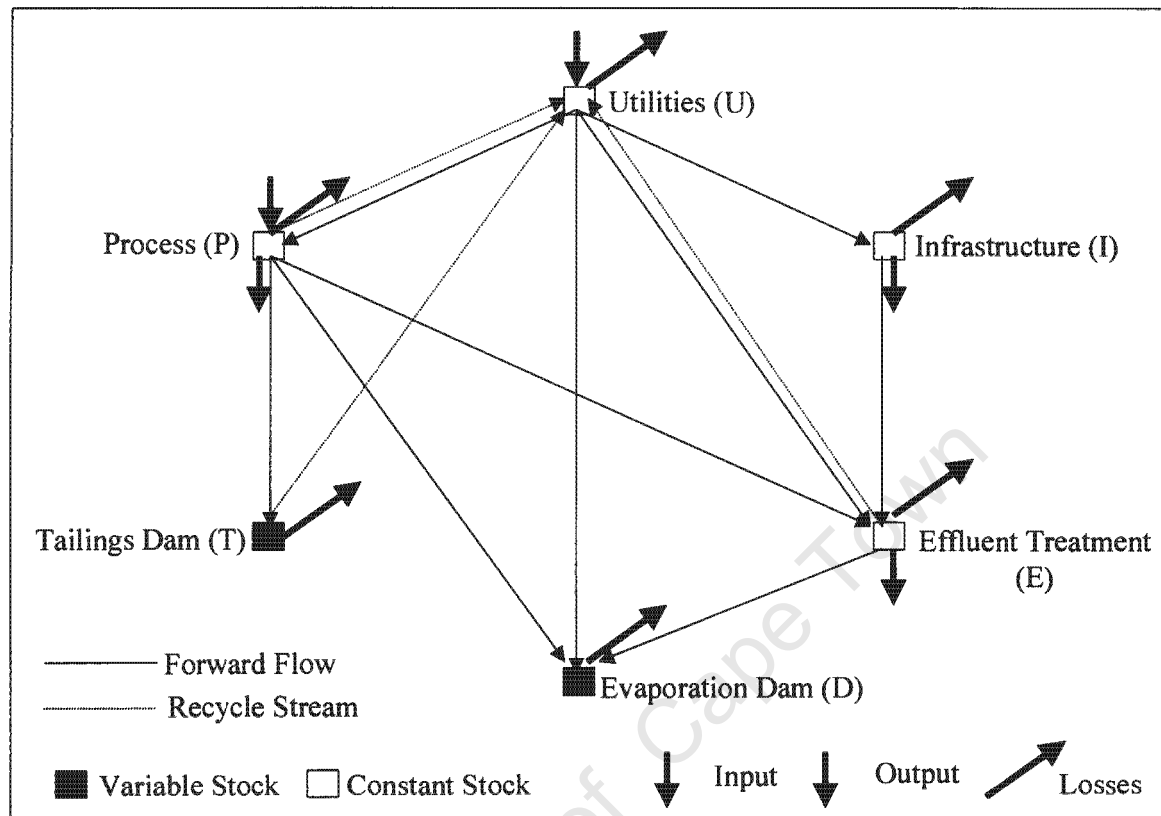
From the network perspective, the Evaporation Dam node represents a total sink and all flows to this node can be considered as an output from the water streams available for integration with the rest of the plant. Since the constituents flowing to the Evaporation Dam will remain on site, this represents an environmental hazard that will not be accounted for in this analysis since the current analysis concentrates on releases to riverine systems. For the current analysis, flows to the Evaporation Dam are considered as a total loss as the volume is made up from sources of new water to the network.

The description of the network is developed from the interactions between the process units by first considering the balances around each unit.

For the Utilities

$$U_{in} = U_{loss} + U_P - U_{PU} + U_{UI} + U_{UE} - U_{EU} + U_{UD} - U_{TU} + U_{accumulation} \quad (4-1)$$

**Figure 4.2: Network Diagram for Water Balance Model**



For the Process Plant

$$UP = P_{out} + P_{loss} - P_{in} + PU + PT + PE + PD + P_{accumulation} \quad (4-2)$$

For the Tailings Dam

$$PT = T_{loss} + TU + T_{accumulation} \quad (4-3)$$

For the Infrastructure

$$UI = I_{loss} + I_{out} + IE + I_{accumulation} \quad (4-4)$$

It should be noted that the term  $I_{out}$  represents the export of a water stream to a water treatment works in the form of raw sewage. If the process facility has a sewage plant on site, the term would not be relevant.

For the Effluent Treatment Plant

$$UE = E_{out} + E_{loss} + EU + ED - PE - IE + E_{accumulation} \quad (4-5)$$

It should be noted that the term  $E_{out}$  represents the return of water to the environment (from the assumption that all water returned to the environment is processed through the effluent treatment plant since treatment of the stream may be required to ensure that the environmental legislative limits are not exceeded).

For the Evaporation Dam

$$D_{loss} = UD + PD + ED - D_{accumulation} \quad (4-6)$$

Since the inventory for the Process, Utilities, Infrastructure and Effluent Treatment are more or less constant in most operations under steady state operating conditions, the terms  $P_{accumulation}$ ,  $U_{accumulation}$ ,  $I_{accumulation}$ ,  $E_{accumulation}$  can be assumed to be zero and will no longer be considered in the current analysis. Further, since no streams flowing to the Evaporation Dam (D) are recovered, these will all eventually be accounted for as  $D_{loss}$ . Thus, all streams to the dam are represented as  $UD_{loss}$ ,  $PD_{loss}$  and  $ED_{loss}$ . The Evaporation Dam is thus no longer considered. The term we are interested in is  $U_{in}$ . This represented the water consumption of the Site.

Taking a balance over the site and condensing the equations, the expression of water consumption becomes:

$$U_{in} = U_{loss} + P_{out} - P_{in} + P_{loss} + E_{out} + E_{loss} + T_{loss} + T_{accumulation} + I_{out} + I_{loss} + PD_{loss} + ED_{loss} + UD_{loss} \quad (4-7)$$

This can be simplified by grouping all the evaporation dam losses as a single term  $D_{loss}$ .

$$U_{in} = U_{loss} + P_{out} - P_{in} + P_{loss} + E_{out} + E_{loss} + T_{loss} + T_{accumulation} + I_{out} + I_{loss} + D_{loss} \quad (4-8)$$

Attention is brought to the losses from the various unit operations. Further, minimising the consumption is related to minimising the return to the environment represented by

$E_{out}$ . The recovery of water from the tailings dam is highlighted as an important area. The increase in inventory of the tailings stock, as a result of an increase in the volume of interstitial water in the tailings stock pile, will result in a related increase in the hold-up of the node. This, for example, is an area where Rossing Uranium reduced their water consumption as described in Chapter 3.2.1. The description of the accumulation factor for both the tailings dam and the evaporation dam requires further investigation. These are not considered further in this work. The intent of equation 3.8 is to demonstrate how the net water inflow requirement is affected by the effluent discharge and the tailings dam accumulation (both of which are under the direct control of site management personnel and can be predicted as design quantities). This suggests that the site water balance, coupled as it is to process water requirements, should provide a basis to connect process-level information with that pertaining to the catchment into which effluent is released.

#### ***4.1.5 Benefits of the Water Model in Design***

The Water Flow Model provides an accounting methodology that incorporates all the flows on the site and accounts for some of the flows that are usually not considered, such as the fire water requirements, safety showers, ablution requirements and infrastructural consumption amongst others. The majority of these flows are small in volume, but their cumulative consumption contributes to the total consumptive impact on the water source. These leaky flows are captured and a complete picture of the site water consumption is compiled. The model methodology enables the inclusion of the flow of chemical species and thus the model provides a basis for a site chemical and environmental accounting tool. Only the model methodology is described in this thesis. This is to provide the reader with an understanding of how design level information can be collated and used to provide input information to a fate and transport model, which determines an ecological impact of an emission to a riverine system. This model also provides the input data that could be used in mass exchange networks. As discussed in Chapter 1, this thesis does not engage with mass exchange networks, but seeks to provide information that could be used in these networks.

One of the greatest benefits of the Water Model is that it can be used at all levels of the design process, from "order of magnitude" studies to detailed design. The nature of the model provides an opportunity for the design engineer to review whether all flows are accounted for, and provides a higher level of accuracy in the water consumption

estimates through the design process. Changes to the process and the selection of process technologies or process equipment can be evaluated efficiently with respect to their effect on the overall water consumption of the site and the nature of the effluents they produce. This provides an opportunity to include water considerations in the design process.

The Water Model also tracks the composition of the effluent streams providing data for the evaluation of the environmental impact of releases from the site and thus input into the process design process at an earlier stage than happens commonly as part of the accompanying Environmental Impact Assessments (EIA) exercise, which is generally performed during the detailed design stage. At this stage, the process has been finalised and the considering the environmental impacts does not contribute to the process design, rather placing external constraints and additional effluent treatment facilities to the flowsheet.

#### **4.1.6 Water Indicators for Design**

As discussed in Chapter 2.4, indicators for water resources should be considered in two major areas viz. the quantity or volume of water removed from the environment and whether this volume withdrawn is returned or not and the quality of the water returned to the environment, especially regarding impairment due to pollutants or other changes introduced during water use.

Owens (2002) suggests that a water quantity indicator needs to address

- The total quantity entering the system in inputs
- Whether the water sources for these inputs are renewable and/or sustainable
- Whether the water outputs are returned to the original surface basins so that downstream human and ecological users are not deprived of adequate water volumes

The Total Water entering the system is represented by the sum of the utility water input and the process feed stream water ( $U_{in}$  and  $P_{in}$  respectively). An important aspect of the total water being consumed is its relationship to the proportion of water of water which is being recycled or re-utilised, and the quantity of water which is being released from the process as an effluent or loss to effluent dams or other sinks, in proportion to the total water input.

To determine whether the inputs are from a renewable source or not and whether the other users in the catchment are impacted requires an understanding of the functioning of the catchment. The current National Water Act of South Africa (Act 38 of 1998) provides water allocations to current and future users in the catchment. These allocations are being evaluated in the light of a deeper understanding of the ecological requirements of a river system. As discussed in Chapter 2.1, programmes such as the Building Block Method and DRIFT which have been developed by the South African Water Research Commission with prominent South African and Australian Water Scientists allow catchment managers to determine the water yield a catchment may offer (King et al in press). These can then be allocated to the various water users in the catchment. The evaluation of a river system to determine the water yield is a complex multidisciplinary procedure and has only been performed on one catchment in Southern Africa thus far (King personal communication). Assuming the current process of allocation is continued, the water consumption of the process situated within a catchment can be evaluated in terms of the previously unallocated water surplus for the catchment. Further, the water consumption of the process can be evaluated against the total water allocated for consumption. This provides scope for indicators, which provide an understanding of the impact of the process facility to the catchment and other users in the catchment, to be proposed.

The total water available for allocation in South Africa is currently set by the DWAF based on the hydrological flows in the catchment. Current research has shown the shortcomings of this methodology and the DWAF is re-evaluating the methodology in the light of programmes such as the Building Block Method and DRIFT (King et al in press).

It should be noted that any deviation from the local water composition will have an effect on the assemblage of aquatic organisms present downstream of the emission point. Ideally, the concentration of an effluent stream should reflect the compositional bias of the existing chemical species in the river water. If water is discharged to a stream from a process facility, and withdrawn from the same stream by the same process facility, the discharge from the process facility should be upstream of the intake such that the company has to deal with its own pollution (de Bono, op cit). This is the fairest practice considering the needs of all other users in the catchment.

**Table 4.1: Metal Concentration Limits for Emissions to Aquatic Ecosystems (Dallas and Day<sup>+</sup>, 1993, DWAF<sup>#</sup>, 1996,**

Metal	Recommended Concentration Limit (µg/L)	Water Quality Guideline for Aquatic Ecosystems (µg/L)
Fe	200	10*
Cu	2.8 – 6	3
Co	1000	
Ni	10 – 50	
Zn	5 – 50	2
Cd	1 – 2	150
Hg	5 – 10	40
Sn	1000	
As	500 – 1000	10

\* - Value recommended for aquaculture.

NOECs should be determined for the catchment using organisms present in the catchment, preferably endemic or historically local fauna, i.e. not introduced organisms or organisms not occurring in the catchment. Historically, NOEC limits have been established using North American organisms as the majority of toxicity testwork is currently being performed in North America. These limits are not necessarily applicable to organisms from other areas. Further, the local organisms would be acclimatised to the conditions experienced in the particular catchment and not the laboratory conditions.

## 4.2 The River Compartment Model

The River Compartment Model attempts to describe the fate of a metal release to a river. The model is based on the MacKay Type fate models coupled to Life Cycle Impact Assessment (Huijbregts et al., 2000, Goedehoop and Spriesma, 1999). The model is for a point-source emission into a river, modelled as a single compartment plug flow reactor without back mixing. This can be approximated by a series of continuous stirred reactors assuming full mixing in each compartment. Three factors are considered in the

current model. The first is the convective transport of contaminants down the river with the bulk flow. The second is the removal of metal from solution by reaction according to first order kinetics with sediment particles in the water column. The third is the transport of the metals bound to the sediments down the course of the river. In order to establish the model, a number of assumptions are necessary. These are presented below.

#### **4.2.1 Assumptions**

The assumptions upon which the model is based are as follows:

- Effluent discharge (defined by the network model above) is modelled as a continuous point-source emission,
- There is an excess of sediment in the water column onto which metal can adsorb,
- Metal adsorbed onto sediment in the compartment is considered as part of sediment within the compartment,
- Desorption is slow compared to adsorption (due to excess of sediment)
- No groundwater interchange takes place,
- No biological interaction with flora or fauna takes place within the compartment,
- Sediment does not move through the compartment at the same rate as the water. The sediment transport is modelled by viewing the sediment residence time as a function of the water residence time,
- Metal species in the water column and bound to the sediment do not interact with other metal species in the water column or bound to sediments,
- Diffusive transport is small compared to convective river transport.

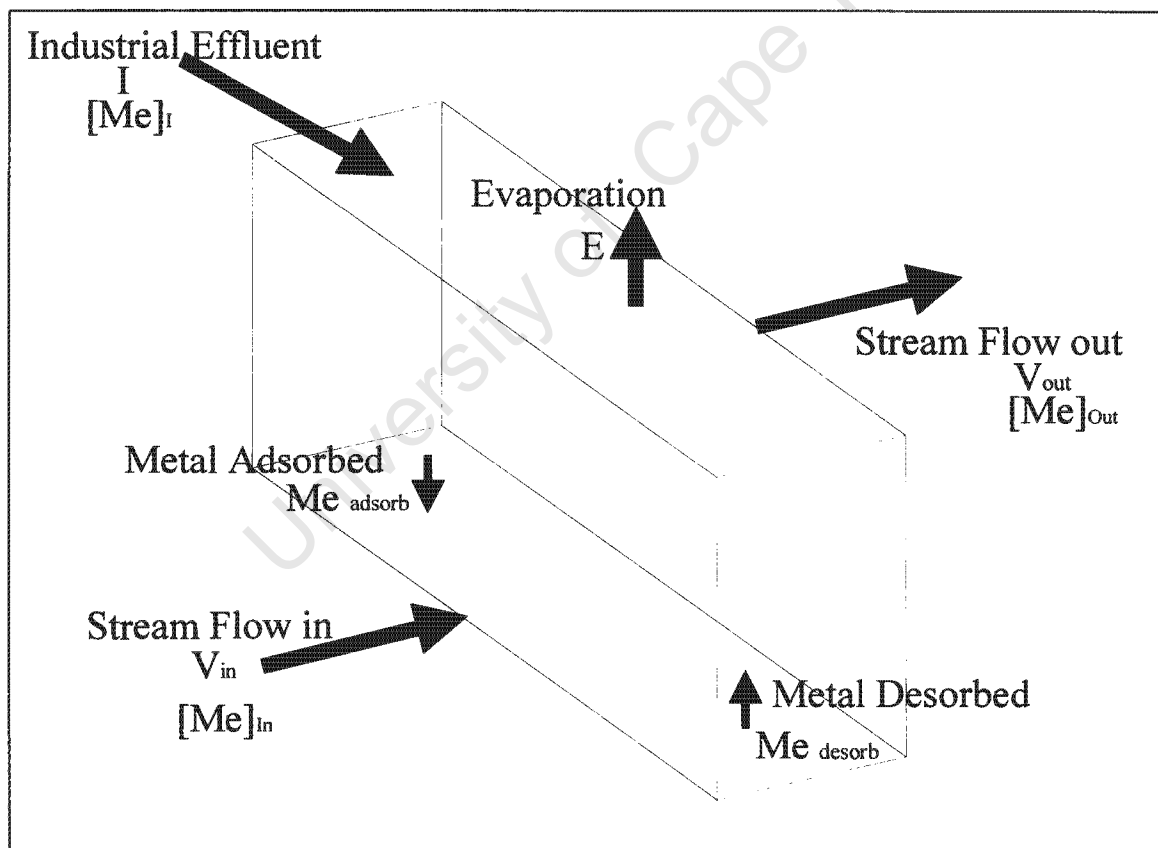
#### **4.2.2 System Description**

The River Compartment Model is a metal species transport model, which calculates the environmental concentration of metals in a river system. The concentration of metals in a compartment is determined by reactions with the sediment, but the nature of these reactions is not detailed.

The compartment is defined by a characteristic length term, in terms of river mean velocity and residence time. A one-hour residence time was selected as the smallest time unit. The volume of the compartment is determined from stream channel

geometry. The model's approach is similar to that of MacKay type fate and transport models, which have been used in conjunction with Life Cycle Impact Assessment approaches such as USES and Eco-Indicator 99 (Huijbregts et al. 2000, Goedeboom and Spriesma, 1999). The MacKay type models are discussed briefly in Chapter 2.2 and in greater detail in Appendix A.5. The difference here is that the compartment is a defined unit based on the flow of the river and the channel geometry while the LCA packages mostly use the entire freshwater compartment and the average concentration of an emission is compared to the entire compartment. The disadvantage of using the entire compartment is that emissions in excess of the NOEC are not observed immediately. A typical compartment is detailed in the Figure 4.3, showing the various flux terms that pertain.

**Figure 4.3: Diagram of a River Compartment**



#### 4.2.3 Compartment Balances

A volumetric balance of the compartment results in the following equation

$$V_{Out} = V_{In} + I - E \quad (4-9)$$

where  $V_{in}$  is the volumetric flow rate of the river into the compartment,  $[Me]_{in}$  is the concentration of metal Me in stream into the compartment,  $V_{out}$  is the volumetric flow rate of the river out of the compartment,  $[Me]_{out}$  is the concentration of metal Me in stream out of the compartment,  $I$  is the volumetric flow rate of the industrial effluent into the compartment,  $[Me]_I$  is the concentration of metal Me in stream into the compartment,  $E$  is the net environmental volumetric flow balanced between evaporation and rainfall.

A volumetric balance is required since rainfall and evaporation are reported in the condensed volumetric terms. This could easily be converted to a mass balance assuming a density for water as rainfall and evaporation.

A metal balance over the water column considering the mass flow of metal Me over the compartment results in the following equation

$$Me_{out} = Me_{in} + Me_I + Me_{desorb} - Me_{adsorb} \quad (4-10)$$

where  $Me_{out}$  is the mass flow of metal Me out of the compartment,  $Me_{in}$  is the mass flow of metal Me into the compartment,  $Me_I$  is the mass flow of metal Me into the compartment from the industrial effluent,  $Me_{desorb}$  is the mass flow of metal Me which is desorbed from the sediment,  $Me_{adsorb}$  is the mass flow of metal Me adsorbed to the sediment.

The concentration within the compartment is assumed uniform throughout the compartment, at the concentration leaving the compartment. The concentration of metals in the compartment would be represented as follows:

$$[Me]_{out} = \frac{V_{in} [Me]_{in} + I [Me]_I + Me_{desorb} - Me_{adsorb}}{V_{out}} \quad (4-11)$$

where  $V_{in}$  is the volumetric flow rate of the river into the compartment,  $[Me]_{in}$  is the concentration of metal Me in stream into the compartment,  $V_{out}$  is the volumetric flow rate of the river out of the compartment,  $[Me]_{out}$  is the concentration of metal Me in stream out of the compartment,  $I$  is the volumetric flow rate of the industrial effluent

into the compartment,  $[Me]_I$  is the concentration of metal Me in stream into the compartment.

For the present model, the metal desorbed from the sediment is not accounted for as the rate of this process is slow relative to others due to the assumption that there is an excess of sediment in the compartment, and therefore can be discounted. Equation 3-11 can thus be re-written as:

$$[Me]_{out} = \frac{V_{in} [Me]_{in} + I[Me]_I - Me_{adsorb}}{V_{out}} \quad (4-12)$$

where  $V_{in}$  is the volumetric flow rate of the river into the compartment,  $[Me]_{in}$  is the concentration of metal Me in stream into the compartment,  $V_{out}$  is the volumetric flow rate of the river out of the compartment,  $[Me]_{out}$  is the concentration of metal Me in stream out of the compartment, and  $Me_{adsorb}$  is the mass flow of metal adsorbed to the sediment. Since the industrial effluent represents a point source emission to the environment, the term  $I[Me]_I$  can be discounted for the remainder of the compartments other than the initial compartment. Equation 4-12 can be written for the remainder of the compartments as:

$$[Me]_{out} = \frac{V_{in} [Me]_{in} - Me_{adsorb}}{V_{out}} \quad (4-13)$$

Since the assumption made for the model is that only adsorption of metal onto sediment occurs in the compartment, the model estimates the metal remaining in the water column from first order reaction kinetics. First order kinetics is used based on the tests conducted by Diamond et al (1990)(cited in di Toro et al (2001a) and Adams et al (2000)). This is used since no other model proposed for the metal concentration was reported in the literature surveyed as discussed in Chapter 2.7. The first order kinetic reaction describes the concentration of metal remaining in solution. This can be used to describe the concentration of metal leaving the compartment. The first order kinetics for the metal remaining in the water column is described by the following equation:

$$[Me]_{out} = [Me]_{in} e^{-kt} \quad (4-14)$$

where  $[Me]_{in}$  is the initial metal concentration of the metal Me,  $t$  is the residence time in the compartment and  $k$  is the first order reaction parameter in units of 'per hour' described as follows:

$$k = \frac{\ln 2}{t_{1/2}} \quad (4-15)$$

where  $t_{1/2}$  is the half life time in hours derived from mesocosm experiments. Values from mesocosm experiments conducted in freshwater lakes in Canada are presented in Table 4.2. These values need to be confirmed for South African conditions. The current model uses the values reported from the Canadian mesocosm experiments as cited in di Toro *et al.* (2001a) and Adams *et al.* (2000).

**Table 4.2: Half-life times from freshwater mesocosm experiments (Diamond *et al.* (1990), cited by di Toro *et al.*, 2001a)**

Metal	Half Life Time (days)
Fe	12
Cu	9.5
Co	5
Ni	25
Zn	20
Cd	16
Hg	16
Sn	11
As	20
Cs	24

#### **4.2.4 Metal Fluxes to Sediment**

Since the total sediment mass in the compartment is not known, the metal concentration of the sediment cannot be calculated. However, the metal flux to the sediment in a specific compartment can be calculated from a metal balance over the compartment. Equation 4-13 can be rewritten as follows:

$$M_{adsorb} = V_{in}[Me]_{in} - V_{out}[Me]_{out} \quad (4-16)$$

where  $M_{adsorb}$  is the metal adsorption flux by the sediment in the compartment (g/hr),  $V_{in}$  is the volumetric flow rate of the river into the compartment ( $m^3/hr$ ),  $[Me]_{in}$  is the concentration of metal Me in stream into the compartment (mg/L),  $V_{out}$  is the volumetric flow rate of the river out of the compartment ( $m^3/hr$ ),  $[Me]_{out}$  is the concentration of metal Me in stream out of the compartment (mg/L). The concentration of metal Me in the compartment is calculated from the equation 4-14.

The units of  $M_{adsorb}$  in equation 4-16 are mass per unit time and this quantity represents the average rate at which metal is adsorbed onto the sediment in the compartment. To calculate the mass of metal adsorbed to the sediment in the compartment, the metal adsorption flux  $M_{adsorb}$  must be multiplied by the residence time of the water in the compartment.

$$Me_{ads} = M_{adsorb} \tau \quad (4-17)$$

where  $Me_{ads}$  is the mass of metal adsorbed to the sediment in the compartment (g),  $M_{adsorb}$  is the metal adsorption flux (g/hr) and  $\tau$  is the residence time of water in the compartment (hr).

#### **4.2.5 Sediment Metal Content**

As discussed in Chapter 4.2.4 above, the metal concentration in the sediment cannot be calculated as the total mass, or volume, of sediment in the compartment is not known. In order to account for the metal that is present in the compartment, a sediment transport term has been included in the model. The transport of sediment is parameterised from the residence time of the sediment in the compartment relative to that of water in the compartment. This assumption implies that sediments are gradually moved down the watercourse of the river at a constant rate. In reality, sediment is transported during periods of high flow and deposited during periods of low flow. The sediment metal content is a steady state approximation of the metal content in the compartment.

The transport of sediment is based on the residence time of the sediment within the compartment. The residence time of sediment cannot be less than the residence time of water in the compartment and thus a minimum of 1:1 has been set for the ratio of sediment residence time with respect to water residence time. The sediment residence time is expressed in multiples of the water residence time. The fraction of sediment being transported to the next compartment is calculated from the sediment residence time ratio as follows:

$$F = \frac{1}{R} \quad (4-18)$$

where  $F$  is the fraction of the sediment being transported to the next compartment and  $R$  is the sediment residence time ratio between sediment and water residence times. The quantity of metal in the sediment of the compartment is calculated from the metal balance on the sediment. Assuming that no desorption from the sediment occurs, a metal balance for the sediment in compartment  $i$  can be written in an equation similar to Equation 4-10:

$$Me_{retained,i} = Me_{Stock} + Me_{in,i} + Me_{ads,i} - Me_{out,i} \quad (4-19)$$

where  $Me_{out,i}$  is the mass of metal  $Me$  in the sediment leaving compartment  $i$ ,  $Me_{in,i}$  is the mass of metal  $Me$  in the sediment entering into compartment  $i$ ,  $Me_{retained,i}$  is the mass metal  $Me$  contained in the sediment which is retained in compartment  $i$ ,  $Me_{Stock}$  is the mass of metal  $Me$  which has accumulated in compartment  $i$ , and  $Me_{ads,i}$  is the mass of metal  $Me$  which is adsorbed from the water column to the sediment in compartment  $i$ .

The mass of metal adsorbed to the sediment,  $Me_{ads,i}$ , is described by equation 4-17. To calculate the mass of metal entering compartment  $i$ , the mass of metal leaving the previous compartment  $i-1$  needs to be calculated. This is a fraction ( $1/R$ ) of the total metal content of the compartment. This is represented in equation 4-18.

$$Me_{out,i} = \frac{1}{R} (Me_{retained(i)}) \quad (4-20)$$

where  $Me_{out,i-1}$  is the mass of metal  $Me$  in the sediment leaving compartment  $i-1$ ,  $Me_{in,i}$  is the mass of metal  $Me$  in the sediment entering into compartment  $i$ ,  $Me_{retained(i-1)}$  is the

mass metal  $Me$  contained in the sediment which is retained in compartment  $i-1$  and  $R$  is the ratio of the residence times for the sediment and the water.

At steady state, there is no change in the metal retained in the compartment. This means that the mass of metal retained in the compartment equals the metal accumulated in the compartment. Equation 4-17 becomes:

$$Me_{in,i} + Me_{ads,i} - Me_{out,i} = 0 \quad (4-21)$$

Substituting equation 4-20 in equation 4-21, the steady state metal content of compartment  $i$ , is described as follows:

$$Me_{retained,i} = R(Me_{in,i} + Me_{ads,i}) \quad (4-22)$$

Substituting in for the metal entering the compartment, the equation becomes:

$$Me_{retained,i} = (Me_{retained,i-1} + RMe_{ads,i}) \quad (4-23)$$

For the first compartment, there is no metal inflow from the previous compartment and thus equation 4-23 simplifies to:

$$Me_{retained,0} = RMe_{ads,0} \quad (4-24)$$

Since the metal accumulated in the first compartment can be calculated, the metal accumulated in all subsequent compartments can be calculated.

#### **4.2.6 Estimating the Environmental Impact**

Ecological toxicity is a product of the fate and exposure risks as discussed in Chapter 2.7.1. The above River Compartment Model provides an estimate of the environmental concentration of metals in the water column of a river. The ecological toxicity of the metals can be estimated down the length of the river provided the exposure pathways of the metal are known. The River Compartment Model does not take the exposure aspects of ecological toxicity into account. The link between environmental toxicity and the environmental concentration has been established, but the synergistic and antagonistic effect of metal cocktails has not established, as discussed in Chapter 2.7.

The toxicity of metals could be calculated assuming that the synergistic and antagonistic effects do not take place, but this would not add significantly to the environmental impact estimates provided by some of the impact assessment models of tools such as LCA. The existence of the synergistic and antagonistic effects are known, but not understood (Dallas and Day, 1993). This reduces the value of the River Compartment Model, at this stage at least, to estimating only the environmental concentration of metals of interest.

Recalling the previous discussion about “proxy” indicators, it is possible to extend the usefulness of the River Compartment Model as follows. Estimating the ecological effect of an effluent released into a river can be accomplished by evaluating the length of river affected by the release. This can be evaluated from two perspectives.

The first is evaluating the length of stream or river with metal concentrations above the NOEC level i.e. disturbance above NOEC. This approach should reflect zero results, as the emissions to the river system should not exceed the NOEC levels.

The second methodology for the Affected Stream Length calculates the length of stream or river required to reduce the water column metal concentration to reach the levels upstream of the inflow of the effluent. This method estimates the effective river length which is required to restore the environmental concentration of metals in the river to the level prior to the introduction of the effluent. This approach assumes that the organisms utilising the river water are able to survive at the concentration of metals in the water column prior to the introduction of the effluent. The current knowledge base cannot predict whether these organisms would survive at any altered metal concentration as toxicity testing, even if it has been performed on the same species, probably has not been performed on individuals from the population in the river section of interest. However, this method retains some consistency with the increasingly prevalent use of Load Based Licensing regulations, in which the overriding concern is the critical carrying capacity of a catchment.

Both of the proposed methods of evaluating the ecological impact by the affected stream length are “proxy” estimates of environmental impact. Proxy indicators are introduced in Chapter 2.4. Examples of similar methods of estimating the environmental impact include Hansen’s “Affected Land Footprint” describing

groundwater contamination (Hansen et al., 2002). Both these methods produce an Affected Stream Length resulting from the release of the effluent into the stream. The Affected Stream Length could provide a means for the comparison of a number of effluent streams to estimate the environmental impact of the individual effluents.

#### 4.2.7 Affected Stream Length

The River Compartment Model proposed in this Chapter assumes first order reaction kinetics for the removal of metal species from the water column. This assumption is based on the lake mesocosm results produced by Diamond et al. (1990). River mesocosm experiments are required to determine the order of the reaction kinetics for the removal of metal species from riverine water columns, as they are more dynamic than lake systems. A summary of the reaction rate orders is presented in Table 4.3. The reaction rate constant ( $k$ ) would be determined and substituted in the relevant reaction. Desorption of metals from the sediments has not been included in the current model. This could be included by determining the reverse reaction order and adding the resolution reactions to the River Compartment Model and the Affected Stream Length calculation.

**Table 4.3: Concentration Profile Reactions for Various Orders of Reactions**

Reaction Order	Concentration Profile	Time to reach Target Concentration
0 (Linear)	$C = C_o - kt$	$t = \frac{(C_o - C_{target})}{k}$
1	$C = C_o e^{-kt}$	$t = \frac{1}{k} \ln\left(\frac{C_o}{C_{target}}\right)$
2	$C = \frac{C_o}{C_o kt + 1}$	$t = \frac{1}{k} \left( \frac{1}{C_{target}} - \frac{1}{C_o} \right)$

Where  $C$  is the water column metal concentration (mg/L),  $C_o$  is the initial metal concentration after effluent introduction (mg/L),  $C_{target}$  is the target metal concentration e.g. NOEC limit or concentration prior to effluent introduction (mg/L),  $k$  is the reaction rate constant ( $hr^{-1}$ ) and  $t$  is the time since effluent introduction (hr).

The Affected Stream Length is calculated from the time to reach the target concentration and the velocity of water in the channel. The channel velocity varies seasonally, and along the length of the river. For the purposes of comparison, a velocity of 1m/s is proposed for the instream velocity of rivers. If the flow discharge information for the river is known, the dry season low flow could be used as a basis since under these flow conditions, as the environmental impact is expected to be the greatest here. For site-specific evaluations, the flow discharge curve for the river identified for effluent discharge should be constructed during the initial design stages. The site for a proposed metallurgical plant is usually only chosen during the advanced stages of the design. This poses a challenge as the selection of process route takes place early in the design process. For these cases, the default instream velocity of 1m/s could be used.

#### **4.2.8 Model Inputs**

The inputs required for the model consist of climactic and hydrological data and details of the effluent. The hydrological and effluent data required for the model are:

- River channel dimensions (considered constant for area of model)
- River depth (uniform across the river)
- River width
- River flow (m<sup>3</sup>/s) – wet and dry seasons or monthly average or flow discharge curve
- River metal concentration (the case study in Chapter 5 considers Cu, Co, Zn and Cd) (µg/L)
- Catchment Annual Rainfall (mm) – wet and dry seasons or monthly average
- Catchment Annual Evaporation (mm) – wet and dry seasons or monthly average
- Industrial Effluent Flow (m<sup>3</sup>/hr)
- Industrial Effluent Metal Concentration (Cu, Co, Zn and Cd) (mg/L)
- Metal First Order Reaction Rates (Cu, Co, Zn and Cd) (days)
- Sediment Residence Time Ratio (in relation to the water residence time)
- Compartment Residence Time (hours)

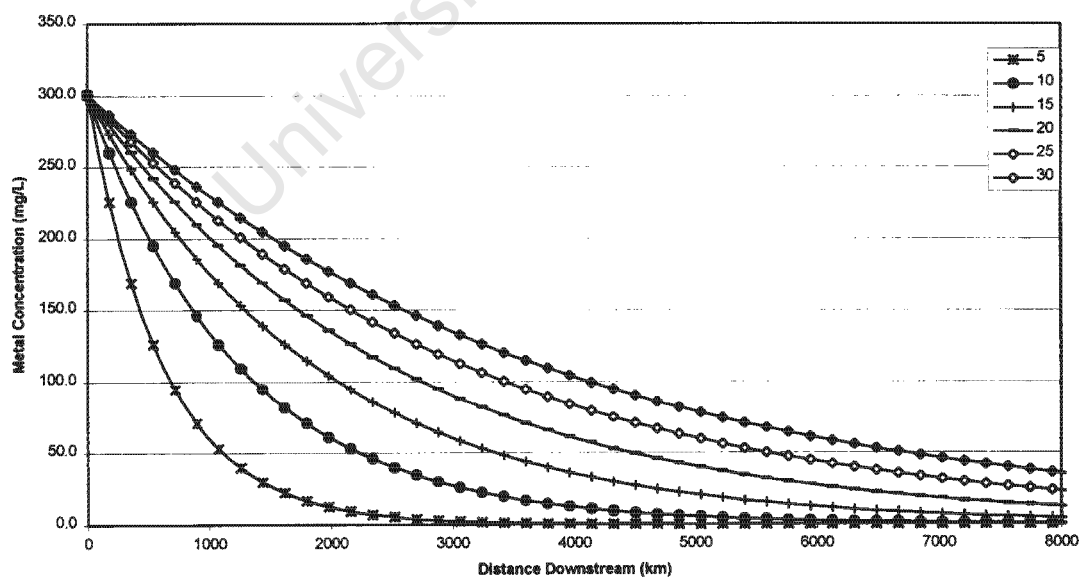
#### **4.2.9 Model Outputs**

The outputs of the model are discussed with respect to the model input parameters. The model produces four outputs. These are the environmental metal concentration,

the metal flux to the sediment, the metal sediment content and the affected Stream Length. The affected stream length is calculated for each metal contained in the effluent and discussed in detail in Chapter 5. The other three outputs produced by the model are discussed here, to give some sense of their relative importance. In so doing, it is also possible to get some idea of the validity of model assumptions.

The first output from the model is the water column metal concentration, which is calculated against both time from release and the distance downstream from emission point. The two most important factors determining the environmental concentrations are the initial metal concentration and the first order rate constant (or metal half-life). The environmental concentration for an initial metal concentration is plotted against distance downstream of the effluent release for a number of first order reaction rate constants. Figure 4.4 provides an indication of the effect of the reaction rate constant. The effect is obvious, the higher the first order rate constant (or metal half life) the higher the environmental concentration. Each concentration profile follows the typical first order decay, which is expected.

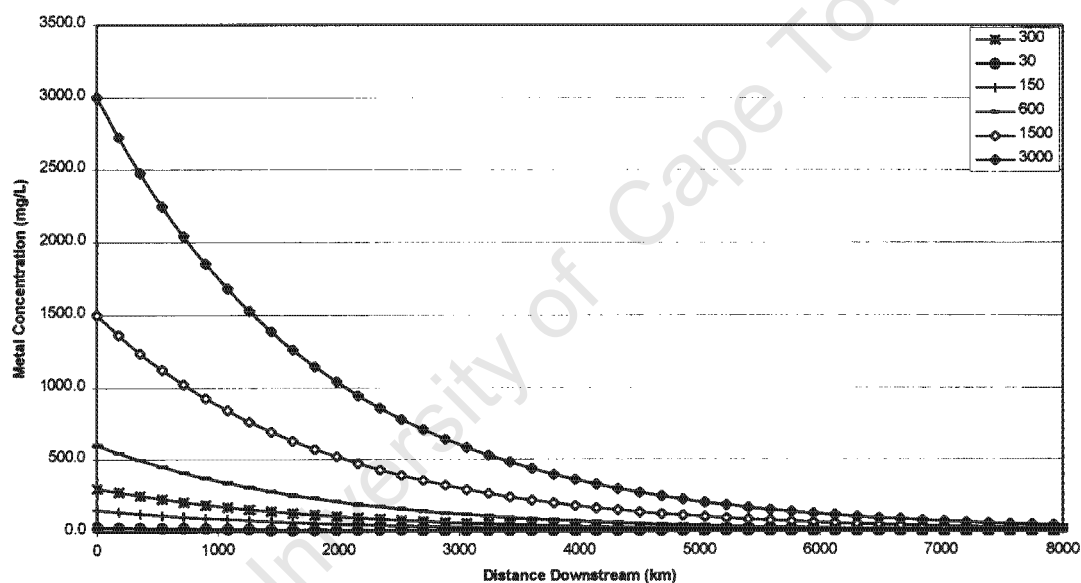
**Figure 4.4: Water Column Metal Concentration at Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days**



Factors affecting the initial environmental concentration after the introduction of the effluent are the ratio between the river flow and the effluent release rate, the

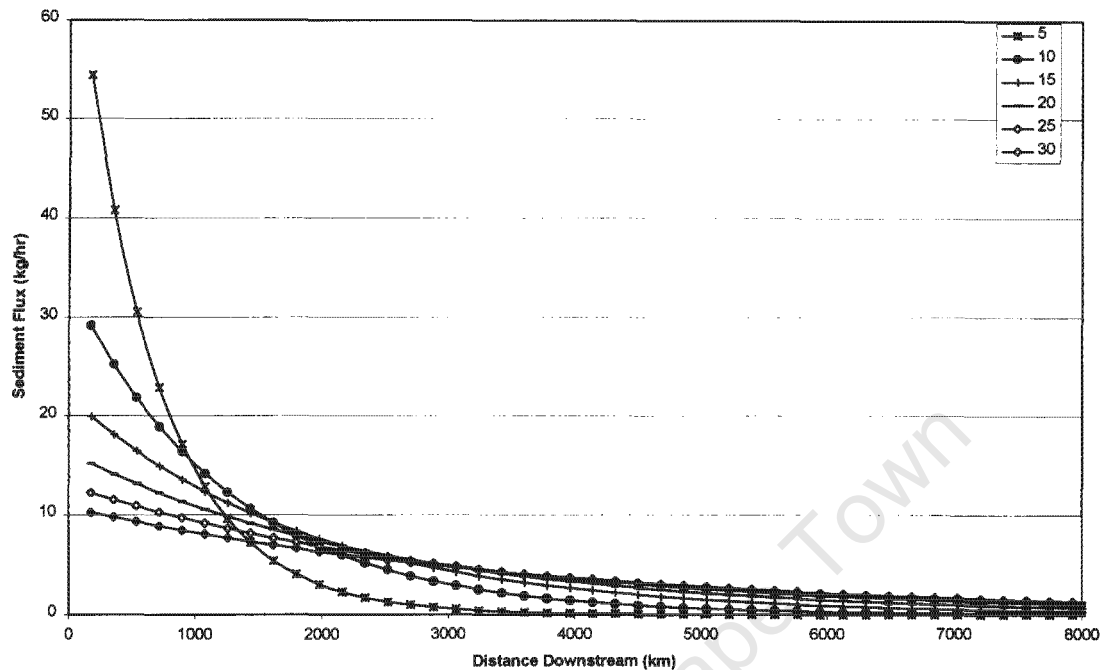
concentration of metals in the river prior to effluent introduction and the effluent concentration itself. Holding the first order reaction rate constant, the resultant environmental metal concentration for a variety of effluent metal concentrations is presented in Figure 4.5. An increase in the initial environmental concentration of metals after the release of an effluent to the river shifts the metal environmental concentration curve up down the length of the river. Increasing the effluent concentration thus increases the length of the river that is affected by the release of the effluent to the river.

**Figure 4.5: Water Column Metal Concentration at Metal Half-Life of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L**



The metal flux to sediment represented the average rate at which metal is departing to the sediment in the compartment. The metal flux to the sediment is calculated for each compartment and summarised in a graphical output, presented in units of kg/hr. The metal flux to sediment for an initial metal concentration is plotted against distance downstream of the effluent release for a number of first order reaction rate constants. Figure 4.6 provides an indication of the effect of the reaction rate constant on the metal flux from the water column to the sediment.

**Figure 4.6: Metal Flux to Sediment at Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days**

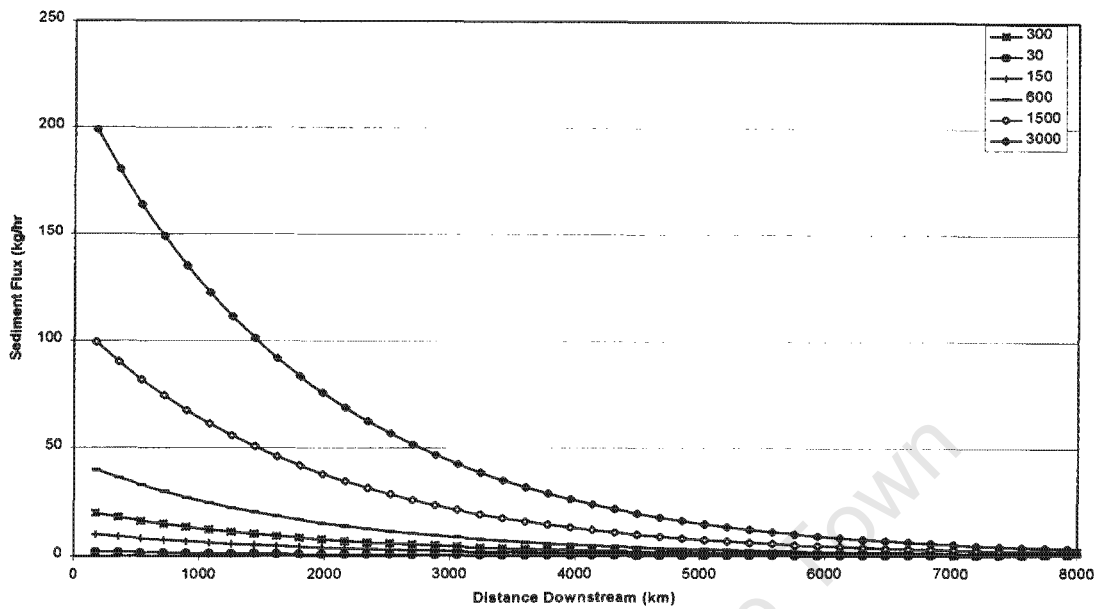


As with the environmental metal concentrations, the initial metal concentration and the first order rate constant are the most significant parameters affecting the metal flux to the sediment. The effect of various effluent metal concentrations on the metal flux to sediment is presented in Figure 4.7. The profiles generated are similar to those for the environmental metal concentration of Figure 4.5. This illustrates the importance of the environmental metal concentration on the metal flux to sediment.

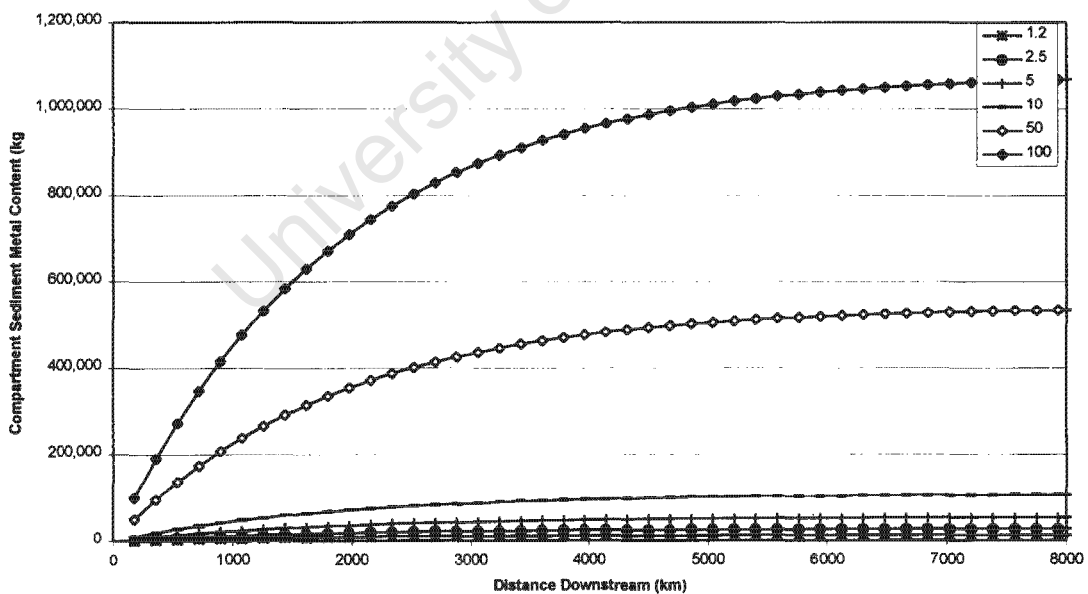
The final output from the model is the metal sediment content. This represents the metal that is contained in the sediment and consistently transported downstream. The actual concentration of metal in the sediment cannot be calculated without knowing the entire sediment volume. The model assumes that the sediment is consistently transported downstream at a rate slower than the residence time of the water in the compartment.

The parameters that affect the metal sediment content are the metal flux to sediment and the ratio of the sediment and water residence times. Metal accumulates in the compartment during low flow periods of the dry season and transported downstream during the wet season.

**Figure 4.7: Metal Flux to Sediment at Metal Half-Life of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L**



**Figure 4.8: Metal Content in Sediment at Sediment Residence Time Ratios of 1.2, 2.5, 5, 10, 50, and 100**

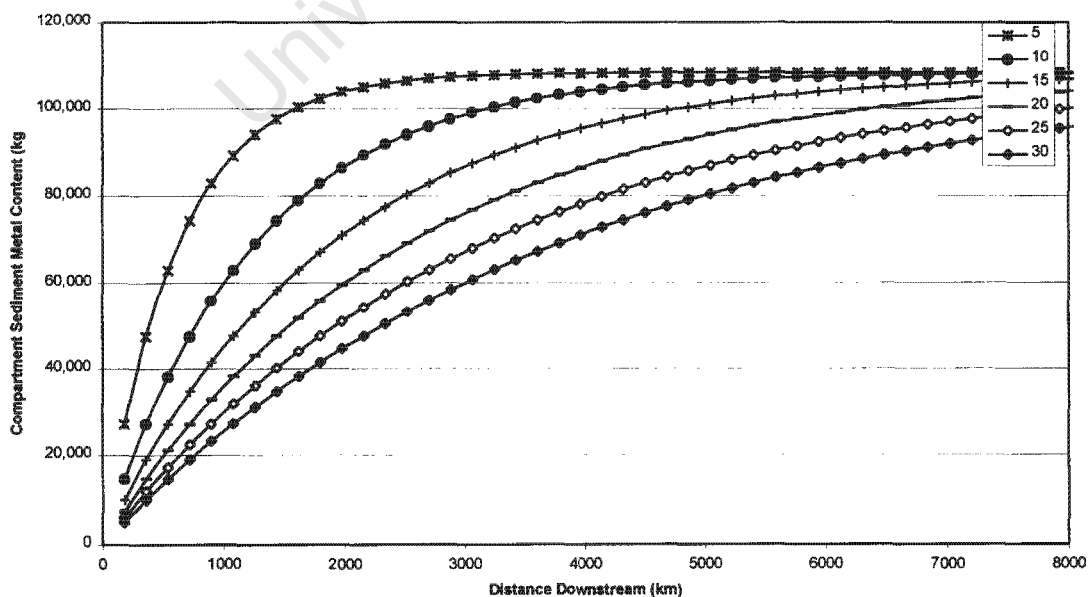


The current model assumes a steady state condition for the metal transport. Variable sediment transport can only be incorporated in the model if the sediment transport dynamics and the seasonal hydrological flow regimes of the flow discharge curve are

known. The sediment residence time ratio determines the magnitude of the metal content in each compartment and affects the magnitude of the metal potentially desorbed from the sediment. Desorption of metal from the sediment is not included in the present model. The effect of the sediment residence time ratio on the sediment metal content is presented in Figure 4.8. For the case study presented in Chapter 5, a value of 10:1 was selected arbitrarily for the sediment residence time ratio.

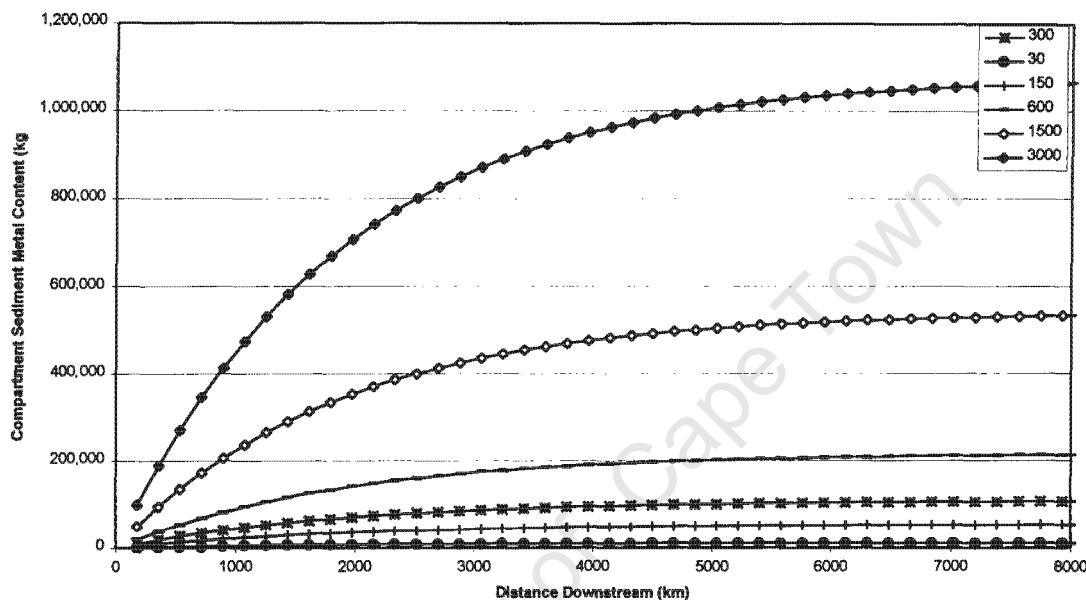
It is clear from Figure 4.8 that the entire river downstream of the effluent release is potentially affected by the metal contained in the sediment transported by the river. The Affected Stream Length concept discussed previously refers only to the environmental concentration of metals in the water column and does not consider the sediment metal content. Should this concept be extended to include the metal sediment content, it is clear that the entire downstream river system is affected by releases of effluents to river systems. The magnitude of the final metal content is determined by the sediment residence time ratio. Figure 4.9 details the effect of the metal first order reaction constant on the sediment residue content. It is clear that the first order reaction constant affects the distance down stream of the effluent release before the maximum metal content is reached, but not the maximum metal content.

**Figure 4.9: Metal Content in Sediment at Sediment Residence Time Ratios of 10 and Metal Half-Lives of 5, 10, 15, 20, 25 and 30 days**



The metal concentration of the effluent also determines the magnitude of the final metal sediment content. This is shown in Figure 4.10. The parameters having the greatest effect on the final sediment metal content are thus the sediment residence time ratio and the initial environmental concentration of the metal.

**Figure 4.10: Sediment Metal Content at Metal Half-Life of 15 days and Effluent Metal Concentrations of 30, 150, 300, 600, 1500 and 3000g/L**



### 4.3 Closure

In this Chapter, two models have been proposed to link design level information to the environmental impact of aqueous emissions from a metals refining operation. The first model, the Water Flow model, links the water consumption of the process and site infrastructure to an over all water consumption and effluent release vector which can be used in determining the effect of the proposed process on the ecological reserve of the catchment. The second model, the River Compartment Model, links the metal release to an environmental concentration for a release of metal containing effluents to a river. These models together provide a basis from which environmental impacts can be evaluated.

The Water Flow model is a network model that summarises the stocks and flows of water over the site. The flows are summarised as vectors containing both flow and content information. Effluent production from the site is thus summarised in the Water

Flow model. Water consumption for the site is also summarised in the Water Flow model.

The River Compartment Model calculates the environmental metal concentration in a river for a continuous point source effluent release to a river system. The River Compartment Model is based on a single compartment fate and transport model using a first order reaction rate for the metal adsorption to the sediment. The metal flux to the sediment is calculated and the metal sediment content calculated. The sediment transport is modelled by selecting a ratio between the sediment and water residence times within the compartment.

The concept of Affected Stream Length is introduced and proposed as a method of evaluating the environmental impact of an effluent on a riverine ecosystem. The Affected Stream Length uses the environmental metal concentration prior to the effluent release to predict the ecological effect of a metal release. The Affected Stream Length predicts the length of stream of the dimensions of the river at the point of release

The parameters influencing the results of the River Compartment Model are evaluated and the first order reaction rate and the initial metal concentration after the introduction of the metal containing effluent were found to have the greatest influence on the environmental metal concentration and the metal flux to the sediment. The sediment transport ratio and the initial environmental metal concentrations were found to have the greatest effect on the final sediment metal content. The first order reaction rate did not influence the final sediment metal concentration, but determined the length of stream required to reach the maximum concentration.

The River Compartment Model is evaluated in a Case Study in Chapter 5 using data obtained from a study conducted by the University of Zambia on the Mwumbashi River in the Kitwe region of the Zambian Copper Belt.

## CHAPTER 5 – EVALUATION OF THE RIVER COMPARTMENT MODEL

Having developed a model which links process design information of water flows and effluent releases to site-wide considerations (and thus to effluent release to riverine systems) and a second model which predicts the fate of metals released to a riverine system, this chapter of the thesis explores the use of the River Compartment Model for the fate of metals in riverine systems. A case study is used to evaluate the River Compartment Model and the proposed proxy environmental impact indicator of "Affected Stream Length". The case study uses results of an environmental monitoring study conducted by the University of Zambia on particular river catchments in the Zambian Copper Belt.

The effect of mining on the Mwambashi River Catchment was evaluated by Simukanga et al (2002), by monitoring metal concentrations at 10 discrete sites within the catchment (wherein is situated a number of copper concentration and refining operations). The available information did not allow an evaluation of the parameters of the model since the flow data was not available for the Mwambashi main stem and tributaries. That said, the case study provides a valuable opportunity to explore the use of the Affected Stream Length as a "site-generic" indicator for impact assessment of minerals and metals, as is now being proposed by the LCA community (UNEP / SETAC Life Cycle Initiative, 2003). The objective of this case study is to explore how the measured concentrations can be used to develop, in reverse, a pseudo-picture of effluent discharges that could have given rise to these local concentrations.

No detailed knowledge of the processing conditions at the various refining sites is known. However, each can be thought of as mirroring a particular combination or choice of design parameters – including technology type, operating conditions etc. If, to a first approximation, the hydro-geological conditions prevailing within the catchment can be treated as uniform, thus differences in the calculated dispersion of the various metals (predicted by the River Compartment Model) suggest a relationship between technology operation and environmental impact. This provides some justification for the use of the model in design studies. It is this premise that is explored further in this chapter, through the case study.

Following the presentation of the results of the Case Study, the usefulness of the River Compartment Model in Design is discussed. The shortcomings and advances of the River Compartment Model are explored.

## **5.1 Case Study Area**

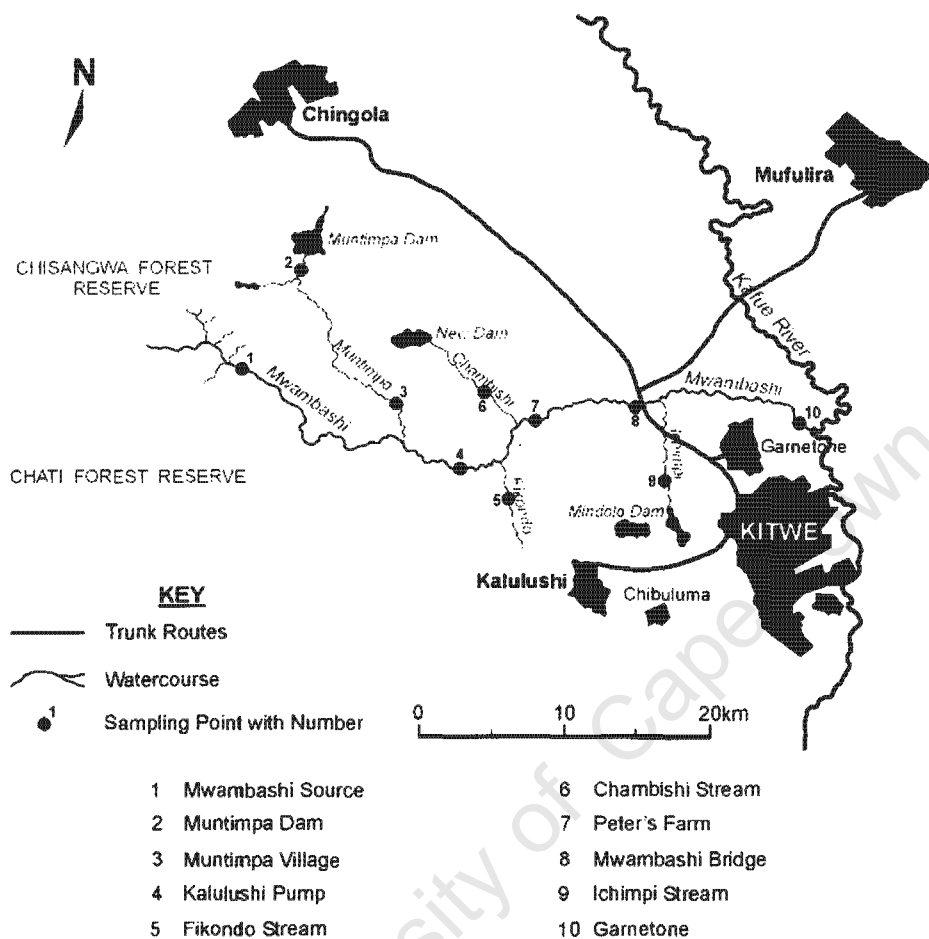
Zambia is a country known for its copper and cobalt production. Most of Zambia's mining and minerals processing facilities are situated on the Copper Belt. The facilities have been established for a long time and environmental management principles have only been established in the recent years. The Mwambashi River is a tributary of the Kafue River, which is in turn a major tributary of the Zambezi River. The local mining industry discharges effluents into the Mwambashi River via its tributaries. The Mwambashi catchment area also supports a number of important socio-economic activities including small and large scale commercial farming and fishing. One water purification plant is situated on the Mwambashi River and it supplies the town of Kitwe with drinking water. Commercial and subsistence farmers also abstract water from the Mwambashi River for irrigation and drinking water (Simukanga et al., 2002). The Mwambashi catchment is depicted in Figure 5.1.

The University of Zambia has conducted a survey in the Mwambashi catchment to determine the levels of contamination originating from the mining activities in the catchment. This study was conducted under the direction of the Pilot Environmental Fund of the Zambian Ministry of Tourism, Environment and Natural Resources (Simukanga et al., 2002).

### ***5.1.1 Mining Activities in Mwambashi Catchment***

The tributaries of the Mwambashi receive mining effluents from the local mining and minerals processing operations. The Muntimpa stream receives effluents from Nchanga mine of Konkola Copper Mines, the Chambishi stream receives effluents from Chambishi Metal Processing Plant of Chambishi Metal plc, the Fikondo stream receives effluents from the mines in Kalulushi, while the Ichimpi stream receives effluents from Mindola dam of Mopani Copper Mines, Kitwe (Simukanga et al., 2002). The primary product from these mining operations is copper with cobalt as a secondary product from operations such as Chambishi Metals. The metallurgical operations in the Mwambashi catchment include copper concentrators, copper smelters, roast leach electrowin copper cobalt refineries and copper electro-refining facilities.

**Figure 5.1: Mwambashi Catchment Area (Simukanga et al., 2002)**



### **5.1.2 Measured Environmental Metal Concentrations**

Simukanga and co-workers sampled the tributaries and main stem of the Mwambashi River at ten sample points indicated in Figure 5.1 in both the wet and dry seasons of 2001. The results of the sampling exercise for the dry season are presented in Appendix B1. Four metals were selected from the raw data. Zinc and Cadmium data was used to augment that of copper and cobalt (the primary products), based on some knowledge of their adsorption and toxicity behaviour from Lake mesocosm experiments conducted by Diamond and co-workers as cited in di Toro et al (2000). The arithmetic average concentration for each of the metals at each of the sample sites is presented in Table 5.1.

**Table 5.1: Metal Concentration in the Mwambashi Catchment during the Dry Season (Simukanga, 2002)**

		Cu (µg/L)	Co (µg/L)	Zn (µg/L)	Cd (µg/L)
Mwambashi Source	1	55	0.054	0.049	0.17
Muntimpa Dam	2	132	10	0.25	0.68
Muntimpa Village	3	98	4.5	0.058	0.56
Kalalushi Pump Station	4	331	4.5	0.075	0.31
Fikondo Stream	5	1083	7.9	0.080	0.22
Chambishi Stream	6	79	14	0.075	0.92
Peer's Farm	7	270	4.5	0.034	0.23
Mwambashi Bridge	8	289	0.87	0.056	0.26
Gametone	10	318	1.1	0.067	0.24

Sample point 9 was omitted for the dry season as it produced a spurious result when the simulated effluent was calculated.

### **5.1.3 Rainfall and Evaporation**

The hydrological data for the area is summarised in Table 5.2. The hydraulic data (mean flow velocities, sediment transport rates etc.) for the respective streams was not available from the monitoring data. The average for the months of April to September have been chosen to represent the Dry seasons.

**Table 5.2: Rainfall and Evaporation Data for the Mwambashi Catchment**

Month	Mean Monthly Rainfall (mm)	Mean Monthly Evaporation (mm)
January	292	144
February	234	134
March	221	130
April	76	125
May	5	163
June	0	147
July	0	171
August	1	220
September	4	253
October	30	257
November	155	178
December	323	150
Annual	1341	2072

## 5.2 Case Study

### 5.2.1 Assumptions

In order to make some meaningful use of the measured data, a number of assumptions needed to be made. These pertain to the challenge of interpreting the various dissolved metal values in terms of hypothetical effluent discharges from processing plants in the area, and in terms of the catchment hydrogeology.

It was assumed that the environmental metal concentrations were because of an effluent release to the Mwambashi Stream Source. The effluents were reconstituted by assuming the headwater composition of the Mwambashi as the condition prior to effluent release, and that the effluent release constitutes 0.1% of the total volumetric flow, thus not significantly impacting the hydraulic dynamics of the stream. The metal concentrations calculated for some of the effluents are above the NOEC concentrations. This situation would not occur except in countries where dilution of the effluent using water from natural systems is allowed to reach the legislative limit. This practice is allowed in Zambia (S Livingstone, personal communication, 2000). The effluent concentrations calculated to reach the measured environmental concentrations are presented in Table 5.3.

**Table 5.3: Simulated Effluent Release to the Mwambashi Catchment**

		[Cu] (mg/L)	[Co] (mg/L)]	[Zn] (mg/L)	[Cd] (mg/L)
Effluent	D1	77	10	0.20	0.52
Effluent	D2	43	4.4	0.008	0.39
Effluent	D3	276	4.5	0.026	0.15
Effluent	D4	1028	7.9	0.031	0.053
Effluent	D5	24	14	0.013	0.75
Effluent	D6	215	4.4	0	0.059
Effluent	D7	234	0.81	0.007	0.090
Effluent	D8	263	1.1	0.017	0.066

The effluent composition was back-calculated from the above assumptions and the measured environmental concentration. These simulated values were entered into the River Compartment Model, and the resulting profile of metal concentration along the river was calculated. In addition, the metal flux to sediment and the metal sediment content per compartment were calculated.

For the calculation of the Affected Stream Length, an instream velocity is required. For this case study, a value of 1m/s was chosen. This value should represent the average dry season low flow instream velocity across the stream channel. Site-specific information was not available for the Mwambashi Catchment.

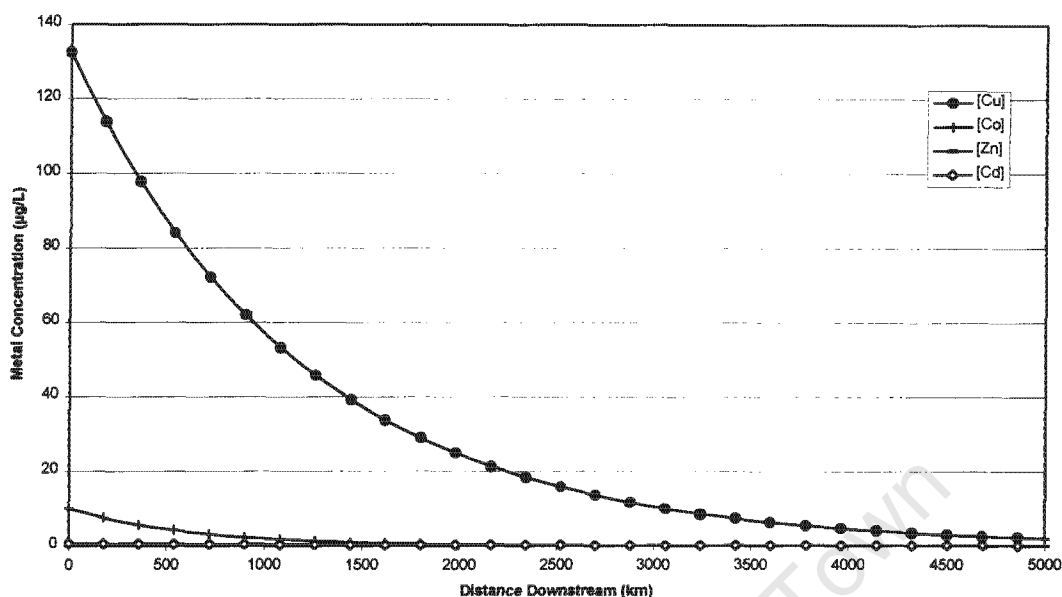
The sediment transport is approximated in the model by the steady state transport of sediment through the compartments at a rate several order of magnitude higher than the water residence time of the compartment. For the case study, a sediment residence time ratio of 10:1 was chosen. This could be too low for the dry season where sediment transport is at a minimum and too high for the wet season where sediment transport is at a maximum.

### **5.2.2 Results**

The data from the simulated effluents were input into the model and the result for each effluent is presented in Appendix B.2. The results of Effluent D1 are presented here to detail the results of the model. Comparisons between the environmental metal concentrations for each effluent are reproduced below to provide a means for comparison between the effluent streams.

The predicted environmental concentration of the metals for Effluent D1 is presented in Figure 5.2. As discussed in Chapter 4, the major influences on the environmental concentration are the initial concentration and the first order reaction rate constant. The initial concentration is determined by the concentration of the metal in the effluent and the dilution achieved by mixing the effluent with the river water. The environmental metal concentration is dominated by copper due to the high concentration of copper in the effluent and the source water and the relatively small half-life time of 9.5 days. This value was measured in Canadian Lakes and should be determined for local conditions. The flow patterns, the water chemistry, the local geology and the sediment composition of the Mwambashi catchment would all affect the metal first order reaction rate. This parameter should be confirmed for local catchments before it is applied in these calculations. This dominance by copper (in terms of its mass concentration) potentially masks the importance of the release of other metals to the environment, as these may be more bio-available, resulting in increased toxicity potentials.

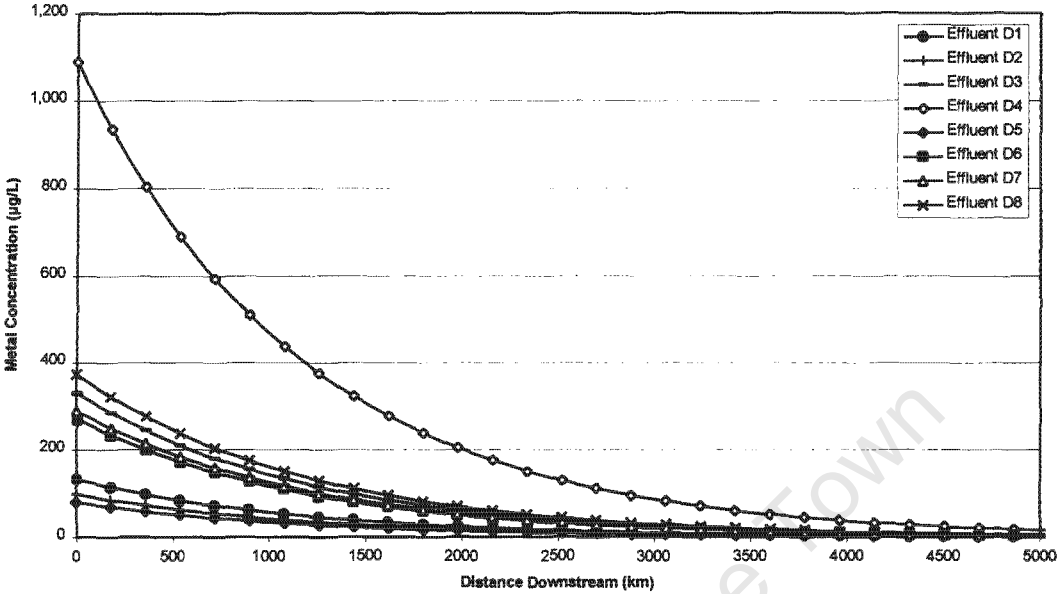
**Figure 5.2: Predicted Environmental Concentration for Effluent D1**



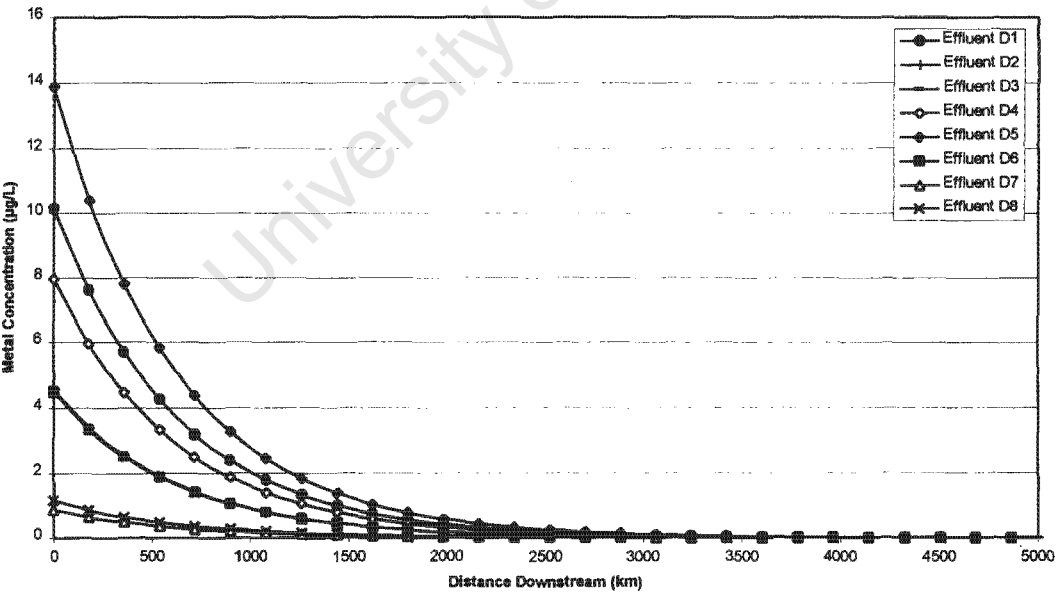
The predicted environmental concentration, as a function of distance downstream from the point of emission release, can be compared to a target parameter such as the NOEC concentration. The NOEC concentration or any particular legislative requirement (based on an effects analysis or water quality indicator), giving the distance of stream required to achieve the target concentration determined. Alternatively, the concentration of metals in the water column prior to effluent addition could be used as a reference to determine the length of stream required to mitigate the effect of the introduction of the effluent into the river system. This latter view is acceptable if it is argued that the local biological populations have adjusted to whatever concentration profile exists in the headwaters. In both cases, the stream length is a proxy indicator of the real environmental impact of this effluent release, but is more meaningful than indicators currently employed by assessment tools such as LCA.

Figures 5.3, 5.4, 5.5 and 5.6 present the model results for copper, cobalt, zinc and cadmium respectively. These provide a measure of comparison between the various effluents. It would be easy to propose that the effluent with the highest concentration of a single metal species would have the greatest environmental effect. Whether the selected metal species, copper in the case of Figure 5.3, has a greater effect than one that has not been considered is not easy to determine from this form of the model output.

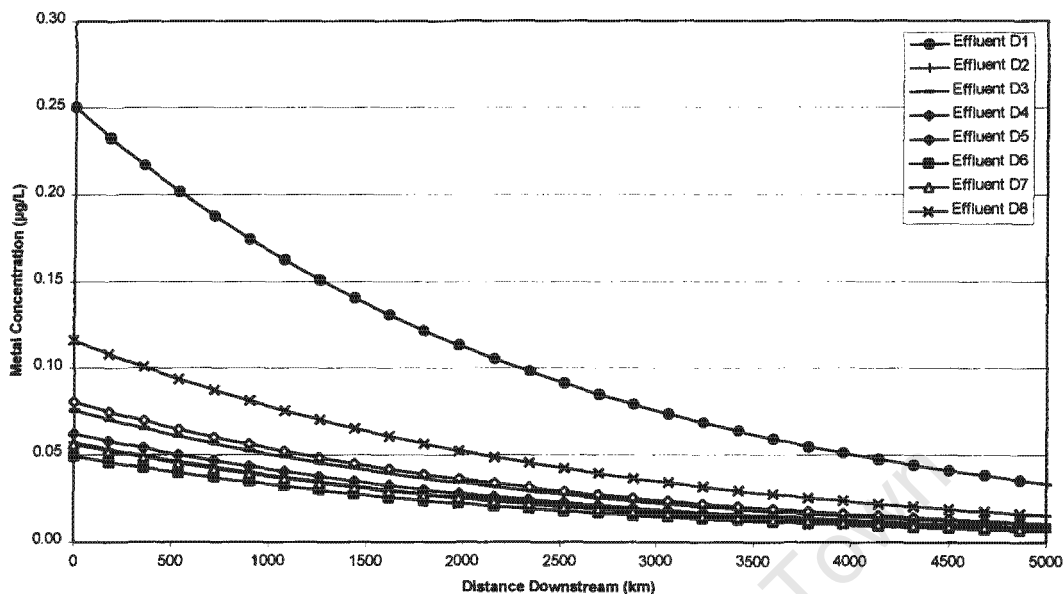
**Figure 5.3: Predicted Environmental Concentration for Copper**



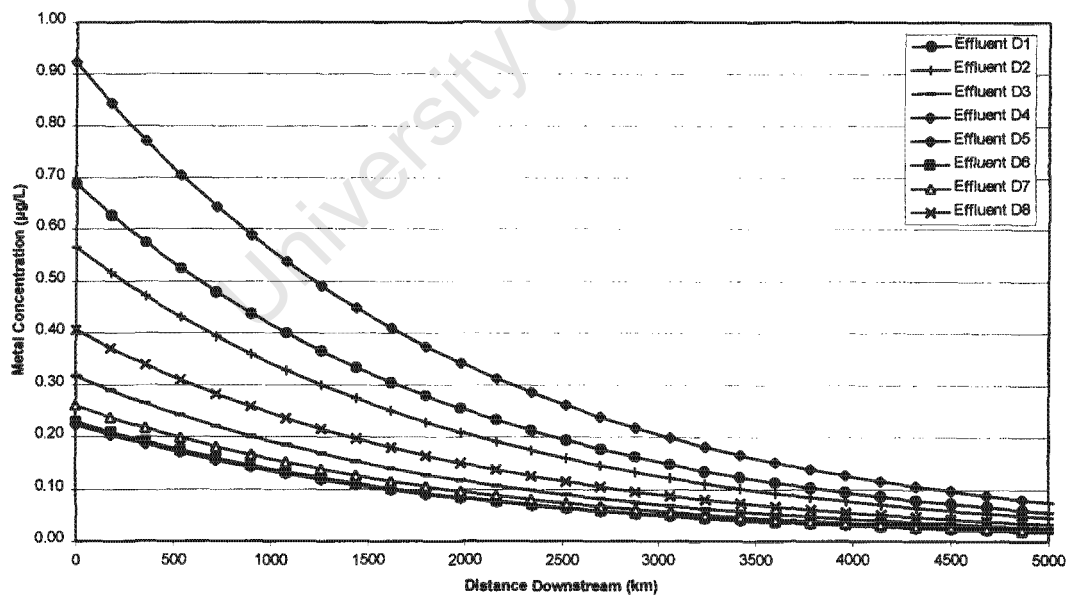
**Figure 5.4: Predicted Metal Environmental Concentration for Cobalt**



**Figure 5.5: Predicted Metal Environmental Concentration for Zinc**



**Figure 5.6: Predicted Metal Environmental Concentration for Cadmium**



From a comparison of these figures, it is clear that different metals influence the ranking of various effluents in these figures. For copper, Effluent D4 maintains the highest environmental concentration, while for cobalt and cadmium Effluents D5 and D1

have the highest environmental concentrations. For zinc, Effluent D1 has the highest environmental concentration.

The comparison of these results requires additional information to allow the analyst to determine which metal has the greatest effect and which effluent would result in the greatest environmental impact. Does zinc at 0.25µg/L have a greater environmental impact than copper at 1050µg/L? A calculated value representing the distance downstream required to reach a target concentration provides a more suitable mechanism by which the effluents can be compared. This is the concept of the Affected Stream Length.

### 5.2.3 Affected Stream Length

The Affected Stream Length is the distance of river required to mitigate the effect of the introduced effluent. This value is calculated from the equations presented in Table 4.3. The current model uses a first order reaction kinetics as a basis and the distance to reach the target concentration is based on an instream velocity of 1m/s. Table 5.4 presents the results of the Affected Stream Length calculation for the hypothetical effluents being released into the Mwambashi headwaters. The maximum Affected Stream Length is a proxy for the impact of that metal that has the greatest effect on the downstream biota.

**Table 5.4: Affected Stream Length using Environmental Concentration as Target Concentration**

		Cu (km)	Co (km)]	Zn (km)	Cd (km)	Max (km)	Metal	Average (km)
Effluent	D1	830	2600	3200	2200	3200	Zn	2200
Effluent	D2	550	2200	300	1800	2200	Co	1200
Effluent	D3	1700	2200	850	990	2200	Co	1400
Effluent	D4	2800	2500	980	440	2800	Cu	1700
Effluent	D5	350	2800	470	2700	2800	Co	1600
Effluent	D6	1500	2200	0	480	2200	Co	1000
Effluent	D7	1600	1400	270	680	1600	Cu	980
Effluent	D8	1800	1500	1700	1400	1800	Cu	1600

Note: Results reported to two significant figures.

The results of the evaluation of the hypothetical effluents shows that the effluents which have the lowest Affected Stream Length are D7, D6, D2 and D3 in order of

increasing Affected Stream Length. Cobalt and copper have the greatest impact on the Affected Stream Length.

The magnitude of the attenuation distances predicted by the Affected Stream Length appear to be excessive. It should be remembered that the Affected Stream Length is a proxy indicator and that the calculated distances are based on the stream at the point of effluent introduction. The Affected Stream Length is thus specific to the system being evaluated and provides a proxy indicator for the ecological impact of an effluent release on the stream. It is obvious that the larger the receiving body, the lower the related Affected Stream Length. The case study is based in the headwaters of the Mwambashi catchment. At this point, the stream is small. The calculated values for the Affected Stream Length can not be mapped to the considerably larger Kafue and Zambezi Rivers.

Can the Affected Stream Length be used as a metric to compare the impact of a suite of effluents on a river system? Returning to the question whether zinc at  $0.25\mu\text{g/L}$  has a greater environmental impact than copper at  $1050\mu\text{g/L}$ , the Affected Stream Lengths calculated for Effluent D1 show that zinc has an Affected Stream Length of 3200km while that of copper is 830km. It is thus evident that zinc has a considerably greater (four times) effect on the river system than copper. A similar case can be posed for comparing two or more effluents.

The significance of the Affected Stream Length is that it highlights the metals which have the greatest environmental impact in the effluent, and provides an indication of the impact by reporting an affected stream length. The design team can address these particular metals and modify the process design, or testwork programme, to address the reduction of the predicted environmental impacts of the specific metals. Additional process steps, or alternative operating conditions, can be evaluated to reduce the environmental impact of the process plant on the river system.

It should be noted that desorption of metals from the sediment is not currently included in the model. The inclusion of desorption reactions would increase the Affected Stream Length by decreasing the net adsorption of metals onto the sediment. This is assuming that the adsorption reaction rate is greater than the corresponding desorption reaction rate. Both reactions are based on the difference in metal concentration between the water column and the sediment. An equilibrium will be reached between the adsorption

and desorption reactions. This has not been included in the current format of the model.

#### **5.2.4 Metal Flux to Sediment**

The high metal flux to the sediment close to the point of effluent release could potentially have the highest effect on the benthic invertebrates and those living in the sediment. For the purpose of this work, the assumption was made that the metal in the sediment is not bioavailable to both water column or benthic organisms.

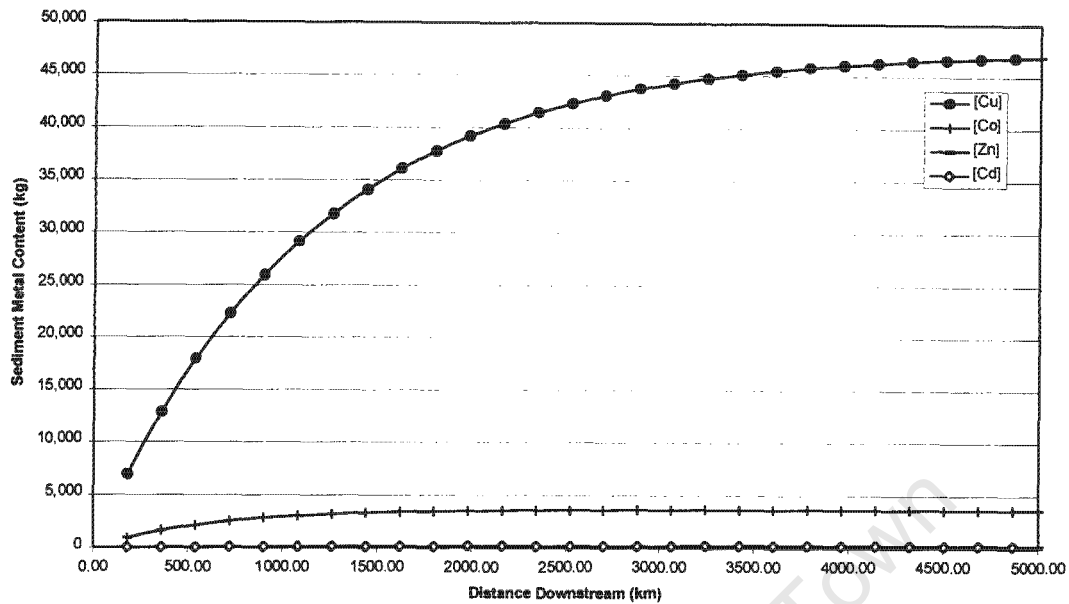
The metal flux does not provide a means of predicting the effects of metal released to the sediments. The profiles achieved mirror those of the environmental metal concentration since the metal flux is influenced by the same factors which affect the environmental metal concentration viz. initial concentration and first order reaction rate. The metal flux to sediment is used in the calculation of the sediment metal content and would not be reported as a model result. This work concentrates on the water column environmental concentration while reporting the sediment metal content, assuming the metal in the sediment is not bioavailable.

#### **5.2.5 Metal Sediment Content**

Consistent with the results for the River Compartment Model of the effluent release evaluated, copper dominates the predicted sediment metal content. The model used a sediment residence time ratio of 10:1, which could be an underestimate for the dry season. As discussed in Chapter 4, the factors that have the greatest effect on the sediment metal content are the initial metal concentration, the first order rate constant and the sediment residence time ratio.

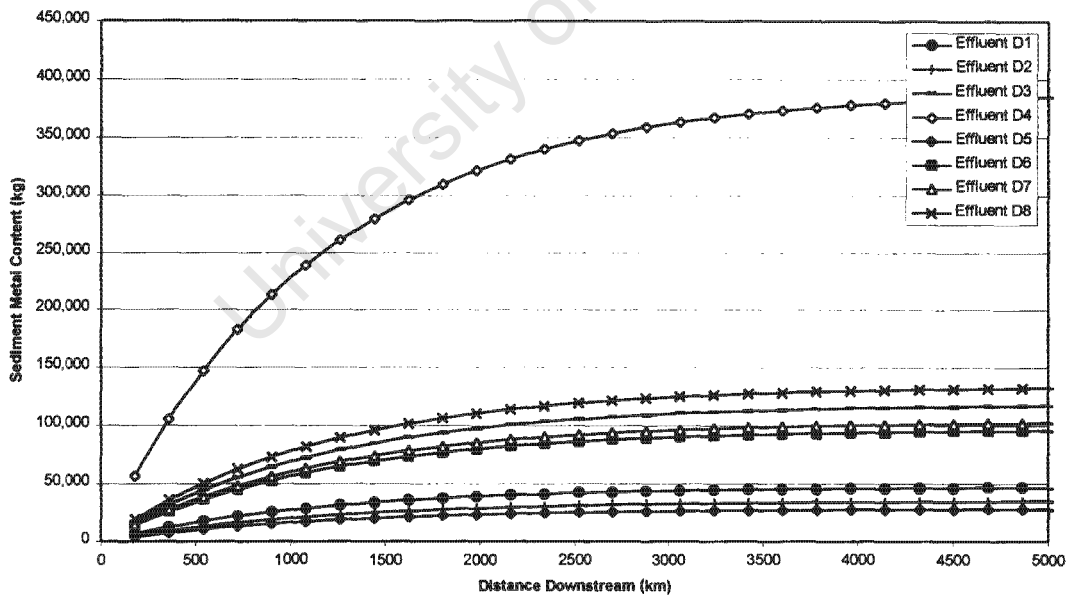
Figure 5.7 presents the predicted sediment metal content for Effluent D1. The Affected Stream Length predicted that zinc resulted in the greatest environmental impact. This is not evident from Figure 5.7. What is evident from this figure is that the entire downstream reaches of the river will be affected by the release of the effluent.

**Figure 5.7: Predicted Sediment Metal Content\* for Effluent D1**



\* -Based on a sediment residence time ratio of 10

**Figure 5.8: Predicted Dry Season Sediment Metal Content\* for Copper**

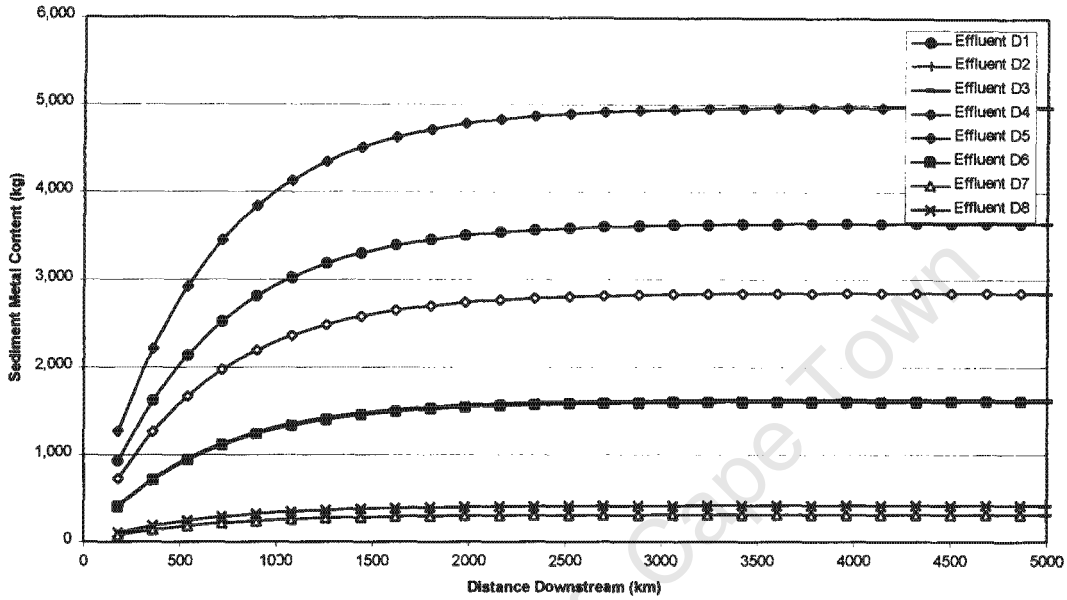


\* -Based on a sediment residence time ratio of 10

Figures 5.8, 5.9, 5.10 and 5.11 show the metal sediment content for copper, cobalt, zinc and cadmium respectively. Since it has been assumed that metal bound to the sediment is not bio-available, the metal sediment content represents a potential

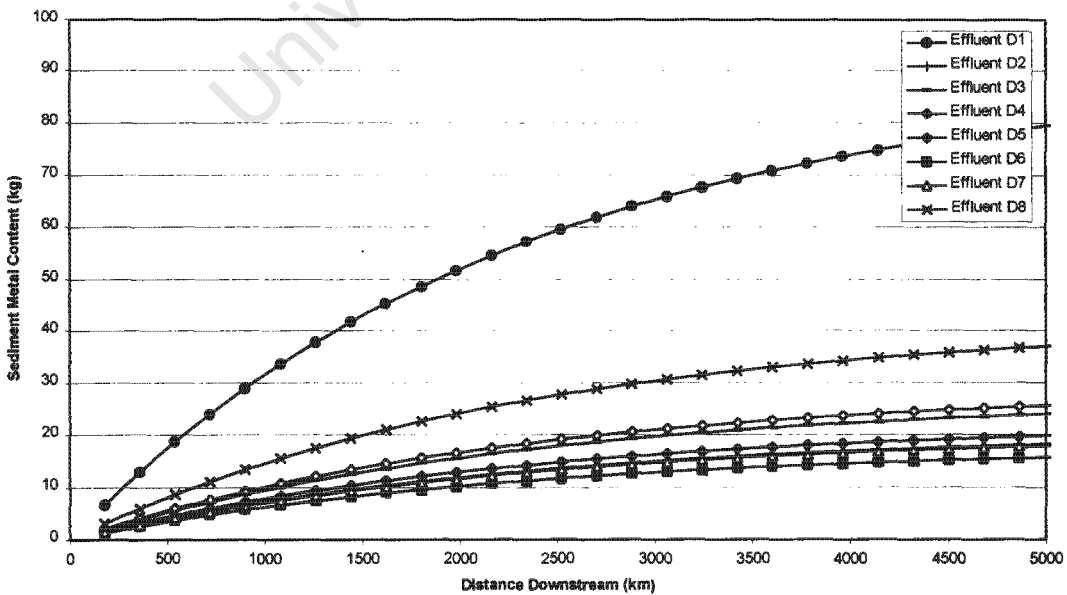
environmental risk should the metal become bio-available through a change in environmental conditions e.g. the introduction of acid mine drainage into the river could result in the remobilisation of the metals.

**Figure 5.9: Predicted Dry Season Sediment Metal Content\* for Cobalt**



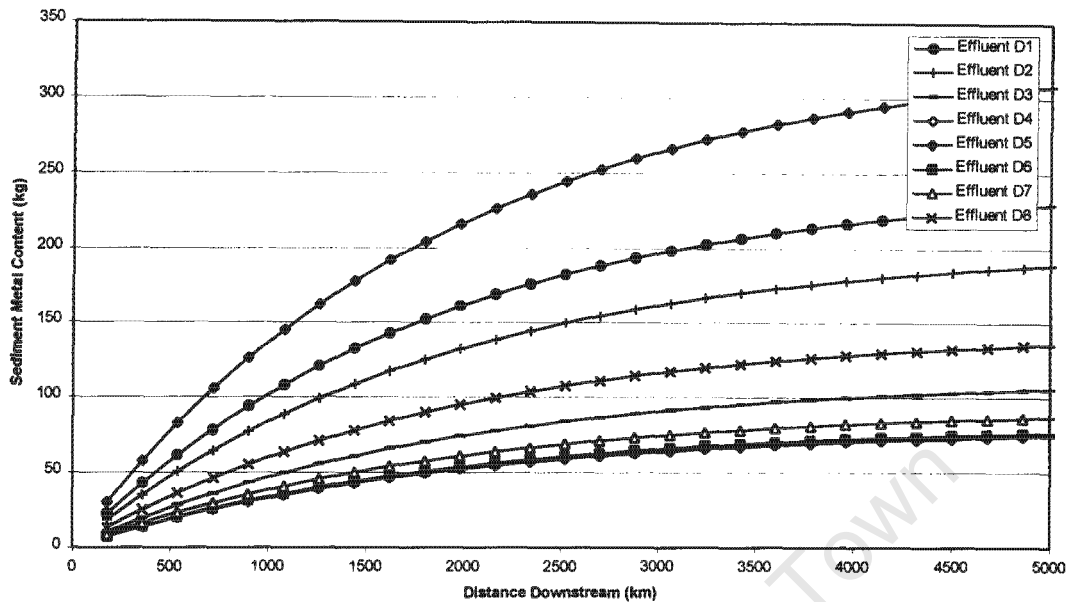
\* -Based on a sediment residence time ratio of 10

**Figure 5.10: Predicted Dry Season Sediment Metal Content\* for Zinc**



\* -Based on a sediment residence time ratio of 10

**Figure 5.11: Predicted Dry Season Sediment Metal Content\* for Cadmium**



\* -Based on a sediment residence time ratio of 10

As discussed in Chapter 4, the sediment residence time ratio determines the final metal concentration in the compartment. The factors influencing the metal flux to sediment, the initial concentration and the first order reaction rate, determine the time for the final concentration to be reached. Sediment transport is seasonal and is affected by the local catchment hydrology. Whereas the environmental metal concentration will be reduced downstream naturally by the confluence of streams and ground water infusion, the metal sediment content is not reduced. It may be distributed through a greater volume of sediment, but the content is not reduced.

The reader is directed to Appendix B.2 to view the full results of all the effluents evaluated. Effluent D1 was discussed in this section to provide an indication of the information that is produced from the model.

### 5.3 Discussion of Case Study Results

The objective of the case study was to demonstrate the use of the River Compartment Model proposed in this work to predict, from design level information, the environmental concentration of metals in a riverine system and the environmental impact of effluent releases to a river system. This section reviews the success of the model in predicting an environmental impact from a point source effluent release to a river system. Each

component of the River Compartment Model is discussed and reviewed with respect to the usefulness output information the model produces.

### **5.3.1 Metal Environmental Concentrations**

The concentrations of metal species in the environment were predicted from the River Compartment Model but were not verified against field data since the data available from the Mwambashi Catchment did not permit such verification. The River Compartment Model should be verified against field data to determine the validity of the parameters used in the model and the predictions produced by the model. As discussed in Chapter 4.2, lake mesocosm results were used from Canada generated by Diamond and co-workers. The verification of the lake mesocosm results and their applicability to rivers, and in particular Southern African rivers, is required before the model can be accepted for general use. The uniqueness of each river system may require that the parameters used in the model may need to be verified for each catchment for which the model is used.

The applicability of the proposed first order reaction for the removal of metal from the water column needs to be verified. This would form part of the complete verification of the model.

The results predicted by the model need to be related to a toxicity model for the system to allow further interpretation or evaluation of the environmental impact. The predicted environmental concentration from the model provides a better interpretation of the toxic effect of a metal release to an ecosystem than the current methodology used in LCA fate and transport models such as USES LCA. USES LCA assumes that the release of an effluent is diluted by the entire volume of the freshwater compartment (Huijbregts et al, 2000), and therefore gives only an average value. Further, the entire river downstream of the release is potentially affected by the release and thus the environmental concentration of the contaminants along the profile of the river needs to be determined. The concept of Potentially Affected Fraction (PAF) and Potentially Disappeared Fraction (PDF) (Huijbregts et al, 2001), as discussed in Chapter 2.7, could be applied to the environmental concentration predicted by the model to provide a more accurate evaluation of the environmental impact of a metal release. This approach allows the potentially affected fraction to be calculated along the length of the river downstream of the release. The PAF could thus be reported along the profile of the river. Including

the PAF in the model would allow the output from the model to be used directly in an EIA during the design stages. Further, this information could be used as additional information to aid decision-making during the design process in terms of input to process and equipment selection.

This output of the model provides an indication of the metal in the effluent that has the greatest potential environmental impact. If the environmental concentration can be linked to an ecological toxicity prediction, this output could be more meaningful and useful in the design situation. At present, the environmental concentration does not provide a metric that can be used during the design process to aid decision-making.

### ***5.3.2 Affected Stream Length***

The Affected Stream Length provides a proxy indicator for the environmental impact of an effluent release to a river system by predicting the length of stream which is required to mediate the effect of constituents in the effluent. The maximum Affected Stream Length reflects the attenuation of the metal that has the greatest effect on the downstream biota.

Legislative requirements for effluent releases to river systems are currently based on the concentration of the constituents in the effluent. Cano-Ruiz and McRae (1999) propose that the emphasis during the design of chemical plants should shift from the environmental concentration to environmental impact. Current measures of environmental impacts are based on the ratio between the environmental concentration and the NOEC. As discussed in Chapter 2.5, these environmental impacts use ecological toxicity information that is evaluated on standard organisms that do not necessarily occur in the river system of interest. To accurately predict the environmental impact for such river systems, toxicity testing would have to be conducted on the most sensitive organisms from the catchment of interest. This approach would add considerable cost to the proposed Base Metals Refinery. As discussed in Chapter 3, the Environmental Impact Assessment is usually performed between the Definitive Estimate and the Detailed Engineering stages of a project. At these stages of the design, the process has been selected and the inherent environmental impacts designed into the process plant. The flexibility in process selection occurs during the earlier stages of the process plant design when the information to evaluate the environmental impacts of the proposed process is limited. The challenge is to evolve design to the point where environmental

impact of a selected process can be evaluated. The lower the level of information input required by the environmental impact evaluation, the earlier it can be used in the design process.

The copper NOEC level of 0.23 µg/L is considerably lower than the environmental concentration recorder for the dry season at the Mwambashi source of 55 µg/L. This illustrates the dangers of using information from other catchments. The organisms in the Mwambashi system have adapted to higher levels of copper in their environment. This example illustrates an advantage of using the Affected Stream Length estimate as it accounts for the natural environmental conditions and measures the remediation of perturbations to the natural levels. As stated previously, it is uncertain whether organisms from a specific catchment will survive at environmental metal concentrations other than those they currently experience - the concept of catchment critical carrying capacity being germane here.

The metal contributing the greatest to the Affected Stream Length can be identified and measures can be implemented to reduce the impact of the particular metal by instituting process changes or adding additional process steps. This information being available during the design process provides an opportunity to address the potential environmental impacts from effluent releases to river systems. The earlier during the design process the environmental impact information becomes available to the design engineers, the greater the flexibility afforded to the design engineers to address these potential impacts.

### ***5.3.3 Metal Sediment Content***

The metal sediment content could provide an indication of the potential risk posed to aquatic organisms living in or on the sediment. For the purposes of this work, the metal bound to the sediment is assumed not to be bioavailable. The sediment movement through the compartment is modelled by assuming that the sediment residence time in the compartment is a multiple of the water residence time. This provides an estimate of the metal build up in the compartment. As mentioned in Chapter 4.3, the actual concentration of the metal in the sediment cannot be calculated without knowing the sediment load in the river. The sediment transport is seasonal and depends on the runoff. It is possible that a flow discharge curve for a river could be included in the model to predict sediment transport. Should this be possible, it may be possible to

evaluate the possibility of establishing an environmental impact indicator for the metal content of the sediment. This sediment transport aspect of the model requires further investigation.

The current form of the predicted sediment metal content does not provide an environmental impact metric that could be used as a basis for decision-making during the design process. Should the sediment uptake of metals from the sediment be the limiting exposure pathway for local biota, the sediment metal content becomes very important. In such a situation, the sediment transport would need to be described in detail to allow for the calculation of the sediment metal concentration. The bioavailability of the metal in the sediment would need to be modelled and the toxicity, or ecological risk, of the metal in the sediment calculated.

Desorption of metal from the sediment is not included in the current River Compartment Model. The current model assumes that sediment is in excess and thus not limiting to the adsorption of metals to the sediment. The validity of this assumption should be verified by further studies.

#### **5.4 Application of the Affected Stream Length**

This thesis has sought to establish a measure of environmental impact which could be used during the design of base metals refineries to measure the impact of metals on river systems, beyond the relatively straightforward use of emission-level information. The Water Flow model provides a link between the process and site level information available during the design phases of a project and summarises water consumption requirements and the effluent composition and magnitude for the metallurgical plant. The River Compartment Model provides a fate and transport model which predicts the environmental concentration of metals released in an effluent from a base metals refinery. A product from the River Compartment Model is the Affected Stream Length estimate of the environmental impact of a metal release to a riverine system.

In this section, the Affected Stream Length estimate for the environmental impact of a metal release to a river system is evaluated in terms of the validity of the proposed impact indicator and in terms of the applicability of the indicator for use during the design process.

#### ***5.4.1 Using the Affected Stream Length Estimate in Design***

As discussed in Chapter 5.3.2 above, the Affected Stream Length can be used as a criterion for determining the environmental impact of an effluent release to a riverine ecosystem. The target metal concentration is determined by the level of information available at the specific stage in the design process. In the early stages of design, the site selection process may not have been completed and site-specific environmental information may not be available. A surrogate site may be selected using a local stream or river to evaluate the various effluents. At the early stages of design, it could be assumed that the processing facility would be near the ore body, but the required information may not be available for the area in which the ore body is situated.

Later in the design stages when the site has been selected, the information required in the model should be available, especially if the EIA has been compiled. At these stages of the design, the Affected Stream Length concept can be used as an aid in decision-making regarding effluent treatment technologies or equipment selection.

The Affected Stream Length is a simple concept to determine the environmental effect of various effluent options. This simple concept can obviously be criticised from a number of perspectives, which are discussed below.

#### ***5.4.2 Criticising the Affected Stream Length Estimate***

The Affected Stream Length does not account for dilution due to tributaries or the confluence with the main river stem. This is not seen as a disadvantage as the aim of the Affected Stream Length is to aid decision-making by providing a proxy indicator for an environmental impact. As discussed in Chapter 5.3.2, a comparison between effluents can be made and a suite of effluent, and associated technologies, can be evaluated regardless of the downstream dilution of the water column. Dilution will effect the various options being considered in the same manner. Dilution is an effective way of reducing the environmental concentration of metals in the water column but has not been included in the current River Compartment Model.

The methodology assumes a constant channel width for an inordinate length of the river. This is not realistic. The Affected Stream Length is a concept for comparison, and does not represent an actual stream length, but a hypothetical stream length

required to reach the target metal concentration, or mitigate the effect of the metal release to the river. As a means for comparison, it is a valid measure.

The Affected Stream Length is currently based on lake mesocosm data. How relevant is this data to riverine systems? This is a valid criticism of the model. The possibility of reaction kinetics other than first order kinetics has been discussed above. The validity of first order kinetics needs to be determined. This is beyond the scope of the current work. The evaluation of metal reaction kinetics in streams and the desorption of metals from the sediments need to be determined for river systems. This could form the basis of further studies related to this work.

How does the Affected Stream Length account for antagonistic and synergistic effects of metals in evaluating the environmental effect? The compounding effects of metals are really an unknown at this stage and have not been included in the model.

#### ***5.4.3 Evaluating the Affected Stream Length Estimate***

Hauschild and Pennington (2000) set out criteria to evaluate ecotoxicity effect indicators for their applicability and proposed the following aspects be included:

- Scientific validity
- Environmental relevance
- Reproducibility
- Transparency
- Quantification of uncertainty
- Complexity
- Feasibility
- Data availability

There is currently insufficient data available for the parameters required for the calculation of the Affected Stream Length and thus, it is difficult to evaluate the scientific validity of the model. Parameters that influence the affected stream length are the first order reaction rate constant, the initial concentration, the target concentration and the average instream velocity. The initial concentration can be determined by calculating the result of the mixing between the effluent introduced and the environmental concentration in the river prior to effluent introduction. During the design process, uncertainty exists with respect to the metal concentration of the

effluent. This can vary by more than 100% through the design process. Should the metal concentration be twice the original estimate, the Affected Stream Length would increase by an additional  $\frac{V}{k} \ln(2)$  where V is the instream velocity (m/hr) and k is the first order reaction constant ( $\text{hr}^{-1}$ ).

Further uncertainties in the calculation of the Affected Stream Length originate from the first order reaction rate, natural environmental metal concentration and the instream velocity. The instream velocity and environmental metal concentration are variables that can be measured in the field. These can be included in the design information once a site has been selected for the location of the process plant. For the reaction rate, it should firstly be established whether the reaction rate is first order and subsequently validate the first order reaction rate constant from testwork. This reaction rate could vary between catchments due to water chemistry, underlying geology, hydrology and the hydraulics of the stream. As discussed in Chapter 4, the first order reaction rate constant k ( $\text{hr}^{-1}$ ) is defined by

$$k = \frac{\ln 2}{t_{1/2}} \quad 5-1$$

where  $t_{1/2}$  is the measured metal half life in the water column (hr). Should there be an error of +100% in the measured metal half life, the first order reaction rate constant would halve. In calculating the Affected Stream Length, this would result in a doubling of the Affected Stream Length. Similarly, for the instream velocity, a doubling of the instream velocity would result in a doubling of the Affected Stream Length.

It has been shown that effluent release to river systems affects the stream for a distance downstream of the point of emission. The Saprobien system, the first method proposed to describe the effect of pollution in rivers (Davies and Day, 1998, Moss, 1998), detailed the succession of invertebrate communities downstream of an effluent release and the eventual recovery of the river system to clean water organisms. The concept of the river recovering to conditions prior to an emission a distance downstream has been used by river scientists to promote an appreciation of the ecological importance of rivers (Davies and Day, 1998). There is thus a case for the validity of an environmental impact metric to predict the length of stream or river downstream of an effluent discharge, which is affected by the constituents of the effluent. The proposed

Affected Stream Length calculates the length of stream required for the effect of the release to be mitigated. The proposed metric is environmentally relevant in that it is known that the organisms present in the river system can survive at the ambient environmental concentrations, but it is uncertain whether these organisms will survive outside the ambient conditions.

The calculation of the Affected Stream Length is calculated from environmentally measured reference conditions. The model is based on first order kinetics for the removal of metals from the water column that were measured in lake mesocosm experiments. These need to be verified for the area under study. Since the Affected Stream Length is based on experimental data and on a calculation, it is reproducible and transparent. The effect of uncertainty in the Affected Stream Length is discussed above. Uncertainty in the first order reaction rate constants needs to be determined. This could be coupled with the verification of the kinetics of the metal removal from the water column.

The calculation of the Affected Stream Length is not complex. The scientific validity and feasibility of the Affected Stream Length needs to be verified. There is currently insufficient data available to determine the parameters for the Affected Stream Length calculation for areas other than the great lakes region of North America. The verification of the River Compartment Model through testwork would increase the data available and verify its scientific validity.

In summary, the Affected Stream Length environmental impact indicator has environmental relevance. Verification of the River Compartment Model through testwork, confirming the parameters of the model and the order of the reaction kinetics, would provide a basis for the scientific validity and uncertainty to be quantified and the feasibility of the Affected Stream Length environmental impact indicator to be evaluated.

## **5.5 Evaluating the Proposed Models**

Two models are proposed in this work. The first of these is the Water Flow Model, which provides a network analysis of the process and site facility describing the flows as vectors comprising of both flow and composition data. This model methodology can be used to evaluate the water consumption of the site and predict the effluent from the

site. This model links process level information to an effluent discharge from the site and the water requirement. The second model, the River Compartment Model, describes the fate and transport of metals in river systems, predicts the metal flux to the sediment, and predicts the metal sediment content. Associated with the River Compartment Model is the Affected Stream Length prediction of environmental impact of a metal release to a river system.

The success of these models needs to be evaluated against the metrics proposed by Cano-Ruiz and McRae (1999) for effectively evaluating environmental impacts during the design of chemical plants. The requirements are that the approach should:

- include waste treatment infrastructure within the analysis boundaries,
- facilitate integration of mass exchange processes,
- be adaptable to a life cycle analysis framework for considering environmental impacts, and
- shift the emphasis from effluent concentration to environmental impacts

By the nature of the definition of the Water Flow Model, as discussed in Chapter 4.1, the model considers all flows on the site. The Water Flow Model sets a structure, which requires that all flows of water through the process plant and site facility are included in a network model. The Water Flow Model thus satisfies the first requirement.

The Water Flow Model details every flow on the site as a vector containing flow and composition data that could be used in a mass exchange evaluation. This property of the Water Flow Model promoted the integration of mass exchange on the site by providing valuable information to the process. The Water Flow Model thus satisfies the second requirement.

The Water Flow Model summarises all the stocks and flows of water on the site. The flows are described by a vector which comprises both flow and composition data. These flows are similar to the information used to establish a Life Cycle Inventory of a process facility of commodity. The Water Flow Model is thus adaptable to a Life Cycle analysis framework. The environmental impacts predicted by Life Cycle Assessment for freshwater are deficient as discussed in Chapter 3.4. The environmental impacts used for water applicable to metals are consumption and ecological toxicity (Owen, 2002) and there is sufficient uncertainty in predicting the environmental concentration of metals in

river systems and the ecological toxicity of these metals as discussed in Chapter 2.5. The bioavailable metal concentration is a more appropriate measure upon which toxicity should be based (Jensen et al, 2000). The Affected Stream Length proposed by this work provides a measure of the environmental impact of a metal release to a river system, which can be linked to refining capacity (and therefore units of production). It should be noted that the Affected Stream Length was never intended to be part of LCA, rather to present a different way of looking at impacts which could complement that information available through LCA.

The final requirement of an environmental methodology is that it shifts the emphasis from effluent concentration to environmental impact. The Water Flow model calculates the effluent concentration of a site. The River Compartment Model uses this effluent data to predict the environmental concentration, the metal flux to the sediment and the sediment metal content within the catchment downstream of the effluent release. The environmental concentration and the sediment metal content can be used as an input to an environmental impact prediction based on the ecological toxicity in the water column and the sediment. The River Compartment Model does not make this link, as there is currently a high level of uncertainty relating to the prediction of ecological toxicity. The model proposes an Affected Stream Length as an environmental impact where the length of stream required returning to the water column concentrations prior to the introduction of an effluent is calculated. The model does predict an environmental impact and thus satisfies the final condition. The validity of the Affected Stream Length is discussed in Chapter 5.4.3 above.

It can be concluded that the models proposed in this work together satisfy all the requirements set out by Cano-Ruiz and McRae (1999) for the effective evaluation of environmental impacts during the design of chemical plants.

## **5.6 Closure**

The Case Study was designed to demonstrate the use of the River Compartment Model and the ecological impact estimate of the Affected Stream Length. The model was not verified by the case study, as the information required to verify the model parameters was not available. The verification of the proposed River Compartment Model is required before the model can be accepted as an ecological impact estimate for applications such as Life Cycle Assessment. That said, the methodology behind the

model is generic, and can be used for any particular combination of design-related information and catchment geo-hydrology. The model predicts the environmental metal concentration down the length of a river assuming no change in the flow other than evaporation and rainfall. The model could be modified to include tributaries joining the current branch of the river, but this requires knowledge of the catchment being studied and the hydraulic flow discharge curve of each branch of the river system. This level of detail can be included in the model once the parameters for the model have been verified.

Sediment transport could be linked to the flow discharge curve at various points in the catchment. The advances in sediment transport modelling in a river system were not investigated as part of this work. The current method of modelling sediment transport based on the ratio of the compartment residence times for water and sediment is an estimate. It is expected that the residence time ratio will vary seasonally and thus this method should be evaluated and, if possible, linked to a flow discharge curve for points in the river system.

The Affected Stream Length provides an estimate of ecological impact of a metal release to a river system. The estimate presents additional information to a design team evaluating the ecological impact of a proposed process technology. The Affected Stream Length estimate is dependent on the validity of the River Compartment Model and thus the verification of the River Compartment Model is required to confirm the validity of the Affected Stream Length. The Affected Stream Length should be evaluated from the basis of the environmental concentrations prior to the introduction of an effluent containing stream into the river.

The conditions proposed by Cano-Ruiz and McRae (1999) for effectively considering environmental impacts during design were used to evaluate the proposed combination of the Water Flow Model and the River Compartment Model. Mostly, these design conditions are met by the combination of models developed in this thesis.

## CHAPTER 6 – CONCLUSIONS AND RECOMMENDATIONS

This thesis set out to explore the hypothesis that designers of Base Metals Refineries should consider both site and catchment wide impacts of water consumption and metal releases to aquatic systems by the inclusion of suitable environmental impact measures in the design process. The challenges in accomplishing this include understanding the behaviour of metals in aquatic systems, the resultant environmental impacts, and being able to relate the level of information available at the various stages of the design of base metals refineries to the proposed environmental impacts metric. This chapter of the thesis reviews the work completed towards accepting or rejecting the hypothesis and proposes further work identified in the process of testing the hypothesis.

### 6.1 Testing of the Hypothesis

This thesis sought to evaluate the following hypothesis:

***The design of base metals operations for effective and efficient water usage and management requires consideration of both site- and catchment-wide effects of metal releases to freshwater aquatic systems, and their incorporation into the design process through suitable performance measures.***

The hypothesis is reviewed with respect to the literature reviewed discussing environmentally conscious design.

#### 6.1.1 Environmental Considerations in Design

1. There is a need for engineers involved in the design of base metals refineries to understand the impacts of their designs on the environment rather than meeting effluent release concentration limits.
2. Including waste treatment facilities within the site boundary and producing information suitable for inclusion in a Life Cycle evaluation were required for environmentally conscious design.

3. It has been reported that 85% of the life cycle costs of a chemical plant are determined during the design phases and estimated that 50% of capital expenditure on new process plants is associated with environmental issues.
4. Formal environmental assessments such as Environmental Impact Assessments are only performed between the Definitive Estimate and the Detailed Engineering phases of the project, or concurrently with the Detailed Engineering Phase, which is often too late to significantly incorporate environmental constraints in the core process. Remedial waste treatment processes are added onto the core process to meet legislative requirements. Early assessment of environmental impacts is required from the information available at the specific stage of the design process.
5. Tools such as Life Cycle Assessment are currently available to evaluate the impact of releases, but these are deficient when considering the impact of releases to riverine ecosystems, specifically metal releases.

#### **6.1.2 Result of Hypothesis Testing**

1. Literature indicates that there is a requirement to consider environmental impact of a proposed base metals refinery during the design process. This requires a link between the level of information available at the various stages of the design process and predicted environmental impacts.
2. Five major impacts of mining and minerals operations on freshwater systems have been identified. These are acid mine drainage, metals in the environment, cyanide, sedimentation and water use. These five impacts constitute environmental impacts outside the site boundary and thus classify as catchment environmental impacts.

The review of the literature thus supports the hypothesis and thus the hypothesis is not rejected.

## **6.2 Restating the Hypothesis**

Having accepted the hypothesis from a literature review, the hypothesis was restated to hone into one specific aspect of the original hypothesis, the description of metal related impacts in riverine systems. Riverine systems are important in areas such as

Southern Africa and thus the restated hypothesis focuses on the environmental impact of metals in riverine systems during the design of Base Metals Refineries.

***The environmental impact of metal releases to riverine systems can be modelled and incorporated into the design of Base Metals Refineries through the development of a suitable proxy indicator, or set of proxy indicators.***

This restated hypothesis was evaluated by:

- Proposing the Water Model to link design level information to releases to riverine systems.
- Proposing the River Compartment Model to link metal releases into riverine systems to environmental metal concentrations.
- Proposing the Affected Stream Length as a proxy indicator to represent the environmental impact of metal releases to river systems.
- Evaluating the proposed River Compartment Model and the proposed Affected Stream Length proxy indicator in a Case Study.

### **6.2.1 Riverine Ecosystems**

1. Rivers are linear systems and releases to river systems affect the entire river system downstream of the release.
2. Every catchment is unique and any change to the water quality (physiochemical and flow) have a detrimental effect on the catchment downstream of the disturbance.
3. Factors important in maintaining the functioning of a riverine ecosystem include maintaining flow regimes and preventing elevated (or out of natural range) physiochemical stressors in the system.
4. Biomonitoring provides a comprehensive means for evaluating the state of a riverine ecosystem and establishing a benchmark state of a river, but does not prove to be useful during the design stages since the information used in biomonitoring cannot be linked to the information available during the design process. Biomonitoring should be employed during the evaluation of the operational performance of the base metals refinery and to evaluate the impact of the refinery during its operation.

5. In the design context, minimising the environmental impact of the proposed process by maintaining the natural flow regimes and minimising the effect of physiochemical stressors should be set as objectives.
6. The modelling environmental impacts in rivers require a linear model of the river system. This approach allows the environmental concentration to be evaluated along the length of the river system.

### **6.2.2 Metals in Freshwater Aquatic Ecosystems**

1. The toxicity of metals in aquatic ecosystems is dependent on the concentration of dissolved free metal ions. Toxicological interactions are complex and dependent on factors such as temperature, dissolved organics, inorganic ligands, pH, hardness, alkalinity, organic and inorganic particles and ionic strength.
2. The result of laboratory toxicity testing of metals is influenced by the adaption and acclimatisation of the test organisms. Ideally, organisms from the site selected for building a process plant should be used in the toxicity testing.
3. Metals exert synergistic or antagonistic toxic effects when combined with other metals.
4. The bioavailable concentration of a metal is a good measure of the toxic potential of the metal.
5. Metals are persistent in the environment because they do not degrade. Their bioavailability does vary according to the environmental physiochemical conditions. Metals can become more, or less, bioavailable as a result of changes in the physiochemical condition of the environment.
6. Where the bioavailability of the metal is not available, the environmental concentration of the metal can be used as an indication of the bioavailability.
7. Lake mesocosm experiments conducted in Canada showed that the persistence of metal ions in the water column is dependent on the sediment loading of the water column. Metals exhibited first order reaction kinetics in removal from the water column.

Having identified the need to relate process level information to environmental impacts, the prediction of an environmental impact of metal containing effluent on a river system was investigated.

### **6.2.3 Predicting Environmental Concentration of Metals in Rivers**

1. Testwork conducted on lakes suggested that there was a correlation between the amount of sediment in the water column and the removal of metals from the water column by sedimentation onto particulate matter by first order kinetics.
2. In rivers, especially most Southern African rivers, large quantities of sediment are naturally transported in the river systems. It is assumed that there is sufficient sediment being transported to consistently provide sites for metal adsorption.
3. The assumptions were made that the first order kinetics would hold for river systems and that the large volume of sediment transported would provide sufficient matter for the adsorption of the metals in the water column.

From these assumptions, the River Compartment Model was developed to predict the steady state environmental concentration profile for metals along the length of a river downstream of a continuous point source effluent release.

### **6.2.4 River Compartment Model**

1. The sediment transport is seasonal and can be linked to instream velocity. For the purposes of the model, the sediment transport was modelled by assuming that the sediment residence time in a compartment was a multiple of the water residence time (always greater than 1). Modelling sediment transport in this way assumes steady state conditions that generally do not occur in a river system. The flow in the river can be represented by a flow discharge curve, which details the proportion of time a flow is exceeded. Sediment transport is flow related and this could be linked to the flow discharge curve.
2. The model ignores water chemistry and biotic interaction with the metal in the water column. Metal adsorption onto sediments is proposed as a mechanism by which metals are removed from the water column, but the

actual mechanism is not specified. Water chemistry would be expected to be the greatest driver for metals removal from the water column. The overall reaction is: metals are removed from the water column and deport to the sediment. Water chemistry could be included in the model by the addition of speciation models for the metal in the water column. Knowledge of the kinetics for water chemistry related reactions would be required for their inclusion into the model.

3. The model ignores groundwater interchange. Rainfall and evaporation are included in the model.
4. The model also discounts desorption of metals from the sediment assuming that an excess sediment volume would result in a negligible quantities of metals returning to the water column.
5. The River Compartment Model is based on the assumption of first order kinetics for the removal of metals from the water column. This assumption needs to be verified for metals in river systems before the model can be developed further. This verification would require testwork to be conducted in a number of catchments to evaluate the effect of sediment characteristics on the order of the reaction and the reaction kinetics.
6. The River Compartment Model itself does not provide useful output to evaluate the environmental impact of metals released to a river system. The output of the model includes graphical representations of the environmental metal concentration, the metal flux to sediment and the sediment metal content. The sediment metal concentration cannot be calculated without knowledge of the entire sediment volume of the compartment. The environmental concentration and the sediment metal content could be used to calculate toxicity potentials provided the mechanism for this calculation is available.
7. Parametric analysis of the model revealed that the initial concentration after effluent release and the first order reaction rate have the greatest effect on the environmental metal concentration and the metal flux to sediment. The sediment metal content was affected by the initial concentration, first order reaction rate and the sediment residence time ratio. The maximum value reached was affected by the initial concentration and the sediment residence time ratio. These results emphasise the importance of verifying the kinetics of metal deportment from the water column and the sediment transport.

The use of the model was evaluated in the form of a case study. Since the model has not been verified, the results of the case study are artificial. The outputs of the model provided additional information regarding the environmental impact of a release to the river system, but the information was not useful for making decisions regarding which effluent had the greatest environmental impact since the impact of the metals could not be compared from the model output. An additional metric was required to differentiate between the environmental impacts of the metals contained in the effluents compared.

Although there is great potential in the model, the most significant output of the model in the context of this thesis is the environmental impact predicted by the Affected Stream Length.

#### ***6.2.5 Affected Stream Length***

The sediment metal content showed that the entire river downstream of the effluent release is affected by an increase in the metal contained in the sediment. The Affected Stream Length refers to the length of downstream river that would be required to mitigate the effect of the increased metal concentrations in the water column as a result of the effluent release. The Affected Stream Length assumes that the river does not change in dimensions from the point of effluent introduction. This affected stream length is thus a measure of the environmental impact of the effluent release.

1. The validity of the Affected Stream Length is dependent on the validity of the River Compartment Model and thus the discussion relating to the River Compartment Model applies to the Affected Stream Length.
2. Currently, the environmental impact used to evaluate the freshwater compartment represents the quantity of water required to dilute the emission to the NOEC. This approach is more suitable to lake systems than to river systems. For linear river systems, a concept such as the affected stream length provides a more accurate indication of the impact of an emission to a river system.
3. For the Affected Stream Length, it is proposed that the environmental concentration prior to emission introduction be used as a target concentration

rather than the NOEC. This was illustrated in the case study where the environmental concentration of copper was higher than the NOEC. It is argued that it is uncertain whether organisms existing in the river system can survive at conditions other than the environmental conditions they have been experiencing. The current environmental conditions existing in the river system should thus be used as a basis for calculating the Affected Stream Length of any other environmental impact parameter.

The Affected Stream Lengths calculated during the case study provided results which were considered excessive in length. Affected Stream Lengths in excess of 3000km were calculated. This could result from assumptions made during the case study due to the limited information available.

4. The factors affecting the result of the Affected Stream Length calculation are the average instream velocity of the river, initial concentration, the target concentration and the first order reaction rate constant.
5. For consistency in Affected Stream Length results, 1m/s was proposed as an average instream velocity for the river channel. This would need to be verified from field data, which should include a flow discharge curve for the river and dimensions of the river channel.
6. The case study illustrated that the Affected Stream Length calculation could be used to identify the metal contained in an effluent which would have the greatest environmental impact.
7. This metric could also be used to compare the environmental impact of a range of effluent streams to predict which effluent would have the greatest potential environmental impact.
8. The Affected Stream Length provides additional information to decision makers adding to the body of information available for environmentally conscious design.

It should be remembered that this work has been conducted in the context of the design of Base Metals Refineries. Linking an environmental impact to information available at the various levels of design is required to promote the use of environmental considerations in the design decision making process. Greater flexibility in design options is available at the early stages of the design process while the information used to determine the environmental impact during the EIA is only

available during the definitive estimate and detailed design stages. To bridge this gap, a Water Model is proposed to summarise information relating to water consumption and effluent release from the process facility for used at all levels of design detail.

#### **6.2.6 Water Model**

The Water Model is a steady state network analysis of the water stocks and balances over a process facility. The methodology proposed reports water consumption in various component units and the flow between them. Being a steady state methodology, this model only accounts for nodes where accumulation takes place. The constant stocks are not considered. The flows between the nodes are represented by vectors which contain both flow and stream composition data. This information can be used to determine the total water consumption of the site, or individual nodes, and the quantity and composition of the effluent which would be released from the site.

1. The Water Model contains information that could be used for mass integration methodologies, includes all process areas including waste treatment and is compatible with Life Cycle Assessment methodologies.
2. The model does not implicitly report an environmental impact, rather, it reports the concentrations at the site boundary. This information can be used in conjunction with the River Compartment Model or the Affected Stream Length concept to produce an environmental impact indicator.
3. The Water Model proposed a conceptual methodology to link design level information to an environmental impact. Mass balance information generated during the design process provides the input to the model.
4. The information required by the methodology accounts for all process and site streams.
5. The model can be used at all levels of design and thus can be used to incorporate environmental information into the design decision-making process.
6. Base Case and Alternative flowsheets can be compared based on their environmental impact relating to water use and effluent production.

Although only conceptual, the Water Model provides the link required between the design level information and a predicted environmental impact throughout the design process. This model, in conjunction with the River Compartment Model and the Affected Stream Length concept allows for the consideration of catchment level indicators from design level information.

### ***6.2.7 Testing the Restated Hypothesis***

The testing of the restated hypothesis concludes that:

- The proposed Water Model links design level information to releases from a site that include releases to riverine systems.
  - The model is conceptual and needs to be developed further before it can be used.
  - The model can be structured to monitor all releases from a site, which can be linked to environmental impact indicators.
- The proposed River Compartment Model links metal releases to riverine systems to environmental metal concentrations.
  - The model is representative of a river system.
  - The assumptions made in establishing the model need to be verified.
    - The assumption of first order kinetics for metal removal from the water column.
    - The assumption of sufficient sediment sited for metal adsorption.
    - The assumption that adsorption of metals from the sediment is greater than desorption from the sediment.
    - The assumption regarding sediment transport.
- The proposed Affected Stream Length as a proxy indicator represents the environmental impact of metal releases to river systems.
  - The Affected Stream Length proxy indicator provides a measure of environmental impact for the release of a metal containing effluent to a river system.
  - The validity of the Affected Stream Length requires the verification of the River Compartment Model.
  - The Affected Stream Length provides additional information that can aid decision making during the design of Base Metals Refineries.

In order to accept the restated hypothesis, the assumption that the River Compartment Model is verified needs to be made. The work provides a link between design level information and environmental impact indicators through the River Compartment Model. The verification of the assumptions made for the River Compartment Model is required before it could be accepted that the models proposed satisfy the restated hypothesis. In concept, the hypothesis has been satisfied since a link between design level information and an environmental impact has been established, but the validity of the link remains to be demonstrated.

### **6.3 Recommendations for Further Work**

In this section, the work required to verify the models and their application to the design of Base Metals Refineries is discussed.

#### ***6.3.1 Environmental Impact of Metals in the Freshwater Ecosystems***

The thesis discussed two environmental impacts of Base Metals Refineries on riverine systems. These are the metals in the environment and water consumption. This thesis has concentrated on the issue of metals in the environment. The environmental impact of water consumption needs to be addressed and incorporated in the models proposed. The environmental impact of stream flow reduction activities is being investigated by limnologists and aquatic scientists. The results of these investigations could be evaluated to determine whether the information can be used to develop a proxy indicator for water consumption.

- With respect to metals in the environment, there is potential to extend the environmental impacts to include toxicity concepts such as those proposed for the Potentially Affected Fraction and the Potentially Disappeared Fraction.
- The assumption of first order kinetics for metals removal from the water column in rivers needs to be verified. This could be done by first repeating the mesocosm testwork using river water in agitated standing tanks and then constructing a river mesocosm to verify the kinetics in a simulated river system. This testwork should be conducted with river water from a series of catchments to evaluate the effect of sediment type on the kinetics of metals removal.

- The effect of water chemistry on the kinetics of metals removal from the water column should also be evaluated in mesocosm testwork.

### **6.3.2 River Compartment Model**

The River Compartment Model is central to satisfying the restated hypothesis. The current status of the River Compartment Model does not satisfy the restated hypothesis because the assumptions made during the development of the model were not verified in this work. The validity of the assumptions needs to be verified.

- As stated above, the assumption of first order kinetics can be verified in mesocosm testwork. River water and associated sediment from a number of catchments should be evaluated to determine the effect of water chemistry and sediment type on the kinetics of metals removal from the water column. Confirming the kinetics of metals removal from the water column is central to establishing the validity of the River Compartment Model.
- The sediment transport should be modelled using flow discharge curves to simulate seasonal variations in instream flows. The relationship between instream velocity/flow and the sediment transport may need to be established from limnological studies of river systems. Modelling of the seasonal variations in sediment transport may be required.
- The environmental metal concentration could be related to toxic effects such as Potentially Affected Fraction or Potentially Disappeared Fraction.
- Groundwater infusion could be incorporated into the model from catchment hydraulic models.
- The interaction of metals with the biotic component of the river system could be incorporated using models developed for fate and transport models such as ChemCan and Simplebox models.
- The mechanism for metals removal from the water column should be established. The effect of water chemistry and speciation could be investigated.
- The sediment metal content could be converted to sediment metal concentration should the transport characteristics of the sediment be established. The speciation of the metal bound to the sediment could then

be determined. From this, the toxicological potential of the sediment could be determined and reported as an environmental impact.

- The results of the River Compartment Model should be compared to those observed in polluted river systems such as the Mwambashi catchment in Zambia.

The usefulness of the River Compartment Model in its current form is limited. It is a vehicle for the calculation of the Affected Stream Length. Should the environmental concentration be linked to a toxicity potential or indicator, the model could be used to determine the length of river which could be affected by the release of metals to the river. This would add additional information to the environmental impact study which could determine whether vulnerable or threatened species are known to exist in the Affected reach of river. Biomonitoring programmes could then be established to monitor the effect of releases to the river system on these threatened species. Should a link to sediment toxic potential be established, the usefulness of the River Compartment Model increases in that it could be used to predict the sediment toxic potential of releases to the river system. The threat to benthic organisms could be determined and a biomonitoring programme established to determine the effect of the effluent release.

### ***6.3.3 Affected Stream Length***

The Affected Stream Length is a good representation of an environmental impact because it produces an impact measure that can be conceptualised. The Affected Stream Length is an output from the River Compartment Model and is thus dependent on the verification of the River Compartment Model for its validity. The only variable not derived from the River Compartment Model is the instream velocity that is used to convert the time required to reach the target concentration to an Affected Stream Length.

- The instream velocity varies seasonally and can be related to the flow discharge curve for the catchment of interest.
- The reach of river in which the release takes place also affects the instream velocity. In the upper reaches, the instream velocity is higher than in the lower reaches due to the higher hydraulic gradients in the upper reaches.

The Affected Stream Length could be associated to specific hydraulic gradients, which characterise the various reaches of the river.

#### **6.3.4 Water Model**

The Water Model is still a conceptual model. This methodology needs to evolve further into defining the rules for each of the streams and nodes. The sub models describing the nodes at which accumulation takes place, e.g. the Tailings Dams and the Evaporation Dam need to be developed to allow the compilation of the complete model.

- A water consumption environmental impact should be developed to complement the Water Model. This could be achieved by using the models developed by river scientists such as the Building Block Methodology or DRIFT and incorporating them in condensed format into the Water Model. The difficulty in engaging with these models is that they are the result of multidisciplinary evaluations of catchments and require field work to verify the parameters of the sub models. This is beyond the scope of the early stages of design and a generic catchment model should be considered as a surrogate for the selected site. Regional variability in catchments would also need to be accounted for.
- Development of sub models to describe the accumulation terms for the Tailings Dam and the Evaporation Dam.
- Definition of the rules governing streams and nodes.
- Development of a software version for the model.

The Water Model can be integrated into the design process by summarising the mass balance for the site in terms of the Water Model. This is equivalent to the water balance which usually accompanies the mass balance during the design stages. The Water Model could be used to:

- Evaluate process alternatives to the base case process
- Evaluate the effect of equipment selection on the water consumption and effluent production from the process selected.
- Evaluate process operation strategies for the proposed process plant.
- Set up a Water Management Strategy for the site during the design process.

## 6.4 Closure

This work has provided a conceptual methodology by which environmental impacts of metal containing effluents to river systems can be evaluated during the design process. The models proposed provide this link for all levels of design. The shortfall in the thesis is that the proposed models have not been validated and that the River Compartment Model is based on results of testwork conducted in lakes. The significance of these shortfalls can only be determined by verification of the assumptions stated for the River Compartment Model.

The significance of the work lies in that the models proposed have demonstrated a methodology that can link design level information to an environmental impact of an effluent release on a river system. Using the Water Model and the River Compartment Model in conjunction allows design engineers to evaluate the performance of process and equipment selection alternatives during the design process, predicting the environmental impact of the proposed alternatives. This allows environmental impacts to be used as additional information during design decision-making. The models have been developed specifically for metals and thus provide the minerals design community an indication of the environmental impact early in the design process, before an EIA has been compiled.

The majority of the work conducted on freshwater systems has concentrated on the behaviour of pollutants in lake systems. This work examines the behaviour of pollutants in river systems. The River Compartment Model has been specifically developed for river system, adding to the suite of environmental management tools available to design engineers and plant operators to monitor and manage the environmental performance of their respective operations.

The Affected Stream Length provides an environmental impact indicator that could be used to differentiate between the environmental impacts of releasing a suite of effluents to a river system. Alternatives regarding process or equipment selection could be compared based on the Affected Stream Length for their respective effluents.

There is still a fair amount of work which needs to be completed before the proposed models can be used in design applications. The verification of the River Compartment Model is essential for the future application of the proposed models in the design of Base Metals Refineries.

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## **APPENDICIES**

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## **APPENDIX A – SUPPLEMENTARY LITERATURE**

### **A.1 Water Quality Variables**

#### **Aquatic Ecosystems**

The South African Water Quality Guidelines (SAWQG) (DWAF 1996) define aquatic ecosystems as:

*The abiotic (physical and chemical) and biotic components, habitats and ecological processes contained within rivers and their riparian zones, reservoirs lakes and wetlands and their fringing vegetation.*

SAWQG notes that terrestrial biota, other than humans, dependent on aquatic ecosystems for survival are included in this definition. This definition of aquatic ecosystems includes three primary abiotic and biotic components, namely, sediments (bottom and suspended), water and the riparian zone. The current SAWQG only consider the water component, excluding the ground water, subsurface water and water in bank storage components (DWAF, 1996).

#### **Water Quality Criteria**

Water Quality Criteria are scientific and technical information provided for a particular water quality constituent, in the form of a numerical and qualitative that describe its potential effects on the health of aquatic ecosystems and the fitness of water for other users (DWAF, 1996). The derivation of criteria was based on the best available information, using the species representative of the major trophic groups occurring in aquatic ecosystems. The criteria used in the SAWQG were derived by assuming continuous long term exposure to water quality given.

Three broad classes of criteria can be identified for aquatic ecosystems (DWAF 1996):

- Constituent-specific criteria – level of ecological risk associated with the presence of that constituent in water
- Criteria for complex mixtures – the toxicity of complex mixtures containing several constituents
- Biological criteria – describe the biological status of the aquatic ecosystem

### **Constituent Specific Criteria**

The constituent specific criteria have been divided into four categories based on the effects that the constituents may have aquatic biota, and on the methodologies of derivation used in the criteria (DWAf 1996):

- Toxic constituents – which seldom occur in high concentrations in un-impacted systems. Criteria are given as single numerical values associated with a specific level of risk, or a value below which no adverse effect is expected. Examples are :
  - Inorganic constituents, e.g. Al, As, Cd, Cu, F<sup>-</sup>, Hg, Mn, NH<sub>4</sub><sup>+</sup>
  - Organic constituents, e.g. phenol, atrazine
- System variables – which regulate essential ecosystem processes such as spawning and migration such as temperature, pH and dissolved oxygen. The biotas of aquatic ecosystems are usually adapted to the natural seasonal cycles of changing water quality which characterise these systems. Changes in the amplitude, frequency and duration of the cycles may cause severe disruptions to the ecological and physiological functions of aquatic organisms and hence the ecology of the system.
- Non-toxic inorganic constituents – which may cause toxic effects at extreme concentrations, generally “system characteristics”, in that their natural concentrations depend on localised geochemical, physical and hydrological processes such as total dissolved solids (TDS) and total suspended solids (TSS).
- Nutrients – which are generally not toxic, but which stimulate eutrophication if present in excess - such as inorganic nitrogen (nitrite, nitrate, ammonium) and inorganic phosphorous (ortho-phosphate)

The WQG criteria approach assumes (Burton 1999):

1. single critical acute and chronic average exposure period which does not account for pulse or repeated exposure for shorter time periods
2. single bioavailability normalisation factor (such as hardness, total organic carbon, acid volatile sulphides)
3. laboratory derived toxicity values (used to develop these criteria) on surrogate test species are protective and predictive of indigenous species effects
4. effects based on single chemical exposures and do not account for interactive effects with multiple chemicals
5. chemical values derived from single to a few grab samples are representative of actual organism exposure in situ.

Chemical analysis can provide very accurate measures of the amounts of individual substances in the water, but a monitoring system of this kind suffers from the following drawbacks (Day 2000):

- The results reflect the conditions in the river only at the instant of sampling and short lived, catastrophic pollution is easily missed
- There are thousands of chemical substances which might be present in the water and it is impossible to measure all of them
- Some of the most toxic substances occur in minute quantities, often below the detection limits of even the most sophisticated analytical techniques
- Chemical analysis is expensive
- Some very toxic substances break down easily when removed from the aquatic environment.

### Classification of Substances

The Harmonised system of classification of chemicals harmful to aquatic ecosystems proposed by OECD (OECD 2001a) defines the acute and chronic toxicity levels for substances. The classification system for Acute Toxicity is presented in Table A1.1 while that for Chronic Toxicity is presented in Table A1.2.

Table A1.1: Classification System for Acute Toxicity (OECD 2001a)

Classification	Acute I *	Acute II	Acute III **
Acute Toxicity			
96 hr LC <sub>50</sub> (for fish)	≤ 1 mg/l and/or	>1 - ≤ 10 mg/l and/or	>10 - ≤ 100 mg/l and/or
48 hr EC <sub>50</sub> (for crustaceans)	≤ 1 mg/l and/or	>1 - ≤ 10 mg/l and/or	>10 - ≤ 100 mg/l
72 hr ErC <sub>50</sub> (for algae or other aquatic plants)	≤ 1 mg/l	>1 - ≤ 10 mg/l	and/or >10 - ≤ 100 mg/l

Note \* Category Acute I may be subdivided for some regulatory systems to include a lower band at L(E)C<sub>50</sub> ≤ 0.1 mg/l

Note \*\* Category Acute III Some regulatory systems may extend this range beyond an L(E)C<sub>50</sub> of 100 mg/l through the introduction of another category

Table A1.2: Classification System for Chronic Toxicity (OECD 2001a)

Classification	Chronic I	Chronic II	Chronic III
Acute Toxicity			
96 hr LC <sub>50</sub> (for fish)	≤ 1 mg/l and/or	>1 - ≤ 10 mg/l and/or	>10 - ≤ 100 mg/l and/or
48 hr LC <sub>50</sub> (for crustaceans)	≤ 1 mg/l and/or	>1 - ≤ 10 mg/l and/or	>10 - ≤ 100 mg/l
72 hr LC <sub>50</sub> (for algae or other aquatic plants)	≤ 1 mg/l and the substance is not rapidly degradable and/or the log Kow ≥ 4 (unless experimentally determined BCF < 500)	>1 - ≤ 10 mg/l and the substance is not rapidly degradable and/or the log Kow ≥ 4 (unless experimentally determined BCF < 500), unless the chronic toxicity NOECs are > 1mg/l	and/or >10 - ≤ 100 mg/l and the substance is not rapidly degradable and/or the log Kow ≥ 4 (unless experimentally determined BCF < 500) , unless the chronic toxicity NOECs are > 1mg/l

A **Chronic IV** classification is applied for poorly soluble substances for which no acute toxicity is recorded at levels up to the water solubility, and which are not rapidly degradable and have log Kow ≥ 4, indicating a potential to bio accumulate, unless other scientific evidence showing classification to be unnecessary. Such evidence would include an experimentally determined BCF < 500, or a chronic toxicity NOECs > 1 mg/l, or evidence of rapid degradation in the environment (OECD 2001a).

### Classification of Metals

Metals and their compounds have a number of specific criteria such as biodegradability and octanol/water partitioning coefficient cannot be applied although the principle of lack of destruction via degradation, and bioaccumulation remain important concepts. Thus it is necessary to adopt a different approach. Metals and metal compounds can undergo interactions with the media which affect the solubility of the metal ion, partitioning from the water column, and the species of metal ion that exists in the water column. In the water column, it is generally the dissolved metal ion which are of concern for toxicity. The interaction of the substance with the media may either increase or decrease the level of ions and hence toxicity. It is thus necessary to consider whether metal ions are likely to be formed from the substance and dissolve in the water, and if so, whether they are formed rapidly enough to cause concern (OECD 2001a).

### Classification of Metal Compounds

Where the L(E)C<sub>50</sub> for the metal ions of concern is greater than 100 mg/l, the metal need not be considered further in the classification scheme. (OECD 2001a)

- If solubility  $\geq L(E)C_{50}$ , classify on the basis of the soluble ion
- If solubility  $< L(E)C_{50}$ , classify default Chronic IV

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## A.2 Modelling Metals in Aquatic Systems

### Metal Transformation and Dissolution Kinetics Models

The dissolution and transformation of metals in the environment can be described by a number of kinetic models. The most common of these are the linear, first order, second order and reaction kinetic equation models. These parameters for these models can be derived experimentally by plotting the results of short term dissolution/transformation tests against time and determining the transformation/dissolution kinetics (OECD 2001b).

#### Linear Model

The linear model is described by the equation:

$$C_t = C_0 + kt \quad \text{A2-1}$$

where :

$C_0$  is the initial dissolved metal concentration at time zero (mg/L)

$C_t$  is the initial dissolved metal concentration at time t (mg/L)

k is the linear rate constant (mg/L-days)

#### First Order Model

The first order model is described by the equation:

$$C_t = A(1 - e^{-kt}) \quad \text{A2-2}$$

where :

A is the limiting dissolved metal concentration at apparent equilibrium (mg/L)

$C_t$  is the initial dissolved metal concentration at time t (mg/L)

k is the first order rate constant (1/days)

#### Second Order Model

The second order model is described by the equation:

$$C_t = A(1 - e^{-at}) + B(1 - e^{-bt}) \quad \text{A2-3}$$

where :

$A + B = C$ , the limiting dissolved metal concentration (mg/L)

$C_t$  is the initial dissolved metal concentration at time  $t$  (mg/L)

$a$  is the first order rate constant (1/days)

$b$  is the second order rate constant (1/days)

### Reaction Kinetic Equilibrium Model

The reaction kinetic equilibrium model is described by the equation:

$$C_t = a \left[ 1 - e^{-bt} - \left( \frac{c}{n} \right) \left\{ 1 + \frac{(be^{-nt})}{(n-b)} \right\} \right] \quad \text{A3-4}$$

where :

$C_t$  is the initial dissolved metal concentration at time  $t$  (mg/L)

$a$  is regression coefficient (mg/L)

$b, c, d$  are regression coefficients (1/days)

$n = c + d$

### **Modelling Metal Persistence in Aquatic Environments**

From the mesocosm experiments described by di Toro *et al* (2001a) and Adams *et al* (2000), the results indicate that the half life for metals in the water column is directly related to the fraction of the metal that is sorbed to particles. The particulate fraction defined as :

$$f_p = \frac{C_p}{C_p + C_d} \quad \text{A2-5}$$

where  $f_p$  is the particulate fraction,  $C_d$  is the concentration of dissolved metal (g/L) and  $C_p$  is the concentration of particulate metal (g/L).

The particulate fraction is a function of the partition coefficient  $K_d$  defined as

$$K_d = \frac{C_p}{C_d m} \quad \text{A2-6}$$

where  $K_d$  is the partition coefficient (L/kg) and  $m$  is the suspended solids fraction (kg/L).

The expression for the particulate fraction then becomes

$$f_p = \frac{K_d m}{1 + K_d m} \quad \text{A2-7}$$

The first order removal rate coefficient is defined as follows :

$$K_s = \frac{w_s}{H} \quad \text{A2-8}$$

where  $K_s$  is the first order removal rate coefficient ( $\text{day}^{-1}$ ),  $w_s$  is the settling rate of the particles (m/day) and  $H$  is the depth of the water column (m)

The half life (days) for the metal is then defined as follows

$$t_{1/2} = \frac{0.693}{-K_s f_p} \quad \text{A2-9}$$

and the initial concentration of the metal is defined by the following:

$$C_o = \frac{M}{V} \quad \text{A2-10}$$

where  $C_o$  is the initial concentration of the metal in the water column (g/L),  $M$  is the mass of metal released into the water column (kg) and  $V$  is the volume of the water column ( $\text{m}^3$ )

The hydraulic residence time of the system is given by

$$t_o = \frac{V}{Q} \quad \text{A2-11}$$

where  $t_o$  is the hydraulic residence time (days),  $V$  is the volume of the water in the water column ( $\text{m}^3$ ) and  $Q$  is the inflow rate equal to the outflow rate ( $\text{m}^3/\text{day}$ )

The steady state concentration for a constant input is defined by:

$$C_{ss} = \frac{W_T / Q}{(1 + K_s f_p t_0)} \quad \text{A2-12}$$

where  $C_{ss}$  is the steady state concentration (g/L),  $W_T$  is the metal loading (kg/day) and  $Q$  is the inflow rate equal to the outflow rate ( $\text{m}^3/\text{day}$ )

The total metal concentration  $C_T$  over time ( $t$ ) in a completely mixed volume can be described by the following equation proposed by di Toro *et al* (2001a)

$$C_T = C_{ss} \left( 1 - e^{-\left(K_s f_p + \frac{1}{t_0}\right)t} \right) + C_0 e^{-\left(K_s f_p + \frac{1}{t_0}\right)t} \quad \text{A2-13}$$

For the case where there is an instantaneous release of metal with no inflow or outflow, the solution becomes:

$$C_T = C_0 e^{-K_s f_p t} \quad \text{A2-14}$$

These equations are developed further in Section 4 which describes the development of a model for the removal of metal from the water column in an stream.

### **A.3 Physical and Biological Factors Affecting Metal Bioavailability**

#### Water Hardness and Alkalinity

Hardness, contributed in most natural waters by calcium and magnesium, but also by other similar cations, effects ecotoxicity and bioavailability by competing with metal cations for binding sites on the gills and anions in the water. The metals most affected by hardness include cadmium, chromium, copper, silver and zinc (Parametrix 1995).

Alkalinity affects bioavailability in a manner analogous to hardness but it involves the carbonate anions instead of the calcium and magnesium cations. Alkalinity is also know to have a greater influence than hardness on the bioavailability of copper and lead (Parametrix 1995).

#### Ionic Strength

The high ionic content of saline water may compete for uptake with the ionic metal species or may influence the thermodynamic equilibria altering the ratios of metal species in solution (Parametrix, 1995, Dallas and Day, 1993).

#### REDOX Potential and pH

The pH and Eh of water controls the solubility and concentrations of the major metal species in aquatic environments (Parametrix 1995, Janssen *et al* 2000). Acidification can influence metal toxicity by either metal speciation or the biological sensitivity of the cell surface. The relative and absolute concentrations of the various cations and anions determine which metal species will occur in waters. Eh/pH diagrams, along with computer based models can be used to make predictions regarding the physical state and chemical form of the metal or metal compound under consideration for a given set of environmental parameters (e.g. pH, Eh, carbonate concentration) (Parametrix 1995, Dallas and Day 1993).

#### Ligands

Ligands are anions or molecules that form co-ordinating compounds or complexes with metals. Ligand influence may be direct, e.g. sequestering the metal by complexation, or indirect, e.g. influence gill function (Parametrix 1995, Dallas and Day, 1993).

#### Suspended Particulate Matter and Organic Carbon

The concentration, size class, and organic carbon content of particulates play a major role in how much of a dissolved metal will complex to solid material and determine availability to aquatic organisms (Parametrix 1995, Janssen *et al* 2000). The influence of organic compounds on metal toxicity is important for highly eutrophic and anthropogenically polluted waters, as they may reduce both acute and chronic toxicity of metals by complexing the free metal ions. Naturally large polyphenolic organic acids are even more efficient at complexing metals and hence reducing the toxicity of metals such as Al and Cu (Dallas and Day 1993).

#### Interactions at the Sediment/Water Interface

The interface between the sediment and water column represents an important environment governing the fate of metals in an aquatic environment. As particulate matter falls from the water column, metals are scavenged and subsequently incorporated into the bottom sediment. With time, such surface sediments, and their associated metals can become buried. At depth, sediments often become anaerobic as a result of microbial decomposition of organic matter. Under anaerobic conditions, iron and manganese are reduced to more soluble forms. Once mobilised, they migrate upwards as reduced ions through the interstitial porewater to be reoxidised and fixed in the aerobic surface layer of the sediments. If other metals or metalloids were co-precipitated with iron and manganese in the sediments and are similarly solubilised under reducing conditions, they too will be subjected to the same mobilisation/re-precipitation mechanism. If anaerobic conditions extend above the sediment/water interface, then the potential exists for metals and metalloids to be released into the overlying water column and be available for uptake by aquatic life (Parametrix 1995).

Bioturbation of sediments by benthic organisms may also influence the bioavailability of metals. Bioturbation can significantly disrupt the sediment water interface and may act to increase availability to benthic organisms (Parametrix 1995).

#### Biological Factors

Factors responsible for determining the response of an organism to a toxic trace metal include its life history stage, age and sex, levels of starvation and activity, the degree of physical protection, tolerance levels and acclimation, all of which may also affect susceptibility of organisms to pollutants other than trace metals (Dallas and Day 1993). Recent research efforts have led to an enhanced understanding of the physiological basis of metal toxicity effects on aquatic organisms. These studies have, in combination with metal

speciation work, led to an improved understanding of how water chemistry affects bioavailability, how metals interact with aquatic organisms to exert toxic effects at the organism site of action, and how toxic effect levels can be predicted (Janssen *et al* 2000).

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## A.4 Freshwater Indicators in LCA

### Life Cycle Assessment Overview

Life Cycle Assessment (LCA) is similar to the common chemical engineering practice of conducting a mass and energy balance for a process flow diagram (PFD), only broader in scope. An LCA practitioner tabulates the emissions and the consumption of resources at every stage in a product's life cycle, from its cradle to its grave (raw material extractions, energy acquisition, manufacturing, use and waste disposal). It is desirable that practitioners can then calculate indicators of the likelihood (risks) and the potential consequences of associated impacts in the context of climate change, stratospheric ozone depletion, tropospheric ozone (smog) creation, eutrophication, nutrification, acidification, toxicological impacts on human health and ecosystems, fossil fuel depletion, water consumption, land use (Pennington and Jolliet 2001).

LCA is well documented and standards are available from the International Standards Organisation for the execution of an LCA. LCA is a decision support tool and as such lends itself to providing information upon which informed decisions can be made – including those pertinent to process design (Hertwich and Hammitt, 2001).

A LCA consists of four phases (Guinee *et al.*, 2001):

- **The goal and scope** definition of an LCA provides a description of the product system in terms of the system boundaries and a functional unit. The functional unit is the important basis on which alternative goods, or processes or services, are comparable.
- **Life Cycle Inventory** (LCI) is a methodology for identifying and evaluating resource consumption and emissions at all the stages in a product's life cycle.
- **Impact Assessment** - evaluates the potential impact of the life cycle of the operation; some consideration of valuation is often attempted here.
- **Interpretation/Improvement** - evaluation of the results, choices and assumptions of the LCA in terms of soundness and robustness and the overall conclusion drawn

In many LCAs a few emissions will dominate the category of human health impacts in the life cycle and the results will be readily interpretable. In others, normalisation (such as

weighting indicators for different impact categories relative to the totals for a given geographical region) and multi-criteria decision making (panel-based weighting methods, economic valuation, etc.) provide useful aids to interpret results.

A large number of indicator methodologies are proposed in the literature for characterising impacts in different impact categories in LCA. Not all these methodologies are suitable, or scientifically defensible, in the context of risks and potential consequences. Methods in LCA software are often outdated, providing conflicting and sometimes misleading results (Pennington and Yue, 2000, Boustead *et al.*, 2000). Guinee *et al.* (2001) provide a summary of the practices used in evaluating the various impact categories currently used in LCA.

LCA is an indicator system which provides a simplified way to condense and to examine an inventory as emissions, wastes, and resources and to use inventory data in an environmental context. The inventory results are generated, classified, and modelled into an indicator. LCA is fundamentally an analysis of systems inputs and outputs leaving and entering the environment and not an analysis of the environmental consequences or effects from the system. The usefulness of the information from the indicator results depends on the accuracy, validity and characteristics of the models and characterisation factors. The usefulness of the information from indicator results also depends on the number and kind of simplifying assumptions and value choices used in the model for the indicator. The quantity of the indicator information among different impact categories varies for a number of reasons such as the complexity of environmental mechanisms between the system boundary and the category endpoint, the spatial and temporal characteristics of the category, and the dose response characteristics. This has important implications for the users of LCA in making decisions (Owens 1999):

- The information provided by LCA for their decisions is not about environmental effects; it is a relative view about the emissions and resource use for a system
- The information may not always be technical. Instead, subjective classification and characterisation may result in scores
- The technical quality and usefulness of the information from different indicators varies considerably.

### **Acidification Potential**

Acidification is caused by releases of protons in the terrestrial or aquatic ecosystems. In the terrestrial ecosystem the effects are seen in softwood forests (e.g. spruce) as inefficient

growth and as a final consequence dieback of the forest. These effects are mainly seen in Scandinavia and in the middle/eastern part of Europe. In the aquatic ecosystem the effects are seen as (clear), acid lakes without any wildlife. These effects are mainly seen in Scandinavia.

The potential effects are strongly dependent on the nature of the receiving ecosystem e.g. nitrogen oxides ( $\text{NO}_x$ ) can be fixed in the ecosystem due to uptake in plants. Boustead *et al.* (2000) point out that it is unclear whether acidification potentials are applied to emissions to water or whether they are applied to emissions to air only.

### **Eutrophication Potential**

Eutrophication (or nutrient enrichment) of aquatic and terrestrial ecosystems can be caused by surplus nitrogen, phosphorus and degradable organic substances. Eutrophication can be defined as: "enrichment of the aquatic ecosystems with nutrients leading to increased production of plankton algae and higher aquatic plants leading to a deterioration of the water quality and a reduction in the value of the utilisation of the aquatic ecosystem" (Guinee *et al.*, 2001).

The primary effect of surplus nitrogen and phosphorus in aquatic ecosystems is growth of algae. The secondary effect is decomposition of dead organic material (e.g. algae) and anthropogenic organic substances. The decomposition of organic material is an oxygen consuming process leading to decreasing oxygen saturation and sometimes anaerobic conditions. The anaerobic conditions in the sediment at the bottom of lakes or other inland waters may furthermore result in production of hydrogen sulphide ( $\text{H}_2\text{S}$ ) which may lead to "bottom up" incidents and liberation of toxic hydrogen sulphide to the surrounding water. The possible effects of the emissions leading to eutrophication depend on the receiving waters i.e. some recipients are sensitive to nutrient supply while others are not.

The effects of eutrophication of terrestrial ecosystem are seen on changes in function and diversity of species in nutrient poor ecosystems as heaths, dune heaths, raised bogs etc. and they are caused by atmospheric deposition and aquatic transport of nitrogen compounds.

### **Ecotoxicity**

Ecotoxicological impacts depend on exposures to and effects of chemical and biological substances. The potential effects on ecosystems depend on the actual emission and fate of

the specific substances emitted to the environment. According to the SETAC Europe working group on Life Cycle impact Assessment, LCIA should include the fate of substances by the following equation (Schultze *et al.*, 2000)

$$S^m = \sum_i F_i^m E_i^m M_i^m \quad \text{A4-1}$$

where  $m$  is the medium in which an effect occurs,  $i$  is the substance,  $S$  is the category indicator (effect score),  $F$  is the Fate and exposure factor,  $E$  is the effect factor, and  $M$  is the mass emitted. The term  $FE$  is referred to as the characterisation factor in the ISO nomenclature. The fate of chemical substances depends on:

- degradation rate (aerobic/anaerobic, hydrolytic/photolytic)
- bioaccumulation
- evaporation
- deposition

The degradation rate will affect both the possibility of the substance to reacting the target organism and the kind of toxic effect. Readily degradable substances can show acute toxic effects depending on the degradation type and rate in the actual medium, whereas substances which are not readily degradable can bioaccumulate in the environment and/or show chronic toxic effects. The rates of evaporation/deposition will affect the transfer of substances between the different mediums e.g. air, water, soil or food chains), e.g. in aeration of leads to evaporation of volatile substances from the water, and thereby protecting the biological processes in the wastewater treatment plant against potential toxic or inhibitory effects but also burdening the surroundings (Schultze *et al.*, 2000).

One way of assessing the potential ecotoxicological effects of chemical substances is to use the criteria for classification of substances as "Dangerous for the Environment" (indicated by the symbol  $N$ ) (Schultze *et al.*, 2000):

- biodegradation
- bioaccumulation
- aquatic toxicity (acute/chronic)
- terrestrial toxicity

A number of methods have been proposed for the evaluation of the eco toxicological impacts of emissions to the environment. There is currently no internationally accepted method. Boustead *et al.*(2000), Schultze *et al.* (2000) and Guinee *et al.* (2001) provide discussion on

a selection of current methods. Schultze *et al.* (2000) compare four methods and their comparison is presented in Tablea A4-2 and A4-3

### **Potentially Affected Fraction**

The methods discussed by Schultze *et al.* (2000) concentrated on assessing ecotoxicological effects based on a threshold value, expressed in the effect factor as the reciprocal of a PNEC or something similar. For such methods, the prevailing background concentration is unimportant. There is, however, a trend towards incorporating concentration effect curves, or the slopes of such curves, in which the effect factor is dependent upon the background concentration. This is the approach used in the Eco-Indicator 99 proposed by Goedkoop and Spriensma (1999). The approach is based on the notion of PAFs (Potentially Affected Fraction), the fraction of species that, given an environmental concentration, is exposed above the No Observed Effect Concentration (NOEC). The higher the concentration, the greater the percentage of species considered to be affected. PAFs are based on substance specific species sensitivity, which, in turn based on the NOECs for these substances for different species (Huijbregts *et al.*, 2001).

The PAF and the PNEC are both based on the same curve. To apply the PAF concept requires additional data, however, for example on current environmental concentrations. As these data are still lacking for most substances, the concept still has little practical use. The fact that the PAF provides a measure of toxicity that is comparable between substances is considered to be its major advantage. However, specific rules of addition hold for combining PAFs, which are difficult to transpose to LCA, because as a baseline LCA integrates over space and time and these addition rules for combined toxicity are of course only valid when the substances are present at the same place at the same time.

While ecotoxicological impact assessment is based on PAFs in the Eco-Indicator 99 method, fate and exposure modelling is based on EUSES. Guinee *et al.* (2001) propose that further research should be directed towards integrating the USES-LCA methodology with the PAF approach, and that the potential for using the PAF approach to aggregate ecotoxicological effects with other effects such as eutrophication and acidification be investigated (Huijbregts *et al.*, 2001).

Huijbregts *et al.* (2001) discuss the PAF concept further. They define the Potentially Affected Fraction which is calculated from the cumulative logistic distribution function at a measured or calculated field concentration  $C_{x,e}$  as follows:

$$PAF_{x,e} = \frac{1}{1 + e^{-\left(\frac{\log_{10} C_{x,e} - \alpha_{x,e}}{\beta_{x,e}}\right)}} \quad A4-2$$

where  $\alpha_{x,e}$  is the location parameter, estimated by the sample mean of the log<sub>10</sub> transformed species toxicity values, and  $\beta_{x,e}$  is the scale parameter, estimated from the standard deviation of the log-transformed species toxicity values, of substance x for ecosystem e.

#### Combined Concentration and Response Addition

The concept of multi-substance Potentially Affected Fraction (msPAF) was introduced by Hamers *et al.* (1996) (cited in Huijbregts *et al.*, 2001). Hamers *et al.* (1996) made the following assumptions:

1. concentration addition is applicable to hydrophobic, chemically inert organic substances (i.e. narcotics)
2. response addition is applicable for all other compounds
3. no correlation in sensitivities or interaction of effects between substances exist.

They calculated the combined PAF of all toxic substances (msPAF) from the combined fraction affected of narcotic chemicals,  $PAF_{\Sigma \text{narcotics},e}$ , and the fractions affected of individual chemicals,  $PAF_x$ , by the following equation:

$$msPAF_e = 1 - \left(1 - PAF_{\Sigma \text{narcotics},e}\right) \times \prod_x \left(1 - PAF_{x,e}\right) \quad A4-3$$

where msPAF<sub>e</sub> is the multi-substance PAF in ecosystem e (e.g. soil, water, sediment);  $PAF_{\Sigma \text{narcotics}}$  is the PAF in ecosystem e for all narcotics after concentration addition; and  $PAF_{x,e}$  is the PAF in ecosystem e of substances with a specific node of action. This model relates to the assignment of compounds with similar and dissimilar toxic modes of action and the prediction of ecotoxicological impacts on the basis of calculation rules as derived from basic toxicology and pharmacology (Huijbregts *et al.*, 2001).

Applying Hamers' rules for calculating marginal PAF-increase requires knowledge of:

1. the chemicals'  $\alpha_x$  values
2. the ambient multi-substance PAF

3. the  $\beta_x$  values and ambient concentrations of substances with a specific mode of action; and
4. the  $\beta_x$  and ambient PAF for narcotics.

#### Concentration Addition Only

An alternative approach for calculating the marginal PAF increase is described by van de Meent *et al.* (2000) (cited in Huijbregts *et al.*, 2001) and applied by Goedkoop and Spriensma (1999). These authors started from a slight modification of Hamers' approach. They applied the rules of concentration addition not only to the narcotics, but they generalised it to all chemicals in general with similar toxic modes of action. Taking this approach, Goedkoop and Spriensma (1999) reasoned that, as a general case, all possible modes of action are represented in the environment already, so that addition of any chemical would imply concentration addition to a mechanism present already. The difficulty remains that one needs to decide which  $\alpha$  values to apply in calculating the concentration-additive PAF increase, and how much of this toxic activity (in terms of toxic units) is present already. This information about the ambient toxic activity is usually not available. Goedkoop and Spriensma's (1999) way around this is to use one (weighted average)  $\beta$  value to concentration additively calculate the marginal PAF increase resulting from addition of chemicals to the environment. This approach effectively uses one general PAF curve, expressed in toxic units, with one average scale factor  $\beta$ . Adopting this concentration additive calculation procedure implicitly assumes that all chemicals considered, ambient as well as added chemicals, toxicologically act similarly. Consequently, the characterisation factor  $QET_{e,x,i}$  is a function of the chemicals'  $\alpha_x$  values, chosen standard  $\beta$  value, and the chosen working point on the generalised PAF curve. This simplifies the previous equation to

$$Q_{ETe,x,i} = \frac{dmsPAF_e}{dM_{x,i}} = \frac{\gamma_e}{10^{\alpha_{x,e}}} \times \frac{dC_{x,e}}{dM_{x,i}} \quad A4-4$$

in which  $\gamma_e$  is the slope factor at the working point of the overall PAF curve for ecosystem *e* (Huijbregts *et al.*, 2001).

Huijbregts *et al.* (2001) compared the two methods for 33 substances in the freshwater ecosystem using background concentrations obtained from the Netherlands for a Western European scale using a modified version of the USES-LCA programme. They found that the concentration addition only approach of Goedkoop and Spriensma (1999) generally produced lower multi-substance PAF values than the Hamers method, up to 2.2 order of magnitude, which could influence the outcome of LCA. They concluded that the selection of a  $\beta$  value

for the 33 substances evaluated was substantially higher than the value of 0.4 chosen as a standard.

Huijbregts *et al.* (2001) propose an alternative approach of a damage function where the results of the analysis are presented in terms of the Potentially Disappeared Fraction of species (PDF) as a preferred indicator in LCA. The PDF can be interpreted as the fraction of species that has a high probability of no occurrence in a region due to unfavourable conditions. PDF like damage indicators for different stressors could then be considered as independent effects, and aggregated according to the rules for response addition, such that

$$msPDF_e = 1 - \prod_x (1 - PDF_{x,e}) \quad A4-5$$

$$Q_{eco,x,i} = \frac{dmsPDF_e}{dS_{x,i}} = \frac{(1 - msPDF_e)}{(1 - PDF_{x,e})} \times \frac{dPDF_{x,e}}{dS_{x,i}} \quad A4-6$$

where  $msPDF_e$  is the multi-stress PDF in ecosystem  $e$  (e.g. soil, water, sediment);  $S_{x,i}$  is the introduction of stressor  $x$  to compartment  $i$  (e.g. air, freshwater, agricultural soil) in kg/year (e.g. use of ground water) or m<sup>3</sup>/year (e.g. land use); and  $PDF_{x,e}$  is the PDF in ecosystem  $e$  of stressor  $x$  (Huijbregts *et al.*, 2001).

Empirical information on the probability of species occurrence, as used in the assessment of ecosystems effects due to acidification, eutrophication and desiccation, could directly be used in the calculation of characterisation factors for ecosystem damage. As an alternative, the  $msPDF$  for ecotoxicity could be derived from  $msPAF$ , using simple linear relationships like

$$msPDF_e = K_{PAF \rightarrow PDF} \bullet msPAF_e \quad A4-7$$

where  $K_{PAF \rightarrow PDF}$  is a proportionality constant for converting PAF into PDF (Huijbregts *et al.*, 2001).

### Model Based Ecological Performance Indicators

A number of methodologies and models exist for the calculation of an Environmental Indicator, which is usually expressed as a single numeric. These include the Eco-Indicator 99 model by Pre Engineering (Goedekoop and Spriesma 1999) and methodologies proposed by the WBCSD, NRTEE, CML and Swedish EPS Method (Steen 1999) representing a wide variety of approaches to the calculation of the indicator. The usefulness of a single figure to represent the environmental performance of an operation has been debated as it could mask potentially disastrous consequences should the performance in certain areas lower the

overall figure. The major concern being that uninformed managers will use the indicators out of context (Boustead *et al.*, 2000).

Arrival at an Eco-indicator methodology requires three steps (Boustead *et al.*, 2000, Goedkoop and Spriensma 1999):

- Inventory – compiling a list of the relevant inputs and outputs of a system
- Classification and Characterisation – evaluating the potential environmental impacts associated with the identified inputs and outputs
- Weighting – weighting the results of the characterised impacts relative to one another

Boustead *et al.* (2000) points out that although errors may arise in each step of the process, Classification and Characterisation and Weighting contain multipliers which normalise the data, thus magnifying the errors in previous steps. These basic flaws in the use of such eco-indicators are the improper use of system analysis and incomplete analysis.

Boustead *et al.* (2000) produced a comparison between various eco-indicator methods. The methods considered were Eco-Indicator 95, MET and EPS by Ford Motor company on six options of vehicles. The various methods produced inconsistent results. In this particular evaluation. The various methods also showed great variation in the normalising ratios used for the various impact categories. Boustead *et al.* (2000) conclude that any model which strives to represent the ecological performance as a single index will contain inconsistencies regardless of whether the issues regarding metals are solved.

The Eco-Indicator 95 programme has been updated to Eco-Indicator 99 and a number of the shortcomings have been addressed. The weighting system has been revised and the so-called "Distance to Target" methodology was replaced with a damage function approach (Goedkoop and Spriensma, 1999).

Table A4.1: Review of weighting systems (Steen, 1999)

Method Name	Environmental Goal or Reference	Weighting Principle	Spatial Extension	Type of Impact Category
Eco-scarcity	National emissions	Relative reduction of distance to target	Switzerland, Netherlands, Sweden or Norway	Emissions
Eco-Indicator 99	Present state	Two step weighting, second step of panel type	Europe	Damage
EDIP	Present state	Separate weighting of	Global and national	Normalised impact potentials

		emissions (political goals), resources (supply horizon) and work environment		(person equivalents)
Environmental themes	National critical loads	Relative reduction of distance to target	Switzerland, Netherlands, Sweden or Norway	Impact potentials based on chemical, physical or biological properties of emitted substances or resources
EPS default	Present state of environment	WTP to avoid changes	Global	End point effects
Tellus	Zero emission (not explicitly expressed)	WTP for flue gas cleaning	USA	Emissions

Note : WTP refers to Willingness to Pay

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Table A4.2: Different methods for the assessment of ecotoxicological impacts. (Boustead *et al.* 1999, Schultze *et al.*, 2000, Guinee *et al.*, 2000)

Method	Effects concerned	Criteria/comments	Reference
The CML Method	1) Terrestrial ecotoxicity 2) Aquatic ecotoxicity	The provisional classification factors for ecotoxicity are derived from NOEC or LC <sub>50</sub> multiplied by a safety factor. The classification factors are expressed by m <sup>3</sup> water/mg substance and kg soil/mg substance leading to results as m <sup>3</sup> polluted water and kg polluted soil Fate, persistence, or mixture toxicity is not addressed. No distinction is made between freshwater, seawater and groundwater.	Heijungs <i>et al.</i> , (1992)
The USES Model	1) Terrestrial ecotoxicity (Agricultural and Industrial soil) 2) Aquatic ecotoxicity	The USES-LCA method uses a nested level III multimedia model and calculates the fate of chemicals by considering inter-media transfer, intra-media transfer, and degradation. The global environment is represented by the arctic, moderate and northern tropic zones Emissions only take place on the continental scale and the chemicals are distributed instantaneously and uniformly in the release compartment. Emissions to each of the five compartments can, via transport processes, cause impacts in all compartments of the model	Guinee and Heijungs, (1993), Guinee <i>et al.</i> , (1996)
EDIP Method	1) Acute, aquatic toxicity 2) Chronic, aquatic toxicity 3) Chronic, terrestrial toxicity 4) Acute toxicity to wastewater treatment plants	The EDIP method is divided into two steps. The first is a screening step which considers exposure and ecotoxicity and determines which substances from the inventory contribute to toxicity impacts. During the second step for aquatic ecotoxicity, characterisation factors for acute and chronic ecotoxicity are calculated The fate analysis includes evaporation, deposition, and degradation. The ecotoxicity factors are based on PNEC for acute aquatic, chronic aquatic and terrestrial toxicity, and LOEC for microorganisms in wastewater treatment plants.	Hauschild <i>et al.</i> , (1997)

Critical Surface Time Method	1) Terrestrial ecotoxicity 2) Aquatic ecotoxicity	<p>The aquatic ecotoxicity potential (AEP), is defined as the product of a fate and an effect factor divided by the corresponding product of the fate and effect factor of zinc as a reference substance for the water compartment.</p> <p>The volatilization and sedimentation processes are included without considering the feedback to the original source compartment. Besides emissions to water emissions to soil are considered; the fraction of the emission to soil that reaches the freshwater is based on the CREAMS-GLEAMS model. Inter-media transfer is included by fractions transferred between air, soil and water, such as <math>f_{wi}</math> in the equation below.</p>	Jolliet and Crettaz (1997)
Method	Effects concerned	Criteria/comments	Reference
USES LCA Model	1) Terrestrial ecotoxicity 2) Freshwater Aquatic ecotoxicity 3) Freshwater Sediment ecotoxicity 4) Marine Aquatic ecotoxicity 5) Marine Sediment ecotoxicity	<p>As with the other models, first substance specific characterisation factors, called aquatic ecotoxicity potentials (AETPs), are determined. This is done by calculating potential PEC/PNEC ratios (risk characterisation ratios, RCRs; PEC is the predicted environmental concentration) for the two target compartments, freshwater and seawater, and for each emission based on a fictional 1000 t/day emission. The AETPs are then calculated for each emission compartment by dividing the so-called freshwater and seawater RCRs by the corresponding RCRs of the reference substance (1,4-dichlorobenzene) emitted to a reference compartment, in the case of water, the continental freshwater compartment.</p> <p>The fate model used in USES-LCA requires a continuous release in units of mass per time as input, whereas in lifecycle inventories, releases are given in units of mass.</p>	
Potentially Affected Species Approach		<p>The approach is based on the notion of PAFs (Potentially Affected Fraction), the fraction of species that, given an environmental concentration, is exposed above the No Observed Effect Concentration (NOEC).</p> <p>The PAF and the PNEC are both based on the same curve. To apply the PAF concept requires additional data. As these data are still lacking for most substances, the concept still has little practical use. The fact that the PAF provides a measure of toxicity that is comparable between substances is considered to be its major advantage.</p> <p>Specific rules of addition hold for combining PAFs, which are difficult to transpose to LCA, because as a baseline LCA integrates over space and time and these addition rules for combined toxicity are of course only valid when the substances are present at the same place at the same time.</p>	

Table A4.3: Different methods for the assessment of ecotoxicological impacts. (Boustead *et al.* (1999), Shultze *et al.* (2000), Guinee *et al.* (2001))

Method	Procedure	Effect Factor	Aquatic Toxicity	Reference
CML Method	<p>Compartments – Water and Soil</p> <p>Restriction – emission to water toxic only to water and similarly for soil</p> <p>Does not include degradation and intermedia transport</p> <p>Does not distinguish between acute and chronic toxicity</p>	<p>The CML method uses an effect factor calculated from the inverse of the maximum tolerable concentration (MTC) as defined by the US EPA.</p> $AETP_i = ECA_i = \frac{1}{MTC_i}$ <p>where <math>ECA_i</math> is the ecotoxicological classification factor for aquatic ecosystems for substance <math>i</math> (<math>m^3/mg</math>) and <math>MTC_i</math> is the maximum tolerable concentration of substance <math>i</math> in water, later referred to as the PNEC (<math>mg/m^3</math>).</p>	<p>The AETS is then calculated by summing the products of the AETPs and the masses of the substances emitted as</p> $AETS = ETP_a = \sum_i ECA_i M_i^w$ <p>where <math>ETP_a</math> is the aquatic ecological toxicity potential (<math>m^3</math>) and <math>M_i^w</math> is the mass of substance <math>i</math> emitted to water (<math>mg</math>).</p>	
EDIP Method Environmental Development of Industrial Product	<p>Compartments Emission air, water, soil</p> <p>Effect soil and water</p> <p>Distinguishes between acute and chronic toxicity</p> <p>Models of degradation and intermedia transport only rudimentary</p>	$AETP_{acute} = EF(etwa)_i = f_{wa,i} ETF_{wa,i}$ $AETP_{chronic} = EF(etwc)_i = f_{wc,i} Bio_i ETF_{wc,i}$ <p>Where <math>EF(etwa)</math> is the equivalency factor ecotoxicity water acute, <math>EF(etwc)</math> is the equivalency factor ecotoxicity water chronic, <math>f_{wa,i}</math> is the final partitioning of substance <math>i</math> between emission compartment and water for acute ecotoxicity (dimensionless), <math>f_{wc,i}</math> is the final partitioning of substance <math>i</math> between emission compartment and water for chronic ecotoxicity (dimensionless), <math>Bio_i</math> is the biodegradation index of substance <math>i</math>, derived from the Organisation for Economic Cooperation and Development or EU tests (dimensionless), <math>ETF_{wa,i}</math> is the acute ecotoxicity (effect) factor, and <math>ETF_{wc,i}</math> is the chronic ecotoxicity (effect) factor (both: inverse PNEC [<math>m^3/mg</math>])</p>	<p>The AETPs (i.e., ecotoxicity potential <math>EP(etwa)</math> or <math>EP(etwc)</math>, in EDIP terminology) are then derived by summing the products of the masses released with respective equivalency factors, as with the CML method. These category indicator results have a unit <math>m^3</math> of the respective compartment, indicating which dilution volume is necessary such that the predicted no-effect concentration (PNEC) values are not exceeded.</p>	

Method	Procedure	Effect Factor	Aquatic Toxicity	Reference
USES 1 Model	<p>Compartments – air, water, industrial soil and agricultural soil</p> <p>Distinguishes between acute and chronic toxicity??? (have to check)</p> <p>Models of degradation and intermedia transport based on the SimpleBox 1.0 model</p>	<p>AETP is based on an arbitrarily chosen 1000 kg/day emission of a substance normalised as a potential in comparison to 1,4-dichlorobenzene (1,4-dcb)</p> $AETP_{i,ecomp} = \frac{PEC_{water,ecomp,i} \cdot E_{aqua,i}}{PEC_{water,water,1,4-dcb} \cdot E_{aqua,1,4-dcb}}$ <p>AETP<sub>i,ecomp</sub> is the aquatic eco toxicity potential as a result of an emission of substance i to the compartment ecomp</p> <p>E<sub>aqua,i</sub> is the effect factor representing toxic impact of substance i on the aquatic ecosystem (reciprocal of the PNEC)</p> <p>PEC<sub>water,ecomp,i</sub> is the predicted environmental concentration in the water compartment from an emission of 1000kg/day of substance i to compartment ecomp</p>	<p>The AETS is then calculated by summing the products of the AETPs and the masses of the substances emitted as</p> $AETS = \sum_i \sum_{ecomp} AETP_{i,ecomp} Mi_{i,ecomp}$ <p>where ETP<sub>a</sub> is the aquatic ecological toxicity potential (m3) and Mi<sub>i,ecomp</sub> is the mass of substance emitted to compartment ecomp</p>	
USES LCA Model	<p>Compartments – air, freshwater (aquatic and sediment), marine (aquatic and sediment) and terrestrial</p> <p>Distinguishes between acute and chronic toxicity</p> <p>Uses scenario analysis to assess the sensitivity of the model to different time and spatial horizons</p> <p>More realistic degradation and intermedia transport routes</p>	$FAETP_{i,ecomp} = \frac{PEC_{freshwater,ecomp,i} \cdot E_{freshwater,i}}{PEC_{freshwater,freshwater,1,4-dcb} \cdot E_{freshwater,1,4-dcb}}$ <p>FAETP<sub>i,ecomp</sub> is the freshwater aquatic eco toxicity potential as a result of an emission of substance i to the compartment ecomp</p> <p>E<sub>freshwater,i</sub> is the effect factor representing toxic impact of substance i on the freshwater aquatic ecosystem (reciprocal of the PNEC)</p> <p>PEC<sub>freshwater,ecomp,i</sub> is the predicted environmental concentration in the freshwater compartment resulting from an emission of 1000kg/day of substance i to compartment ecomp</p>	<p>The AETS is then calculated by summing the products of the AETPs and the masses of the substances emitted as</p> $AETS = \sum_i \sum_{ecomp} FAETP_{i,ecomp} Mi_{i,ecomp}$ <p>where ETP<sub>a</sub> is the aquatic ecological toxicity potential (m3) and Mi<sub>i,ecomp</sub> is the mass of substance emitted to compartment ecomp</p>	

Method	Procedure	Effect Factor	Aquatic Toxicity	Reference
Critical Surface Time Method	Compartments Emission air, water, soil Effect soil and water  Distinguishes between acute and chronic toxicity Models of degradation and intermedia transport only rudimentary	The aquatic effect factor is expressed as the inverse PNEC, which is determined according to the U.S. EPA procedure. The characterisation factor for emission to water is calculated as  $AETP_{water} = AEP_i = \frac{F_i E_i}{F_{Zn} E_{Zn}} = \frac{\frac{\tau_i^w}{V^w} \frac{1}{PNEC_{i^*}}}{\frac{\tau_{Zn}^w}{V^w} \frac{1}{PNEC_{Zn^*}}}$ AEP <sub>i</sub> is the aquatic ecotoxicity potential of the substance i emitted to water (kg zinc/kg substance i emitted to water), $\tau_i^w$ is the residence time in the water compartment (years), $V^w$ is the volume of the water compartment per unit area (m <sup>3</sup> /m <sup>2</sup> ), $PNEC_{i^*}$ is the predicted no-effect concentration (PNEC)(kg/m <sup>3</sup> ),	The category indicator is then $AETS = S_{aquatic} = \sum_i (M_i^s AEP_i + f_i^{sw} M_i^s AEP_i)$ S <sub>aquatic</sub> is the aquatic toxicity score (kg zinc emitted to water), where $M_i^s$ is the mass emitted to medium s according to the inventory (kg of substance i), and $f_i^{sw}$ is the fraction of the emission to soil that reaches water	

## A.5 Environmental Modelling

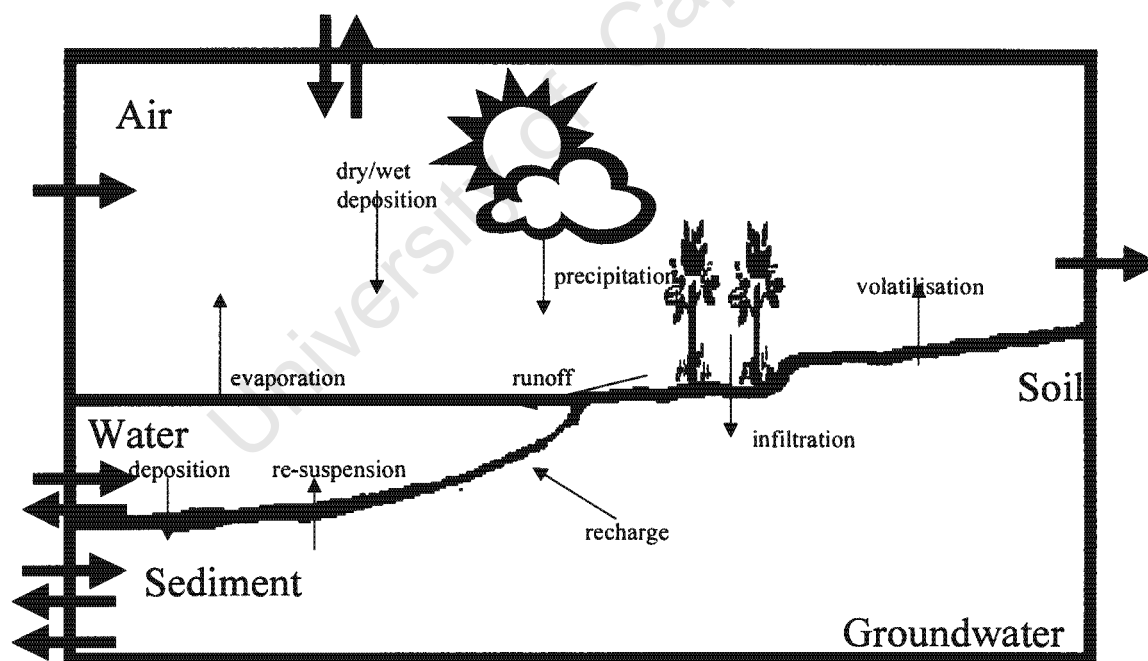
### Levels of Multimedia (Fugacity) Models

Based on the level of complexity desired and on the goal of the modelling efforts, all these advective, reactive and diffusive processes can be accounted for in multimedia models. These considerations were the basis of distinguishing four different levels of fugacity models. Mackay (1991), Coulibaly (2000) and Heijungs (1999) discuss the various levels of Fugacity Models. These are summarised below.

#### Fugacity Model Level I

Level I is the simplest and quickest fugacity calculation that can be used to assess the case of an environmental contamination. It uses only the partition coefficient and an evaluative environment, as shown in Figure A5.1, to predict the chemical distribution between all the phases present

**Figure A5.1: Schematic Representation of a Catchment**



The figure includes five major compartments, subdivided as follows:

1. The air compartment consists of pure air phase and aerosols.
2. The soil compartments consist of soil and terrestrial plants.

3. The water compartment consists of pure water phase, suspended sediment, and aquatic biota including fish, plant and other aquatic populations.
4. The sediment compartment includes the deposited sediment layer.

A Level I simulation is of the equilibrium distribution of a fixed quantity of conserved (i.e. non-reacting) chemical, in a closed environment at equilibrium, with no degrading reactions, no advective processes, and no inter-media transport processes (e.g. no wet deposition, or sedimentation). The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The Level I model assumes a simple, evaluative, closed environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended sediment, fish and aerosols.

This model is useful for establishing the general features of a new or existing chemical's behaviour. A Level I calculation gives the general impression of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium. The results of changes in chemical and environmental properties may be explored.

#### Fugacity Model Level II

A Level II simulation describes a situation in which a chemical is continuously discharged at a constant rate and achieves a steady-state and equilibrium condition at which the input and output rates are equal. Degrading reactions and advective processes are the loss or output processes treated. Inter-media transport processes (eg. no wet deposition, or sedimentation) are not quantified. The medium receiving the emission is unimportant because the chemical is assumed to become instantaneously distributed to an equilibrium condition.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The Level II model assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended sediment, biota and aerosols.

This model is useful for establishing the general features of a new or existing chemical's behaviour. A Level II calculation gives an indication of the likely media into which a chemical will tend to partition and an indication of relative concentrations in each medium. The distribution between media is the same as in Level I. The results of changes in chemical and environmental properties may be explored.

Three persistences are calculated, an overall value,  $T_O$ , and individual persistences attributable to reaction only,  $T_R$ , and advection only,  $T_A$ .

Consideration of advection and reaction rates allows for the calculation of chemical persistence. It provides a first estimate of overall environmental persistence, which is a critical property of the chemical. It also shows which loss processes are likely to be most important. A fast reaction or short half-life may not be significant if relatively little of the chemical is subject to this reaction by virtue of its partitioning. The potential for the chemical to be subject to long-range atmospheric transport is also indicated by the magnitude of the air advection loss. The global chemical persistence is best indicated by the reaction persistence, whereas the local persistence is indicated by the overall persistence.

### Fugacity Model Level III

A Level III simulation describes a situation which is one step more complex and realistic than the Level II model. Like the Level II model, chemical is continuously discharged at a constant rate and achieves a steady state condition in which input and output rates are equal. The loss processes are degrading reactions and advection. Unlike the Level II model, equilibrium between media is not assumed and, in general, each medium is at a different fugacity. A mass balance applies not

only to the system as a whole, but to each compartment. Rates of inter-media transport are calculated using D values which contain information on mass transfer coefficients, areas, deposition and resuspension rates, diffusion rates, and soil runoff rates.

Mass balances are calculated for the four bulk media of air (gas + aerosol), water (solution + suspended sediment + biota), soil, (solids + air + water), and sediment (solids + pore water). Equilibrium exists within, but not between media. For example, sediment solids and pore water are at equilibrium, but sediment is not necessarily at equilibrium with the overlying water.

Physical-chemical properties are used to quantify a chemical's behaviour in an evaluative environment. Three types of chemicals are treated in this model: chemicals that partition into all media (Type 1), involatile chemicals (Type 2), and chemicals with zero, or near-zero, solubility (Type 3). The model can not treat ionising or speciating substances which limits the usefulness of these models when considering metals and ionic species. The Level III model assumes a simple, evaluative environment with user-defined volumes and densities for the following homogeneous environmental media (or compartments): air, water, soil, sediment, suspended sediment, fish and aerosols.

This model gives a more realistic description of a chemical's fate including the important degradation and advection losses and the inter-media transport processes. The distribution of the chemical between media depends on how the chemical enters the system, e.g. to air, to water, or to both. This mode of entry also affects persistence or residence time.

Three persistences are calculated, an overall value,  $T_O$ , and individual persistences attributable to reaction only,  $T_R$ , and advection only,  $T_A$ .

The rates of inter-media transport are controlled by a series of 12 transport velocities. Reaction half-lives are requested for all 7 media. The advective residence time selected for air also applies to aerosols and the residence time for water applies to suspended sediment and fish. The advective residence time of aerosols, suspended sediment and fish cannot be specified independently of the air and water

residence times. Change in contaminant mass is equal to the total input minus the total output:

$$dM/dt = V_i Z_i \frac{df_i}{dt} = I_i + \sum (D_{ij} f_j) - \sum (D_{Ti} f_j) \quad A5-1$$

where  $V_i$  represents the volume,  $Z_i$  the bulk fugacity capacity,  $D_{ij}$  the inter-media input transfers,  $D_{Ti}$  the inter-media output transfers and  $I_i$  the direct input in the compartment  $i$ . The subscript  $j$  represents the other compartments contributing to the mass input into the compartment of interest  $i$ . Since steady state conditions are assumed, the first term  $df/dt$  is equal to zero and the resulting system of equations can be solved for the different fugacity parameters.

#### Fugacity Model Level IV

The level III fugacity model used to solve a steady state problem can be extended to handle unsteady state situations. The additional complexity has the cost of more input data as initial conditions are now required to perform the simulation. Level IV can be very advantageous, especially when long-term scenarios need to be considered. Also it may indicate to decision-makers the required time for an environment to return to an acceptable level of contamination. The term  $V_i Z_i df_i/dt$  is not zero in the unsteady state level IV, thus the chemical fugacity and concentration are allowed to change with time.

The inter-media transfers discussed above constitute the main difference between the multimedia models and the spatial models. The advantages in using a multimedia approach include the ability to add and compare all the  $D$  values (MTC) individually while keeping computations relatively easy to follow. Also, all the MTCs can be added in series or in parallels to determine the overall contaminant fate. These MTCs values contain a great deal of information as to which process would dominate the ultimate fate of the contaminant and thus lead to effective decision making.

#### **Description of Generic Fugacity Model**

The multimedia approach predicts the fate and transport of contaminants by incorporating, not only the single medium fate and transport, but also the inter-medium transfers in the form of a comprehensive model. A contaminant is thus modelled using not only its chemical-physical characteristics, but also by considering

the characteristics of the environment (including all phases that are present). One popular multimedia model that is used by researchers is the Mackay model. The Mackay type model is to be used as the framework of this research. These models are based on the well-accepted thermodynamics concepts such as fugacity and equilibrium.

Fugacity is denoted by the symbol  $f$ , and has units of pressure (Pascal). It is related to concentration as follows:

$$C = f \cdot Z \quad \text{A5-2}$$

where,

C is the concentration in mole/m<sup>3</sup>

$f$  is the fugacity in Pa

Z is the fugacity capacity in mole/m<sup>3</sup>.Pa

Although the fugacity concept is not meaningful when considering the behaviour of inorganic species, the concept of partition coefficients may be used when considering the behaviour of metals at equilibrium with the environment.

### **Toxicological Databases**

Toxicological databases are currently available in two forms. The original form is a library of data which summarises the relevant toxicological data such as the HAZCHEM Data and ECOTOX database. Recently, the toxicological databases have been linked to multi-media fate models. Examples of such databases are CalTOX, ChemCAN, HAZCHEM and the USES Database which uses the Simplebox Model. These models were described by Cowan *et al*/(1995) as follows:

1. CalTOX is a fugacity based model that combines Level IV soil layer compartments with a steady state Level III model containing four compartments. The CalTOX model was developed to assist California Environmental Protection Agency to estimate chemical fate and human exposure in the vicinity of hazardous waste sites. CalTOX also includes indirect algorithms and tools to quantify and assess uncertainties in model outputs
2. ChemCAN is a steady state Level III model, developed by Health Canada, which uses the fugacity and equivalence approach to predict a chemicals fate

in any of the 24 regions of Canada. The model contains four main environmental compartments and a number of sub-compartments. It is very similar to the equilibrium criterion series of models which deduce chemical fate in a hypothetical 105 km<sup>2</sup> region and to the basic MacKay model (MacKay 1991)

3. HAZCHEM is a steady-state Level III model with five compartments, two of which are soils. It is based on the same fugacity model as ChemCAN but contains a number of modifications. It uses matrix inversion to find the steady-state solution. It was developed as a regional scale model for all EU member states.
4. SimpleBOX is a steady-state Level III. It consists of eight compartments, three of which are soils of different uses and properties. It also produces quasi-dynamic (Level IV) output by using an external numerical integrator. Because the model was developed at RIVM as a regional scale model for the Netherlands to be used as part of the Uniform System of Evaluation of Substances (USES), its default environmental characteristics represents the Netherlands. SimpleBOX uses the classical concentration concept to complete mass balances.

Cowan *et al* (1995) compared these models and concluded that :

1. The models produce essentially the same results (within a few percent) only if the relevant mechanisms and parameters are set to the same value
2. If some of the input parameters are left to the discretion of the modeller, different choices can be made yielding different results. These differences in parameters, although understandable and for many scientific purposes insignificant, may be significant in a regulatory decision-making context.
3. Extension of the model definition with a list of values for mass transfer coefficients will eliminate most of the human error differences in model results, but certain structural differences in the model will result in discrepancies.

Kawamoto *et al* (2001) conducted an evaluation of the USES and ChemCAN model in Japan to determine which model should be used, the difference between the model outputs and the accuracy of the model predictions. The study concluded that ChemCAN and USES models give consistent descriptions of the environmental fate of 69 chemicals on two spatial scales calibrated to represent the country of Japan and

Kanagawa prefecture. Predictions from the two models rarely differ by more than a factor of 10. Calculated environmental concentrations cover many orders of magnitude in environmental concentration and the chemicals encompass a spectrum of physico-chemical properties and emission patterns.

The models have been developed to describe the chemical fate of organic compounds in the environment and have not been specifically adapted to metals. Metals are treated as pseudo organic compounds in the models and the speciation and fate of metals in the environment has been recognised as a grey area in the models (Boustead *et al.*, 1999, Huijbregts, 2000)

Table A5.1: Major sources for the differences between HAZCHEM, ChemCAN, SimpleBOX and CalTOX models with respect to water (Cowan *et al* 1995)

Difference	HAZCHEM	ChemCAN	SimpleBOX	CalTOX
Calculation and Mass Balance	Fugacity basis (mass transfer based on D-values derived from partial mass transfer coefficients and z-values)	Fugacity and Equivalence basis (mass transfer based on D-values derived from partial mass transfer coefficients and z-values)	Concentration basis (mass transfer based on D-values derived from partial mass transfer coefficients and z-values)	Fugacity and Equivalence basis (mass transfer based on D-values derived from partial mass transfer coefficients and z-values)
Compartments	Bulk water compartment with equilibrium among sub phases	Bulk water compartment with equilibrium among sub phases	Biota and suspended matter as separate compartments	Bulk water compartment with equilibrium among sub phases
Degradation in Water	On bulk water basis	On bulk water basis	On (dissolved) water phase basis	On bulk water basis
Concentration biota in water	1 mg/l on wet weight basis	1 mg/l on wet weight basis	1 mg/l on dry weight basis	Not used in mass balance
Bioconcentration	$BCF = 0.05 K_{ow}$	$BCF = 0.05 K_{ow}$	$BCF = 0.05 K_{ow}/1.07$ (density biota 1070 kg/m <sup>3</sup> )	$BCF = 0.05 K_{ow}$
Solids-water partitioning	$K_p = f_{oc} 0.41 K_{ow}$	$K_p = f_{oc} 0.41 K_{ow}$	$K_p = f_{oc} K_{ow}$	$K_p = f_{oc} 0.48 K_{ow}$

## **APPENDIX B – CASE STUDY**

### **B.1 Case Study Measure Environmental Concentrations**

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**Appendix B1: Dry Season Water Analysis**

SAMPLE	Cu µg/L	Co µg/L	Zn mg/L	Cd µg/L	Mn µg/L	Fe mg/L	K mg/L	Na mg/L	Mg mg/L	Ca mg/L	Pb µg/L
Mwambashi Source A	51	0.09	0.056	0.169	20	0.51	3.5	0.3	4	3.1	552.25
Mwambashi Source B	56	0.05	0.033	0.175	24	0.5	3.1	0.2	4	2.9	456.5
Mwambashi Source C	54	0.02	0.099	0.172	10	0.51	3.1	0.5	4	3	751.25
Mwambashi Source D	58	0.06	0.014	0.169	20	0.53	3.5	0.3	4	3.9	769.75
Mwambashi Source E	56	0.05	0.045	0.159	10	0.52	3.6	0.4	4	4.63	537.75
	55	0.054	0.0494	0.1688	16.8	0.514	3.36	0.34	4	3.506	613.5
Mutimpa Dam Discharge point A	120	16.18	0.142	0.924	2162	0.23	57.3	29.7	346.9	1111	182.6
Mutimpa Dam Discharge point B	130	10.74	0.299	0.556	2163	0.25	57	29.8	345.2	968	138.2
Mutimpa Dam Discharge point C	150	12.05	0.183	0.65	2120	0.23	58.8	29.8	344.5	1089	207.5
Mutimpa Dam Discharge point D	130	5.77	0.411	0.648	2227	0.27	45.9	29.6	346.3	1109	188.7
Mutimpa Dam Discharge point E	130	5.8	0.213	0.64	2148	0.26	47.6	29.3	348.6	1097	136.9
	132	10.108	0.2496	0.6836	2164	0.248	53.32	29.64	346.3	1074.8	170.78
Mutimpa Village A	100	2.73	0.045	0.601	97	0.11	40.2	21.1	232.6	831	105.9
Mutimpa Village B	100	4.66	0.062	0.555	86	0.12	39.9	20.8	231.3	859	109.4
Mutimpa Village C	100	4.94	0.061	0.522	89	0.13	40.5	20.9	232.7	838	116.9
Mutimpa Village D	100	5.18	0.066	0.565	96	0.12	40.8	21	231.1	834	154.8
Mutimpa Village E	90	4.88	0.054	0.565	97	0.14	42	20.2	233.9	421	188.3
	98	4.478	0.0576	0.5616	93	0.124	40.68	20.8	232.32	756.6	135.06
Kakulushi Pump Station A	272	4.31	0.073	0.272	90	0.2	31	13.9	517	140.8	58.9
Kakulushi Pump Station B	278	4.35	0.035	0.287	80	0.19	21.1	14	498	137.6	33.02
Kakulushi Pump Station C	280	4.83	0.102	0.374	100	0.19	22.9	14.7	553	151	20.4
Kakulushi Pump Station D	357	5.08	0.087	0.327	120	0.13	24.6	15.1	580	157.8	43.57
Kakulushi Pump Station E	467	4.1	0.08	0.312	80	0.2	21.6	13.6	591	161.7	44.06
	330.8	4.534	0.0754	0.3144	94	0.182	24.24	14.26	547.8	149.78	39.99
Fikondo A	1050	<0.10	0.104	0.206	30	0.05	24	7.1	453	75.1	40.2
Fikondo B	1070	13.64	0.073	0.248	30	0.06	24.7	17.3	908	146.1	60.5
Fikondo C	1068	2.04	0.07	0.236	20	0.05	25.4	17	927	147	30.6
Fikondo D	1087	7.81	0.092	0.209	20	0.05	26.6	17.4	905	148.4	64.34
Fikondo E	1142	8.14	0.061	0.212	30	0.06	27.5	17.8	429	70.3	48.17
	1083.4	7.9075	0.08	0.2222	26	0.054	25.64	15.32	724.4	117.38	48.762
Chambishi A	60	14.9	0.07	0.961	68	0.24	104.9	92.7	400	514	123.7
Chambishi B	90	14.79	0.069	0.974	93	0.18	103.5	94.1	398.5	512	86.3
Chambishi C	70	13.28	0.065	1.052	117	0.15	104.6	93.4	372.2	242	147.3
Chambishi D	90	13.08	0.051	0.657	75	0.16	105.4	93.4	390.1	499	23.2
Chambishi E	86	13.05	0.059	0.95	70	0.17	106.9	86.6	510	390.5	238
	79.2	13.82	0.0628	0.9188	84.6	0.18	105.06	92.04	414.16	431.5	123.7
Peter's A	276	9.03	0.027	0.226	30	0.44	19.3	13.3	446	94.1	3241
Peter's B	285	6.5	0.036	0.198	20	0.37	19.9	13.4	445	94.1	42.17
Peter's C	267	4.03	0.022	0.229	30	0.39	19.5	13.2	362	81.6	55.43
Peter's D	265	2.17	0.031	0.26	30	0.38	19.5	13.2	443	91.4	14.42
Peter's E	256	0.61	0.054	0.224	30	0.33	20.3	13	418	89	45.24
	269.8	4.468	0.034	0.2274	28	0.382	19.7	13.22	422.8	90.04	679.652
Bridge A	219	0.42	0.067	0.232	44	0.45	21.9	10.7	344	76.2	31.39
Bridge B	307	0.46	0.062	0.235	10	0.45	22.1	10.7	379	78.3	25.63
Bridge C	301	0.47	0.044	0.246	20	0.43	22.4	10.6	357	79.9	28.86
Bridge D	322	2.26	0.052	0.307	20	0.43	21.8	10	345	79.4	39.3
Bridge E	295	0.73	0.056	0.275	10	0.27	18.7	10.8	363	78.1	34.12
	288.8	0.868	0.0562	0.259	20.8	0.406	21.38	10.56	357.6	78.38	31.86
Ichimpi A	54	0.71	0.016	0.095	10	0.62	10	6.7	152	55.9	12.6
Ichimpi B	4	0.4	<0.001	0.447	10	0.09	11	6.9	141	56	34.6
Ichimpi C	47	1.32	0.009	0.405	30	0.48	12.1	6.9	126	53.9	37.1
Ichimpi D	58	1.15	0.013	0.34	10	0.51	12.5	6.8	161	56.1	62.9
Ichimpi E	56	1.29	0.029	0.295	20	0.51	12.5	7.1	164	55.6	55.99
Ichimpi E	50	<0.10	0.026	0.258	30	0.5	13	7.1	182	55.1	49.3
	43	1.04	0.01925	0.349	20	0.418	12.22	6.96	154.8	55.34	47.978
Gamatone A	327	1.18	0.073	0.249	20	0.48	17.9	9.9	299	68	38.65
Gamatone B	315	1.74	0.064	0.248	20	0.5	18.1	9.8	301	67.5	40.01
Gamatone C	305	0.52	0.071	0.213	50	0.59	20.3	9.9	307	68.7	29.47
Gamatone D	328	1.55	0.05	0.242	10	0.48	18.3	10.2	306	68.5	34.91
Gamatone E	313	0.55	0.075	0.222	43	0.53	20	9.7	305	67.3	48.57
	317.6	1.108	0.0666	0.2348	28.6	0.516	18.92	9.9	303.6	68	38.322

## **B.2 Case Study Model Results**

Please note that the figures quoted in the following tables are computer generated. They have been generated by the River Compartment Model. These figures are only accurate to two significant figures due to the assumptions required for the development of the models.

University of Cape Town

Table B.2.1: River Compartment Model Output - Environmental Metal Concentration

Flows						Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8				
Time	Distance	River	Effluent	Evap	V out	Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				
						[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	
hr	day	km	m3/hr			(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)						
0	0.0	0	36000.00	38.00	81.64	35954.36	132.17	10.12	0.25	0.68	96.12	4.48	0.06	0.56	330.42	4.54	0.08	0.32	1064.78	7.92	0.08	0.22	79.30	13.84	0.06	0.92	270.14	4.47	0.05	0.23	288.37	0.87	0.06	0.26	373.07	1.16	0.12	0.40
20	0.8	72.07	35954.36	0.00	81.64	35872.72	124.37	9.02	0.24	0.66	92.34	3.99	0.06	0.54	310.93	4.04	0.07	0.30	1020.78	7.05	0.08	0.21	74.82	12.33	0.06	0.89	254.21	3.98	0.05	0.22	271.35	0.77	0.05	0.25	351.07	1.04	0.11	0.39
40	1.7	144.14	35872.72	0.00	81.64	35791.07	117.03	8.03	0.24	0.64	86.89	3.56	0.05	0.52	292.59	3.60	0.07	0.29	960.57	6.28	0.08	0.21	70.22	10.06	0.06	0.86	239.21	3.55	0.05	0.21	255.35	0.69	0.05	0.24	330.36	0.92	0.11	0.38
60	2.5	216.22	35791.07	0.00	81.64	35709.43	110.13	7.16	0.23	0.61	81.76	3.17	0.05	0.50	275.33	3.21	0.07	0.28	903.90	5.68	0.07	0.20	66.08	9.78	0.06	0.83	225.10	3.16	0.04	0.20	240.28	0.61	0.05	0.23	310.87	0.82	0.11	0.35
80	3.3	288.29	35709.43	0.00	81.64	35627.79	103.63	6.38	0.22	0.59	76.94	2.82	0.05	0.49	259.08	2.86	0.07	0.27	850.58	4.99	0.07	0.19	62.18	8.72	0.06	0.80	211.82	2.82	0.04	0.20	226.11	0.55	0.05	0.22	292.53	0.73	0.10	0.35
100	4.2	360.36	35627.79	0.00	81.64	35546.15	97.52	5.68	0.22	0.57	72.40	2.52	0.05	0.47	243.80	2.57	0.06	0.26	800.40	4.44	0.07	0.19	58.51	7.97	0.05	0.77	199.33	2.51	0.04	0.19	212.77	0.49	0.05	0.22	275.27	0.65	0.10	0.34
120	5.0	432.43	35546.15	0.00	81.64	35464.51	91.77	5.06	0.21	0.55	68.13	2.24	0.05	0.45	229.42	2.27	0.06	0.25	753.19	3.96	0.07	0.18	55.06	6.92	0.05	0.74	187.57	2.24	0.04	0.18	200.22	0.43	0.05	0.21	259.03	0.58	0.10	0.33
140	5.8	504.90	35464.51	0.00	81.64	35382.86	86.35	4.51	0.20	0.53	64.11	2.00	0.05	0.44	215.88	2.02	0.06	0.24	708.76	3.53	0.07	0.17	51.81	6.16	0.05	0.71	176.50	1.99	0.04	0.18	188.41	0.39	0.05	0.20	243.75	0.52	0.09	0.31
160	6.7	576.58	35382.86	0.00	81.64	35301.22	81.26	4.02	0.20	0.51	60.33	1.78	0.05	0.42	203.15	1.80	0.06	0.24	686.95	3.14	0.06	0.17	48.76	5.49	0.05	0.69	166.09	1.78	0.04	0.17	177.29	0.34	0.04	0.19	229.37	0.46	0.09	0.30
180	7.5	648.85	35301.22	0.00	81.64	35219.58	76.47	3.58	0.19	0.49	56.77	1.59	0.04	0.41	191.17	1.61	0.06	0.23	627.80	2.80	0.06	0.16	45.88	4.89	0.05	0.66	156.29	1.58	0.04	0.16	166.84	0.31	0.04	0.19	215.84	0.41	0.06	0.28
200	8.3	720.72	35219.58	0.00	81.64	35137.94	71.96	3.19	0.19	0.48	53.42	1.41	0.04	0.39	179.89	1.43	0.06	0.22	590.58	2.49	0.06	0.15	43.17	4.36	0.05	0.64	147.07	1.41	0.04	0.16	158.99	0.27	0.04	0.18	203.11	0.37	0.09	0.29
220	9.2	792.79	35137.94	0.00	81.64	35056.29	67.71	2.84	0.18	0.46	50.27	1.26	0.04	0.38	169.28	1.27	0.05	0.21	555.74	2.22	0.06	0.15	40.63	3.88	0.05	0.62	138.40	1.28	0.04	0.15	147.73	0.24	0.04	0.17	191.13	0.33	0.08	0.27
240	10.0	864.86	35056.29	0.00	81.64	34974.65	63.72	2.53	0.18	0.44	47.30	1.12	0.04	0.36	159.29	1.13	0.05	0.20	522.96	1.98	0.06	0.14	38.23	3.46	0.04	0.60	130.23	1.12	0.03	0.15	139.02	0.22	0.04	0.17	179.85	0.29	0.06	0.26
260	10.8	936.94	34974.65	0.00	81.64	34893.01	59.96	2.25	0.17	0.43	44.51	1.00	0.04	0.35	149.88	1.01	0.05	0.20	492.11	1.76	0.06	0.14	35.97	3.06	0.04	0.58	122.55	1.00	0.03	0.14	130.82	0.19	0.04	0.16	169.24	0.26	0.08	0.25
280	11.7	1009.01	34893.01	0.00	81.64	34811.37	56.42	2.01	0.17	0.41	41.89	0.89	0.04	0.34	141.05	0.90	0.05	0.19	463.08	1.57	0.05	0.13	33.85	2.75	0.04	0.58	115.32	0.89	0.03	0.14	123.10	0.17	0.04	0.16	159.26	0.23	0.08	0.24
300	12.5	1081.08	34811.37	0.00	81.64	34729.73	53.09	1.79	0.16	0.40	39.42	0.79	0.04	0.33	132.73	0.80	0.05	0.18	435.76	1.40	0.05	0.13	31.86	2.45	0.04	0.54	108.52	0.79	0.03	0.13	115.84	0.15	0.04	0.15	149.87	0.21	0.08	0.24
320	13.3	1153.15	34729.73	0.00	81.64	34648.08	49.96	1.59	0.16	0.38	37.09	0.71	0.04	0.32	124.90	0.71	0.05	0.18	410.05	1.25	0.05	0.12	29.06	2.18	0.04	0.52	102.12	0.70	0.03	0.13	109.00	0.14	0.04	0.15	141.02	0.16	0.07	0.23
340	14.2	1225.22	34648.08	0.00	81.64	34566.44	47.01	1.42	0.15	0.37	34.90	0.63	0.03	0.30	117.53	0.64	0.05	0.17	385.87	1.11	0.05	0.12	28.21	1.94	0.04	0.50	96.09	0.63	0.03	0.12	102.57	0.12	0.03	0.14	132.71	0.18	0.07	0.20
360	15.0	1297.30	34566.44	0.00	81.64	34484.80	44.24	1.27	0.15	0.36	32.84	0.58	0.03	0.29	110.80	0.57	0.04	0.16	363.10	0.99	0.05	0.12	26.54	1.73	0.04	0.48	90.42	0.56	0.03	0.12	96.52	0.11	0.03	0.14	124.88	0.15	0.07	0.21
380	15.8	1369.37	34484.80	0.00	81.64	34403.16	41.63	1.13	0.14	0.34	30.91	0.50	0.03	0.28	104.08	0.51	0.04	0.16	341.68	0.88	0.05	0.11	24.88	1.54	0.04	0.46	85.09	0.50	0.03	0.11	90.63	0.10	0.03	0.13	117.51	0.13	0.07	0.20
400	16.7	1441.44	34403.16	0.00	81.64	34321.52	39.17	1.00	0.14	0.33	29.08	0.44	0.03	0.27	97.94	0.45	0.04	0.15	321.53	0.79	0.04	0.11	23.50	1.37	0.03	0.45	80.07	0.44	0.03	0.11	85.47	0.09	0.03	0.13	110.58	0.12	0.06	0.20
420	17.5	1513.51	34321.52	0.00	81.64	34239.87	36.06	0.89	0.14	0.32	27.37	0.40	0.03	0.26	92.16	0.40	0.04	0.15	302.56	0.70	0.04	0.10	22.12	1.22	0.03	0.43	75.35	0.40	0.03	0.11	80.43	0.08	0.03	0.12	104.06	0.10	0.06	0.19
440	18.3	1585.56	34239.87	0.00	81.64	34158.23	34.69	0.80	0.13	0.31	25.75	0.35	0.03	0.25	86.72	0.36	0.04	0.14	284.71	0.62	0.04	0.10	20.81	1.09	0.03	0.42	70.90	0.35	0.03	0.10	75.68	0.07	0.03	0.12	97.92	0.09	0.06	0.18
460	19.2	1657.66	34158.23	0.00	81.64	34076.59	32.64	0.71	0.13	0.30	24.23	0.31	0.03	0.25	81.61	0.32	0.04	0.14	267.92	0.58	0.04	0.10	19.59	0.97	0.03	0.40	66.72	0.31	0.03	0.10	71.22	0.06	0.03	0.11	92.14	0.08	0.06	0.18
480	20.0	1729.73	34076.59	0.00	81.64	33994.95	30.72	0.63	0.12	0.29	22.80	0.28	0.03	0.24	76.79	0.28	0.04	0.13	252.11	0.49	0.04	0.09	18.43	0.86	0.03	0.39	62.78	0.28	0.02	0.10	67.02	0.05	0.03	0.11	86.71	0.07	0.06	0.17
500	20.8	1801.80	33994.95	0.00	81.64	33913.30	28.90	0.56	0.12	0.28	21.46	0.25	0.03	0.23	72.26	0.25	0.04	0.13	237.24	0.44	0.04	0.09	17.34	0.77	0.03	0.37	59.08	0.25	0.02	0.09	63.07	0.05	0.03	0.11	81.59	0.06	0.06	0.16
520	21.7	1873.87	33913.30	0.00	81.64	33831.66	27.20	0.50	0.12	0.27	20.19	0.22	0.03	0.22	68.00	0.23	0.04	0.12	223.24	0.39	0.04	0.09	16.32	0.69	0.03	0.36	55.59	0.22	0.02	0.09	59.34	0.04	0.03	0.10	76.78	0.06	0.05	0.16
540	22.5	1945.94	33831.66	0.00	81.64	33750.02	25.80	0.45	0.11	0.26	19.00	0.20	0.03	0.21	63.99	0.20	0.03	0.12	210.07	0.35	0.04	0.08	15.38	0.61	0.03	0.35	52.32	0.20	0.02	0.09	55.84	0.04	0.03	0.10	72.25	0.05	0.05	0.15
560	23.3	2018.02	33750.02	0.00	81.64	33668.38	24.09	0.40	0.11	0.25	17.88	0.18	0.03	0.20	60.21	0.16	0.03	0.11	197.68	0.31	0.04	0.08	14.45	0.54	0.03	0.33	49.23	0.18	0.02	0.08	52.55	0.04	0.03	0.09	67.99	0.05	0.05	0.15
580	24.2	2090.09	33668.38	0.00	81.64	33586.74	22.66	0.36	0.11	0.24	16.83	0.16	0.02	0.20	58.66	0.16	0.03	0.11	186.02	0.28	0.03	0.08	13.80	0.49	0.03	0.32	46.32	0.16	0.02	0.08	49.45	0.03	0.02	0.09	63.98	0.04	0.05	0.14
600	25.0	2162.16	33586.74	0.00	81.64	33505.09	21.33	0.32	0.10	0.23	15.83	0.14	0.02</																									

Table B.2.1: River Compartment Model Output - Environmental Metal Concentration

Flows							Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8				
Time	hr	day	Distance	River	Effluent	Evap	V out	Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.				Water Column Conc.			
								[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]
							(µg/l)				(µg/l)				(µg/l)				(µg/l)				(µg/l)				(µg/l)				(µg/l)				(µg/l)				
1340	55.8		4828.82	30565.98	0.00	81.64	30484.33	2.25	0.00	0.04	0.06	1.67	0.00	0.01	0.05	5.62	0.00	0.01	0.03	18.46	0.00	0.01	0.02	1.35	0.01	0.01	0.08	4.60	0.00	0.01	0.02	4.91	0.00	0.01	0.02	6.35	0.00	0.02	0.04
1360	56.7		4900.90	30484.33	8.00	81.64	30402.69	2.12	0.00	0.03	0.06	1.57	0.00	0.01	0.05	5.29	0.00	0.01	0.03	17.37	0.00	0.01	0.02	1.27	0.01	0.01	0.08	4.32	0.00	0.01	0.02	4.62	0.00	0.01	0.02	5.97	8.00	0.82	0.03
1380	57.5		4972.97	30402.69	8.00	81.64	30321.05	1.99	8.00	0.03	0.06	1.48	0.00	0.01	0.05	4.98	0.00	0.01	0.03	16.34	0.00	0.01	0.02	1.19	0.00	0.01	0.08	4.07	0.00	0.01	0.02	4.34	0.00	0.01	0.02	5.62	0.00	0.02	0.83
1400	58.3		5045.04	30321.05	8.00	81.64	30239.41	1.87	0.00	0.03	0.06	1.39	0.00	0.01	0.04	4.68	0.00	0.01	0.03	15.38	0.00	0.01	0.02	1.12	0.00	0.01	0.07	3.83	0.00	0.01	0.02	4.09	0.00	0.01	0.02	5.29	0.00	0.02	0.03
1420	59.2		5117.11	30239.41	0.00	81.64	30157.77	1.76	0.00	0.03	0.06	1.31	0.00	0.01	0.04	4.41	0.00	0.01	0.02	14.47	0.00	0.01	0.02	1.06	0.00	0.01	0.07	3.60	0.00	0.01	0.02	3.65	0.00	0.01	0.02	4.98	0.00	0.01	0.03
1440	60.0		5189.18	30157.77	0.00	81.64	30076.12	1.66	0.00	0.03	0.06	1.23	0.00	0.01	0.04	4.15	0.00	0.01	0.02	13.62	0.00	0.01	0.02	1.00	0.00	0.01	0.07	3.39	0.00	0.01	0.02	3.62	0.00	0.01	0.02	4.88	0.00	0.01	0.03
1460	60.8		5261.26	30076.12	0.00	81.64	29994.48	1.56	0.00	0.03	0.06	1.16	0.00	0.01	0.04	3.90	0.00	0.01	0.02	12.81	0.00	0.01	0.02	0.94	0.00	0.01	0.07	3.19	0.00	0.01	0.02	3.41	0.00	0.01	0.02	4.41	0.00	0.01	0.03
1480	61.7		5333.33	29994.48	0.00	81.64	29912.84	1.47	0.00	0.03	0.06	1.09	0.00	0.01	0.04	3.67	0.00	0.01	0.02	12.06	0.00	0.01	0.02	0.88	0.00	0.01	0.06	3.00	8.00	0.01	0.02	3.21	0.00	0.01	0.02	4.15	0.00	8.01	0.03
1500	62.5		5405.40	29912.84	0.00	81.64	29831.20	1.38	0.00	0.03	0.06	1.03	0.00	0.01	0.04	3.46	0.00	0.01	0.02	11.35	0.00	0.01	0.02	0.83	0.00	0.01	0.06	2.83	0.00	0.01	0.02	3.02	9.00	0.01	0.02	3.00	0.00	8.01	0.03
1520	63.3		5477.47	29831.20	0.00	81.64	29749.56	1.30	0.00	0.03	0.04	0.97	0.00	0.01	0.04	3.25	0.00	0.01	0.02	10.68	0.00	0.01	0.02	0.78	0.00	0.01	0.06	2.66	0.00	0.01	0.01	2.84	0.00	0.01	0.02	3.67	0.00	8.81	0.03
1540	64.2		5549.54	29749.56	0.00	81.64	29667.91	1.22	0.00	0.03	0.04	0.91	0.00	0.01	0.03	3.06	0.00	0.01	0.02	10.05	0.00	0.01	0.02	0.73	0.00	0.01	0.06	2.50	0.00	0.01	0.01	2.67	0.00	0.01	0.02	3.48	0.00	8.01	0.03
1560	65.0		5621.62	29667.91	8.00	81.64	29586.27	1.15	0.00	0.03	0.04	0.86	0.00	0.01	0.03	2.88	0.00	0.01	0.02	9.45	0.00	0.01	0.01	0.69	0.00	0.01	0.06	2.35	0.00	0.01	0.01	2.51	0.00	8.01	0.02	3.25	0.00	0.01	0.02
1580	65.8		5693.69	29586.27	0.00	81.64	29504.63	1.08	8.00	0.03	0.04	0.80	0.00	0.01	0.03	2.71	0.00	0.01	0.02	8.90	0.00	0.01	0.01	0.65	0.00	0.01	0.06	2.22	0.00	0.01	0.01	2.37	0.00	8.01	0.81	3.08	0.00	0.01	0.02
1600	66.7		5765.76	29504.63	0.00	81.64	29422.99	1.02	0.00	0.02	0.04	0.76	0.00	8.01	0.03	2.55	0.00	0.01	0.02	8.37	0.00	0.01	0.01	0.61	0.00	0.01	0.05	2.08	0.00	0.00	0.01	2.23	0.00	0.01	0.01	2.88	8.00	8.81	0.02
1620	67.5		5837.83	29422.99	0.00	81.64	29341.34	0.98	0.00	0.02	0.04	0.71	0.00	0.01	0.03	2.40	0.00	0.01	0.02	7.88	0.00	0.01	0.01	0.58	0.00	0.01	0.05	1.96	0.00	0.00	0.01	2.09	0.00	0.01	0.01	2.70	0.00	8.81	0.02
1640	68.3		5909.00	29341.34	0.00	81.64	29259.70	0.90	0.00	0.02	0.04	0.67	0.00	0.01	0.03	2.26	8.00	0.01	0.02	7.41	0.00	0.01	0.01	0.54	0.00	0.01	0.05	1.85	0.00	0.00	0.01	1.97	0.00	0.01	0.01	2.55	0.00	0.01	0.02
1660	69.2		5981.98	29259.70	0.00	81.64	29178.06	0.85	0.00	0.02	0.03	0.63	0.00	0.01	0.03	2.12	0.00	0.01	0.02	6.98	0.00	0.01	0.01	0.51	0.00	0.01	0.05	1.74	0.00	0.00	0.01	1.85	0.00	0.01	0.01	2.40	0.00	0.01	0.02
1680	70.0		6054.05	29178.06	0.00	81.64	29096.42	0.80	0.00	0.02	0.03	0.59	0.00	0.01	0.03	2.00	0.00	0.01	0.02	6.56	0.00	0.01	0.01	0.48	0.00	0.01	0.04	1.63	0.00	0.00	0.01	1.75	0.00	0.00	0.01	2.26	0.00	0.01	0.02
1700	70.8		6126.12	29096.42	0.00	81.64	29014.78	0.75	8.00	0.02	0.03	0.56	0.00	0.00	0.03	1.88	0.00	0.01	0.01	6.18	0.00	0.01	0.01	0.45	0.00	0.01	0.04	1.54	0.00	0.00	0.01	1.64	0.00	0.00	0.01	2.12	0.00	8.01	0.02
1720	71.7		6198.19	29014.78	0.00	81.64	28933.13	0.71	0.00	0.02	0.03	0.53	0.00	0.00	0.03	1.77	0.00	0.01	0.01	5.81	0.00	0.01	0.01	0.42	0.00	0.01	0.04	1.45	0.00	0.00	0.01	1.55	0.00	0.00	0.01	2.00	0.00	8.01	0.02
1740	72.5		6270.26	28933.13	0.00	81.64	28851.49	0.67	0.00	0.02	0.03	0.49	0.00	0.00	0.02	1.67	8.00	0.01	0.01	5.47	0.00	0.01	0.01	0.40	0.00	0.01	0.04	1.36	0.00	0.00	8.01	1.45	0.00	0.00	1.88	0.00	8.01	0.02	
1760	73.3		6342.34	28851.49	8.00	81.64	28769.85	0.63	0.00	0.02	0.03	0.47	0.00	0.00	0.02	1.57	0.00	0.01	0.01	5.15	0.00	0.01	0.01	0.38	0.00	0.00	0.04	1.28	0.00	0.00	0.01	1.37	0.00	0.00	0.01	1.77	0.00	0.01	0.02
1780	74.2		6414.41	28769.85	0.00	81.64	28688.21	0.59	0.00	0.02	0.03	0.44	0.00	0.00	0.02	1.48	0.00	0.01	0.01	4.84	0.00	0.01	0.01	0.35	0.00	8.00	0.04	1.21	0.00	0.00	0.01	1.29	0.00	0.00	0.01	1.67	0.00	0.01	0.02
1800	75.8		6486.48	28688.21	0.00	81.64	28606.57	0.56	8.00	0.02	0.03	0.41	0.00	0.00	0.02	1.39	0.00	0.01	0.01	4.58	0.00	0.01	0.01	0.33	0.00	0.00	0.04	1.14	0.00	0.00	0.01	1.21	0.00	0.00	0.01	1.57	0.00	0.01	0.02
1820	75.8		6558.55	28606.57	0.00	81.64	28524.92	0.52	0.00	0.02	0.03	0.39	0.00	0.00	0.02	1.31	0.00	0.01	0.01	4.29	0.00	0.01	0.01	0.31	0.00	0.00	8.03	1.07	0.00	0.00	1.14	0.00	0.00	0.01	1.48	0.00	8.01	0.02	
1840	76.7		6630.62	28524.92	0.00	81.64	28443.28	0.49	0.00	0.02	0.02	0.37	0.00	0.00	0.02	1.23	0.00	0.01	0.01	4.04	0.00	0.01	0.01	0.30	0.00	0.00	0.03	1.01	0.00	0.00	0.01	1.07	0.00	0.00	0.01	1.39	0.00	8.01	0.01
1860	77.5		6702.70	28443.28	0.00	81.64	28361.64	0.46	0.00	0.02	0.02	0.34	0.00	0.00	0.02	1.16	0.00	0.01	0.01	3.80	0.00	0.01	0.01	0.28	0.00	0.00	8.83	0.95	0.00	0.00	1.01	8.00	0.00	0.01	1.31	0.00	8.01	0.01	
1880	78.3		6774.77	28361.64	8.00	81.64	28280.00	0.44	0.00	0.02	0.02	0.32	0.00	0.00	8.02	1.09	0.00	0.00	0.01	3.57	8.00	0.01	0.01	0.28	0.00	0.00	0.03	0.88	0.00	0.00	0.01	0.95	0.00	0.00	0.01	1.23	8.00	8.81	0.01
1900	79.2		6846.84	28280.00	8.00	81.64	28198.35	0.41	0.00	0.02	0.02	0.30	0.00	0.00	0.02	1.02	0.00	0.00	0.01	3.36	0.00	0.01	0.01	0.25	0.00	0.00	0.03	0.84	8.00	8.00	0.01	0.89	0.00	0.00	0.01	1.16	0.00	8.01	0.01
1920	80.0		6918.91	28198.35	0.00	81.64	28116.71	0.39	0.00	0.02	0.02	0.29	0.00	0.00	8.02	0.96	0.00	0.00	0.01	3.16	0.00	0.01	0.01	0.23	0.00	0.00	0.03	0.79	8.00	8.00	0.01	0.84	0.00	0.00	0.01	1.08	0.00	8.01	0.01
1940	80.8		6990.98	28116.71	0.00	81.64	28035.07	0.36	0.00	0.02	0.02	0.27	0.00	0.00	0.02	0.91	0.00	0.00	0.01	2.98	0.00	0.00	0.01	0.22	0.00	0.00	0.03	0.74	0.00	0.00	0.01	0.79	0.00	0.00	0.01	1.02	0.00	0.01	0.01
1960	81.7		7063.06	28035.07	0.00	81.64	27953.43																																



Table B.2.2: River Compartment Model Output - Metal Flux to Sediment

Flows				Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8						
Time	Distance	River	Effluent	Evap	V out	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	
Day	km	m <sup>3</sup> /day	m <sup>3</sup> /day	m <sup>3</sup> /day	m <sup>3</sup> /day	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	(µg/hr)	
0	0.0	36000.00	36.00	81.64	35954.39																																	
0	1.8	72.07	35954.36	0.00	81.64	35972.72	14923.91	2021.84	13.75	46.35	10782.91	895.71	3.15	38.08	36309.79	806.91	4.14	21.35	119206.13	1581.79	4.42	15.04	8714.35	2784.33	3.42	62.28	29895.00	860.71	2.71	15.45	31988.54	173.82	3.09	17.55	40697.05	232.43	6.36	27.38
40	1.7	144.14	35972.72	0.00	81.64	35791.07	13637.19	1787.24	13.39	44.61	10124.58	796.20	3.05	36.89	34092.97	806.18	4.10	20.55	111928.25	1406.07	4.28	14.49	8182.31	2457.25	3.32	59.94	27873.56	794.23	2.62	14.87	28753.66	154.33	3.00	16.83	38143.71	189.88	8.00	25.35
80	2.5	216.22	35791.07	0.00	81.64	35708.43	12804.54	1597.58	12.92	42.84	9506.40	770.75	2.95	35.28	32011.34	616.80	3.99	17.97	105094.20	1248.87	4.15	13.94	7682.72	2184.27	3.12	57.89	26171.70	706.17	2.54	14.31	27937.17	137.19	2.91	16.28	36143.71	189.88	8.00	25.35
120	3.3	288.29	35708.43	0.00	81.64	35627.79	12022.87	1420.09	12.53	41.33	8925.82	626.12	2.87	33.98	30056.94	639.69	3.77	19.03	111101.64	1111.01	4.02	13.94	7213.60	1941.80	3.12	55.53	24573.90	627.72	2.47	13.78	26231.27	121.95	2.82	15.85	33536.71	183.25	6.00	24.40
160	4.2	360.36	35627.79	0.00	81.64	35546.15	11286.48	1282.32	12.14	39.78	8380.64	556.23	2.78	32.86	28221.21	566.22	3.66	18.32	12851.06	987.58	3.90	12.91	6772.08	1725.89	3.02	53.44	23072.98	557.08	2.38	13.28	24826.42	108.40	2.73	15.08	31894.31	145.11	5.84	23.45
200	5.0	432.43	35546.15	0.00	81.64	35464.51	10596.08	1122.07	11.77	38.25	7899.02	497.09	2.70	31.85	26497.71	503.31	3.55	17.89	13245.45	877.86	3.78	12.91	6236.45	1504.13	2.83	51.44	21863.88	495.06	2.32	12.76	23125.27	98.36	2.65	14.50	29918.32	128.99	5.47	22.80
240	5.8	504.50	35464.51	0.00	81.64	35382.86	9951.74	967.40	11.41	36.85	7388.41	441.86	2.61	30.27	24879.34	447.39	3.44	16.97	14819.83	800.31	3.87	11.96	5971.04	1363.86	2.84	49.50	20340.74	440.85	2.25	12.28	23030.40	88.55	2.57	13.95	28601.04	114.86	5.10	20.74
280	6.7	576.58	35382.86	0.00	81.64	35301.22	9343.88	888.57	11.07	35.45	6937.12	392.77	2.53	29.14	23359.70	387.88	3.33	16.89	178980.30	693.61	3.58	11.51	5806.33	1212.15	2.76	47.65	19098.32	381.89	2.18	11.82	20386.65	78.13	2.49	13.43	26375.23	101.92	5.14	20.85
320	7.5	648.65	35301.22	0.00	81.64	35219.58	8773.11	808.06	10.73	34.13	6513.37	348.12	2.48	28.04	21932.77	333.48	3.23	15.72	22005.98	616.54	3.45	11.08	5263.87	1077.48	2.87	45.88	17931.70	348.34	2.11	11.38	19141.33	87.87	2.41	12.92	24764.00	90.59	4.98	20.15
360	8.3	720.72	35219.58	0.00	81.64	35137.94	8237.18	730.49	10.40	32.85	6115.47	303.98	2.38	26.89	20562.91	314.21	3.13	15.13	187907.14	548.03	3.34	10.86	4842.30	957.73	2.59	44.13	16836.26	309.63	2.05	10.85	17971.89	60.15	2.34	12.44	23251.28	80.53	4.89	18.39
400	9.2	792.79	35137.94	0.00	81.64	35056.29	7733.82	652.24	10.08	31.61	5741.85	275.84	2.31	25.86	18334.46	279.29	3.04	14.59	15476.72	487.12	3.24	10.26	4460.35	851.30	2.51	42.48	15007.86	275.22	1.98	10.54	18974.00	53.47	2.27	11.97	21830.74	71.59	4.68	18.86
440	10.0	864.86	35056.29	0.00	81.64	34974.65	7281.38	583.45	9.77	30.43	5391.03	245.19	2.24	25.00	16153.46	248.25	2.94	14.01	13959.25	432.89	3.14	9.95	4056.86	756.86	2.43	40.86	14841.83	244.84	1.92	10.14	14874.95	42.54	2.07	11.08	19244.46	58.55	4.40	17.29
480	10.8	936.94	34974.65	0.00	81.64	34893.01	6817.88	514.94	9.48	28.98	5091.61	217.84	2.17	24.06	11944.21	228.86	2.85	13.49	11559.68	384.87	3.04	9.50	3559.68	697.84	2.29	37.87	13953.39	183.28	1.81	9.36	17865.96	37.25	1.93	10.27	18894.24	44.88	4.13	16.01
520	11.7	1009.01	34893.01	0.00	81.64	34811.37	6401.07	437.29	9.19	28.16	4782.31	193.71	2.10	23.13	10802.86	198.14	2.77	12.98	10523.23	342.09	2.95	9.15	3840.84	597.84	2.29	37.87	13953.39	183.28	1.81	9.36	17865.96	37.25	1.93	10.27	18894.24	44.88	4.13	16.01
560	12.5	1081.08	34811.37	0.00	81.64	34729.73	6038.88	388.88	8.91	27.12	4481.88	172.18	2.04	22.28	10224.66	174.34	2.68	12.49	9826.50	304.07	2.86	8.90	3905.92	531.39	2.22	38.44	12283.82	171.80	1.75	9.04	17115.05	28.87	1.94	9.85	15927.41	39.71	4.01	15.41
600	13.3	1153.15	34729.73	0.00	81.64	34648.08	5642.58	345.46	8.63	26.11	4189.18	153.04	1.98	21.45	9146.14	154.96	2.60	12.02	9381.76	270.27	2.77	8.47	3385.54	472.33	2.15	35.07	11533.06	152.70	1.70	8.70	15833.06	28.87	1.94	9.85	15927.41	39.71	4.01	15.41
640	14.2	1225.22	34648.08	0.00	81.64	34566.44	5297.87	307.06	8.37	25.12	3933.12	138.03	1.92	20.84	8324.16	137.73	2.52	11.14	8463.15	240.26	2.89	8.15	3138.54	418.23	2.05	38.78	10816.22	120.64	1.60	8.06	14833.06	20.64	1.82	9.16	14038.79	31.38	3.77	14.27
680	15.0	1297.30	34566.44	0.00	81.64	34484.80	4973.84	272.93	8.11	24.38	3682.70	120.91	1.96	19.87	7624.58	122.42	2.44	11.14	7624.58	213.53	2.81	7.85	2984.30	373.18	2.02	32.49	10186.22	100.80	1.50	7.76	13833.06	16.82	1.62	8.16	13183.06	27.89	3.65	13.74
720	15.8	1369.37	34484.80	0.00	81.64	34403.16	4699.77	242.59	7.86	23.27	3486.85	107.47	1.80	19.12	6924.58	106.81	2.37	10.22	6924.58	118.74	2.53	7.55	2801.86	361.67	1.96	31.27	9544.73	107.23	1.55	7.76	12833.06	12.64	1.57	8.16	12183.06	22.03	3.43	12.72
760	16.7	1441.44	34403.16	0.00	81.64	34321.52	4384.27	215.62	7.62	22.40	3254.98	95.52	1.75	18.40	6280.96	96.72	2.30	10.31	5984.27	108.89	2.45	7.27	2630.58	294.80	1.90	30.09	8661.19	95.31	1.50	7.47	11833.06	18.52	1.71	8.48	11237.61	24.79	3.54	12.72
800	17.5	1513.51	34321.52	0.00	81.64	34239.87	4116.21	191.65	7.39	21.55	3055.97	84.90	1.69	17.41	5629.52	85.96	2.26	9.93	5379.10	149.94	2.37	7.00	2408.73	282.03	1.84	28.96	8143.26	84.71	1.45	7.18	10833.06	16.48	1.66	8.16	11618.94	22.03	3.43	12.72
840	18.3	1585.58	34239.87	0.00	81.64	34158.23	3864.51	170.34	7.16	20.74	2889.11	75.48	1.64	17.04	5061.28	78.41	2.16	9.59	4718.29	139.27	2.30	6.73	2178.29	232.80	1.79	27.87	7888.89	75.29	1.41	6.81	10433.06	14.83	1.61	7.85	10808.47	18.88	3.33	12.25
880	19.2	1657.65	34158.23	0.00	81.64	34076.59	3628.18	151.40	6.95	19.86	2693.66	67.07	1.59	16.40	4507.47	67.91	2.08	9.15	3978.84	118.45	2.26	6.48	2176.91	207.00	1.73	26.82	7415.80	69.92	1.37	6.85	10213.06	13.70	1.58	7.56	10241.38	17.40	3.22	11.78
920	20.0	1729.72	34076.59	0.00	81.64	33995.00	3406.30	132.57	6.73	19.21	2528.82	59.62	1.54	15.78	4051.75	60.39	2.00	8.85	3275.46	105.28	2.18	6.24	2043.78	186.98	1.68	25.81	6952.27	58.48	1.32	6.40	7431.93	11.59	1.51	7.27	9815.05	15.47	3.03	11.94
960	20.8	1801.80	33995.00	0.00	81.64	33913.36	3197.98	118.80	6.53	18.49	2374.24	52.99	1.49	15.19	3594.90	53.85	1.97	8.51	2824.51	92.67	2.10	6.00	1918.78	165.53	1.63	24.84	6552.58</											

Table B.2.2: River Compartment Model Output - Metal Flux to Sediment

Flows				Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8						
Time	Distance	River	Flow	Effluent	Evsp	V out		[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]			
hr	km		m3/hr					(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)	(g/hr)			
1520	69.3	5477.47	28831.20	0.00	81.64	28748.56	126.85	0.29	1.33	2.80	94.25	0.13	0.30	2.13	317.39	0.13	0.40	1.20	1041.98	0.23	0.43	0.84	76.17	0.40	0.33	3.48	258.49	0.13	0.26	0.87	278.99	0.02	0.30	0.98	358.36	0.03	0.62	1.53
1540	64.2	5549.54	23748.88	0.00	81.64	28857.91	119.15	0.26	1.29	2.50	86.48	0.11	0.28	2.85	297.89	0.12	0.38	1.11	917.84	0.18	0.40	0.78	87.10	0.31	0.31	3.23	243.57	0.10	0.25	0.90	258.97	0.02	0.29	0.95	336.33	0.03	0.80	1.47
1560	65.0	5621.62	28887.91	0.00	81.64	28988.27	111.83	0.23	1.25	2.40	83.02	0.10	0.28	2.87	278.57	0.10	0.28	0.97	871.84	0.18	0.40	0.78	87.10	0.31	0.31	3.11	228.57	0.10	0.25	0.90	243.99	0.02	0.28	0.91	315.86	0.03	0.58	1.42
1580	65.8	5693.68	28986.27	0.00	81.64	29054.99	104.95	0.20	1.21	2.31	77.92	0.09	0.28	1.80	262.38	0.08	0.38	1.06	861.42	0.18	0.39	0.75	62.97	0.29	0.30	3.11	214.52	0.08	0.24	0.77	228.99	0.02	0.26	0.84	286.28	0.02	0.58	1.36
1600	66.7	5765.78	29054.69	0.00	81.64	29122.99	96.50	0.18	1.17	2.22	73.13	0.08	0.27	1.83	242.25	0.08	0.35	1.02	808.46	0.14	0.38	0.72	59.10	0.25	0.29	2.89	201.33	0.08	0.23	0.74	214.91	0.02	0.26	0.81	276.04	0.02	0.54	1.31
1620	67.5	5837.89	29122.99	0.00	81.64	29214.34	92.45	0.18	1.13	2.14	68.69	0.07	0.29	1.76	216.11	0.07	0.34	0.90	758.75	0.13	0.38	0.69	55.47	0.22	0.28	2.87	188.93	0.07	0.22	0.71	201.70	0.01	0.26	0.81	244.00	0.02	0.51	1.22
1640	68.3	5907.90	29214.34	0.00	81.64	29299.70	86.76	0.14	1.10	2.06	64.41	0.06	0.25	1.66	261.90	0.08	0.33	0.86	712.09	0.11	0.35	0.67	52.06	0.20	0.27	2.77	177.33	0.08	0.22	0.69	189.30	0.01	0.25	0.78	244.00	0.02	0.51	1.22
1660	69.2	5981.98	29299.70	0.00	81.64	29378.06	81.43	0.13	1.06	1.98	60.45	0.06	0.24	1.68	203.58	0.06	0.32	0.91	668.30	0.10	0.34	0.84	48.86	0.17	0.27	2.66	166.43	0.08	0.21	0.68	177.65	0.01	0.24	0.75	229.64	0.01	0.48	1.17
1680	70.0	6054.05	29378.06	0.00	81.64	29462.42	76.42	0.11	1.03	1.90	56.73	0.05	0.24	1.57	191.04	0.05	0.31	0.88	627.10	0.08	0.33	0.82	45.65	0.15	0.26	2.59	156.19	0.05	0.20	0.69	186.73	0.01	0.23	0.72	215.70	0.01	0.48	1.12
1700	70.8	6126.12	29462.42	0.00	81.64	29544.78	71.72	0.10	1.00	1.83	53.24	0.04	0.23	1.51	179.29	0.04	0.30	0.84	588.62	0.08	0.32	0.59	43.03	0.14	0.25	2.46	146.58	0.04	0.20	0.61	158.47	0.01	0.22	0.66	202.44	0.01	0.46	1.06
1720	71.7	6198.19	29544.78	0.00	81.64	29633.13	67.30	0.09	0.97	1.76	49.87	0.04	0.22	1.45	166.29	0.04	0.29	0.81	552.41	0.07	0.31	0.57	40.38	0.12	0.24	2.37	137.57	0.04	0.19	0.58	148.85	0.01	0.22	0.67	186.96	0.01	0.45	1.04
1740	72.5	6270.28	29633.13	0.00	81.64	29724.49	66.16	0.08	0.94	1.70	46.86	0.04	0.21	1.39	157.91	0.04	0.28	0.78	518.42	0.06	0.30	0.55	37.80	0.11	0.23	2.28	129.10	0.03	0.18	0.57	137.81	0.01	0.21	0.64	178.29	0.01	0.44	1.00
1760	73.3	6342.34	29724.49	0.00	81.64	29818.85	59.28	0.07	0.91	1.63	44.01	0.03	0.21	1.34	146.19	0.03	0.27	0.75	486.52	0.06	0.28	0.53	35.57	0.10	0.23	2.19	121.16	0.03	0.18	0.54	129.33	0.01	0.20	0.62	167.32	0.01	0.42	0.96
1780	74.2	6414.41	29818.85	0.00	81.64	29916.21	55.83	0.06	0.88	1.57	41.30	0.03	0.20	1.28	135.07	0.03	0.27	0.72	456.58	0.05	0.28	0.51	33.38	0.09	0.22	2.11	113.70	0.03	0.17	0.52	121.37	0.01	0.20	0.59	157.03	0.01	0.41	0.93
1800	75.0	6486.48	29916.21	0.00	81.64	30014.57	52.21	0.05	0.85	1.51	38.78	0.02	0.20	1.24	123.51	0.02	0.26	0.70	428.46	0.04	0.27	0.49	31.22	0.08	0.21	2.03	106.71	0.02	0.17	0.50	111.93	0.00	0.19	0.55	138.29	0.01	0.38	0.86
1820	75.8	6558.55	30014.57	0.00	81.64	30112.92	48.99	0.05	0.83	1.45	36.37	0.02	0.18	1.19	112.46	0.02	0.25	0.67	402.11	0.04	0.27	0.47	29.40	0.07	0.21	1.95	100.14	0.02	0.16	0.47	100.31	0.00	0.18	0.55	129.78	0.01	0.37	0.82
1840	76.7	6630.62	30112.92	0.00	81.64	30211.28	45.98	0.04	0.80	1.40	34.13	0.02	0.18	1.15	114.84	0.02	0.24	0.64	377.35	0.03	0.26	0.45	27.59	0.08	0.20	1.88	93.97	0.02	0.16	0.45	94.14	0.00	0.17	0.51	121.78	0.00	0.36	0.79
1860	77.5	6702.70	30211.28	0.00	81.64	30311.64	43.15	0.04	0.78	1.34	32.03	0.02	0.18	1.10	107.86	0.02	0.23	0.62	354.12	0.03	0.25	0.44	25.89	0.05	0.19	1.81	88.19	0.02	0.15	0.45	88.30	0.00	0.17	0.48	114.29	0.00	0.35	0.76
1880	78.3	6774.77	30311.64	0.00	81.64	30412.00	40.49	0.03	0.75	1.29	30.08	0.02	0.17	1.08	101.22	0.02	0.23	0.60	332.32	0.03	0.24	0.42	24.29	0.05	0.19	1.74	82.78	0.02	0.15	0.43	82.84	0.00	0.17	0.48	114.29	0.00	0.35	0.76
1900	79.2	6846.84	30412.00	0.00	81.64	30513.35	38.00	0.03	0.73	1.24	28.21	0.01	0.17	1.02	94.98	0.01	0.22	0.57	311.85	0.02	0.23	0.40	22.80	0.04	0.18	1.67	77.96	0.01	0.14	0.41	80.30	0.00	0.16	0.47	107.25	0.00	0.34	0.73
1920	80.0	6918.91	30513.35	0.00	81.64	30614.71	35.88	0.03	0.71	1.20	26.47	0.01	0.16	0.98	89.14	0.01	0.21	0.55	292.85	0.02	0.23	0.39	21.39	0.04	0.18	1.61	72.88	0.01	0.14	0.40	77.70	0.00	0.16	0.45	100.65	0.00	0.33	0.71
1940	80.8	6990.98	30614.71	0.00	81.64	30716.07	33.46	0.02	0.69	1.15	24.84	0.01	0.16	0.95	83.85	0.01	0.21	0.53	274.62	0.02	0.22	0.37	20.08	0.00	0.17	1.55	68.38	0.01	0.13	0.38	73.00	0.00	0.15	0.44	94.45	0.00	0.32	0.68
1960	81.7	7063.06	30716.07	0.00	81.64	30817.43	31.40	0.02	0.68	1.11	23.31	0.01	0.15	0.91	78.50	0.01	0.20	0.51	257.70	0.02	0.21	0.36	18.84	0.03	0.17	1.49	64.18	0.01	0.13	0.37	68.51	0.00	0.15	0.42	88.83	0.00	0.31	0.65
1980	82.5	7135.13	30817.43	0.00	81.64	30918.79	28.46	0.02	0.64	1.07	21.87	0.01	0.15	0.86	73.96	0.01	0.19	0.48	241.83	0.01	0.21	0.35	17.68	0.08	0.17	1.43	60.22	0.01	0.13	0.36	64.29	0.00	0.14	0.40	86.17	0.00	0.30	0.69
2000	83.3	7207.20	30918.79	0.00	81.64	31020.14	27.85	0.02	0.62	1.02	20.52	0.01	0.14	0.84	69.12	0.01	0.19	0.47	226.98	0.01	0.20	0.33	16.59	0.02	0.16	1.36	58.51	0.01	0.12	0.34	60.32	0.00	0.14	0.39	78.04	0.00	0.29	0.60
2020	84.2	7279.27	31020.14	0.00	81.64	31121.50	25.99	0.02	0.60	0.98	19.80	0.01	0.14	0.81	64.83	0.01	0.18	0.45	212.89	0.01	0.19	0.32	15.59	0.02	0.15	1.27	49.71	0.01	0.11	0.30	56.58	0.00	0.14	0.37	73.19	0.00	0.28	0.58
2040	85.0	7351.34	31121.50	0.00	81.64	31222.85	24.32	0.01	0.58	0.96	18.08	0.01	0.13	0.78	60.90	0.01	0.18	0.44	198.81	0.01	0.18	0.31	14.59	0.02	0.15	1.22	46.52	0.00	0.12	0.29	49.77	0.00	0.12	0.33	68.86	0.00	0.27	0.54
2060	85.8	7423.42	31222.85	0.00	81.64	31324.21	22.81	0.01	0.57	0.91	16.93	0.01	0.13	0.75	57.02	0.01	0.17	0.42	187.21	0.01	0.18	0.30	13.96	0.02	0.14	1.19	43.73	0.00	0.11	0.28	46.68	0.00	0.12	0.32	65.84	0.00	0.25	0.52
2080	86.7	7495.49	31324.21	0.00	81.64	31425.56	21.81	0.01	0.55	0.87	15.88	0.00	0.13	0.72	53.48	0.00	0.18	0.40	175.58	0.01	0.18	0.29	12.84	0.01	0.14	1.17	43.73	0.00	0.11	0.28	46.68	0.00	0.12	0.32	65.84	0.00	0.25	0.52
2100	87.5	7567.56	31425.56	0.00	81.64	31526.92	20.67	0.01	0.53	0.84	14.90	0.00	0.12	0.69	50.17	0.00	0.18	0.39	164.89	0.01	0.17	0.27	12.04	0.01	0.13	1.13	41.01	0.00	0.10	0.28	43.78	0.00	0.12	0.32	65.84	0.00	0.25	0.52
2120	88.3	7639.63	31526.92	0.00	81.64	31628.29	18.82	0.01	0.51	0.81	13.97	0.00	0.12	0.66	47.05	0.00	0.15	0.37	154.48	0.01	0.16	0.26	11.29	0.														

Table B.2.2: River Compartment Model Output - Metal Flux to Sediment

Flows						Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8				
Time	Distance	River	Effluent	Evap.	V out	Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				Metal Sediment Flux				
hr	km		m <sup>3</sup> /hr			[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	
day						(g/hr)				(g/hr)				(g/hr)				(g/hr)				(g/hr)				(g/hr)				(g/hr)				(g/hr)				
3040	126.7	10054.04	24852.40	52.00	81.64	24822.75	1.02	0.00	0.12	0.13	0.78	0.00	0.03	0.11	2.55	0.00	0.04	0.06	8.38	0.00	0.04	0.04	0.61	0.00	0.03	0.18	2.03	0.00	0.02	0.04	2.23	0.00	0.03	0.05	2.88	0.00	0.05	0.08
3080	127.5	11027.02	24822.75	53.00	81.64	24894.11	0.98	0.00	0.11	0.13	0.71	0.00	0.03	0.11	2.40	0.00	0.03	0.06	7.87	0.00	0.04	0.04	0.58	0.00	0.03	0.17	1.96	0.00	0.02	0.04	2.09	0.00	0.03	0.05	2.71	0.00	0.05	0.08
3080	128.3	11068.09	24894.11	54.00	81.64	24898.47	0.90	0.00	0.11	0.12	0.87	0.00	0.03	0.10	2.25	0.00	0.03	0.06	7.39	0.00	0.04	0.04	0.54	0.00	0.03	0.17	1.84	0.00	0.02	0.04	1.98	0.00	0.02	0.05	2.54	0.00	0.05	0.07
3100	128.2	11171.16	24898.47	55.00	81.64	24898.83	0.85	0.00	0.11	0.12	0.83	0.00	0.02	0.10	2.11	0.00	0.03	0.06	6.92	0.00	0.03	0.04	0.48	0.00	0.03	0.15	1.82	0.00	0.02	0.04	1.73	0.00	0.02	0.04	2.24	0.00	0.05	0.07
3120	130.0	11243.23	24898.83	56.00	81.64	24814.18	0.79	0.00	0.10	0.12	0.58	0.00	0.02	0.09	1.99	0.00	0.03	0.05	6.13	0.00	0.03	0.04	0.45	0.00	0.02	0.14	1.53	0.00	0.02	0.04	1.53	0.00	0.02	0.04	1.98	0.00	0.04	0.08
3140	130.8	11315.30	24814.18	57.00	81.64	24789.54	0.75	0.00	0.10	0.11	0.55	0.00	0.02	0.09	1.87	0.00	0.03	0.05	5.76	0.00	0.03	0.05	0.42	0.00	0.02	0.14	1.43	0.00	0.02	0.04	1.44	0.00	0.02	0.04	1.96	0.00	0.04	0.08
3180	131.7	11387.38	24789.54	58.00	81.64	24785.90	0.70	0.00	0.10	0.11	0.52	0.00	0.02	0.08	1.75	0.00	0.03	0.05	5.41	0.00	0.03	0.03	0.40	0.00	0.02	0.14	1.35	0.00	0.02	0.03	1.44	0.00	0.02	0.04	1.75	0.00	0.04	0.08
3180	132.5	11458.45	24785.90	59.00	81.64	24743.25	0.66	0.00	0.09	0.10	0.49	0.00	0.02	0.08	1.65	0.00	0.03	0.05	5.06	0.00	0.03	0.03	0.37	0.00	0.02	0.13	1.27	0.00	0.02	0.03	1.27	0.00	0.02	0.04	1.64	0.00	0.04	0.08
3200	133.3	11531.52	24743.25	60.00	81.64	24721.82	0.62	0.00	0.09	0.10	0.46	0.00	0.02	0.08	1.56	0.00	0.03	0.05	4.77	0.00	0.03	0.03	0.35	0.00	0.02	0.13	1.18	0.00	0.02	0.03	1.19	0.00	0.02	0.03	1.54	0.00	0.04	0.05
3220	134.2	11603.59	24721.82	61.00	81.64	24700.97	0.58	0.00	0.09	0.10	0.43	0.00	0.02	0.08	1.47	0.00	0.03	0.04	4.49	0.00	0.03	0.03	0.33	0.00	0.02	0.12	1.12	0.00	0.02	0.03	1.12	0.00	0.02	0.03	1.45	0.00	0.04	0.05
3240	135.0	11675.66	24700.97	62.00	81.64	24681.33	0.55	0.00	0.09	0.09	0.41	0.00	0.02	0.08	1.35	0.00	0.03	0.04	4.22	0.00	0.03	0.03	0.31	0.00	0.02	0.11	1.05	0.00	0.02	0.03	1.05	0.00	0.02	0.03	1.36	0.00	0.04	0.05
3280	135.6	11747.74	24681.33	63.00	81.64	24662.89	0.51	0.00	0.08	0.08	0.38	0.00	0.02	0.07	1.26	0.00	0.03	0.04	3.98	0.00	0.03	0.03	0.29	0.00	0.02	0.11	0.93	0.00	0.02	0.03	0.89	0.00	0.02	0.03	1.26	0.00	0.04	0.05
3280	136.7	11819.81	24662.89	64.00	81.64	24645.05	0.48	0.00	0.08	0.08	0.36	0.00	0.02	0.07	1.21	0.00	0.02	0.04	3.72	0.00	0.03	0.03	0.28	0.00	0.02	0.11	0.87	0.00	0.02	0.03	0.83	0.00	0.02	0.03	1.20	0.00	0.04	0.05
3300	137.5	11891.89	24645.05	65.00	81.64	24628.41	0.45	0.00	0.08	0.08	0.34	0.00	0.02	0.07	1.13	0.00	0.02	0.04	3.50	0.00	0.03	0.03	0.27	0.00	0.02	0.11	0.83	0.00	0.02	0.03	0.80	0.00	0.02	0.03	1.13	0.00	0.03	0.04
3320	138.3	11963.85	24628.41	66.00	81.64	24612.76	0.43	0.00	0.08	0.08	0.32	0.00	0.02	0.06	1.07	0.00	0.02	0.04	3.29	0.00	0.02	0.02	0.26	0.00	0.02	0.10	0.82	0.00	0.02	0.03	0.77	0.00	0.02	0.03	1.00	0.00	0.03	0.04
3340	139.2	12038.02	24612.76	67.00	81.64	24598.12	0.40	0.00	0.07	0.08	0.30	0.00	0.02	0.06	1.00	0.00	0.02	0.03	3.08	0.00	0.02	0.02	0.24	0.00	0.02	0.09	0.77	0.00	0.02	0.03	0.73	0.00	0.02	0.03	0.94	0.00	0.03	0.04
3360	140.0	12108.10	24598.12	68.00	81.64	24584.48	0.38	0.00	0.07	0.07	0.28	0.00	0.02	0.06	0.94	0.00	0.02	0.03	2.90	0.00	0.02	0.02	0.23	0.00	0.02	0.09	0.68	0.00	0.02	0.03	0.68	0.00	0.02	0.03	0.88	0.00	0.03	0.04
3380	140.8	12180.17	24584.48	69.00	81.64	24571.84	0.35	0.00	0.07	0.07	0.26	0.00	0.02	0.06	0.88	0.00	0.02	0.03	2.73	0.00	0.02	0.02	0.20	0.00	0.02	0.09	0.64	0.00	0.02	0.03	0.64	0.00	0.02	0.03	0.83	0.00	0.03	0.04
3400	141.7	12252.24	24571.84	70.00	81.64	24560.19	0.33	0.00	0.07	0.07	0.25	0.00	0.02	0.06	0.83	0.00	0.02	0.03	2.57	0.00	0.02	0.02	0.19	0.00	0.02	0.09	0.60	0.00	0.02	0.03	0.60	0.00	0.02	0.03	0.78	0.00	0.03	0.04
3420	142.5	12324.31	24560.19	71.00	81.64	24549.55	0.31	0.00	0.07	0.07	0.23	0.00	0.01	0.05	0.78	0.00	0.02	0.03	2.41	0.00	0.02	0.02	0.18	0.00	0.02	0.08	0.58	0.00	0.02	0.03	0.58	0.00	0.02	0.03	0.73	0.00	0.03	0.04
3440	143.3	12396.38	24549.55	72.00	81.64	24539.81	0.29	0.00	0.06	0.06	0.22	0.00	0.01	0.05	0.73	0.00	0.02	0.03	2.27	0.00	0.02	0.02	0.17	0.00	0.02	0.08	0.56	0.00	0.02	0.03	0.56	0.00	0.02	0.03	0.68	0.00	0.03	0.04
3460	144.2	12468.46	24539.81	73.00	81.64	24531.27	0.28	0.00	0.06	0.06	0.21	0.00	0.01	0.05	0.68	0.00	0.02	0.03	2.13	0.00	0.02	0.02	0.16	0.00	0.01	0.06	0.53	0.00	0.01	0.02	0.53	0.00	0.01	0.02	0.65	0.00	0.03	0.03
3480	145.0	12540.53	24531.27	74.00	81.64	24523.63	0.23	0.00	0.06	0.06	0.19	0.00	0.01	0.05	0.65	0.00	0.02	0.03	2.00	0.00	0.02	0.02	0.15	0.00	0.01	0.06	0.50	0.00	0.01	0.02	0.50	0.00	0.01	0.02	0.60	0.00	0.03	0.03
3500	145.8	12612.60	24523.63	75.00	81.64	24516.98	0.24	0.00	0.06	0.06	0.18	0.00	0.01	0.05	0.61	0.00	0.02	0.03	1.88	0.00	0.02	0.02	0.14	0.00	0.01	0.07	0.47	0.00	0.01	0.02	0.47	0.00	0.01	0.02	0.57	0.00	0.03	0.03
3520	146.7	12684.67	24516.98	76.00	81.64	24511.34	0.23	0.00	0.06	0.05	0.17	0.00	0.01	0.04	0.57	0.00	0.02	0.02	1.77	0.00	0.02	0.02	0.13	0.00	0.01	0.07	0.44	0.00	0.01	0.02	0.44	0.00	0.01	0.02	0.54	0.00	0.02	0.03
3540	147.5	12756.74	24511.34	77.00	81.64	24506.06	0.22	0.00	0.05	0.05	0.16	0.00	0.01	0.04	0.54	0.00	0.02	0.02	1.67	0.00	0.02	0.02	0.12	0.00	0.01	0.07	0.41	0.00	0.01	0.02	0.41	0.00	0.01	0.02	0.50	0.00	0.03	0.03
3560	148.3	12828.82	24506.06	78.00	81.64	24500.06	0.20	0.00	0.05	0.05	0.15	0.00	0.01	0.04	0.51	0.00	0.02	0.02	1.57	0.00	0.02	0.02	0.11	0.00	0.01	0.06	0.39	0.00	0.01	0.02	0.39	0.00	0.01	0.02	0.48	0.00	0.02	0.03
3580	149.2	12900.89	24500.06	79.00	81.64	24500.06	0.19	0.00	0.05	0.05	0.14	0.00	0.01	0.04	0.48	0.00	0.02	0.02	1.47	0.00	0.02	0.02	0.11	0.00	0.01	0.06	0.37	0.00	0.01	0.02	0.37	0.00	0.01	0.02	0.46	0.00	0.02	0.03
3600	150.0	12972.96	24500.06	80.00	81.64	24498.77	0.18	0.00	0.05	0.05	0.13	0.00	0.01	0.04	0.46	0.00	0.01	0.02	1.38	0.00	0.02	0.01	0.10	0.00	0.01	0.06	0.34	0.00	0.01	0.01	0.34	0.00	0.01	0.01	0.45	0.00	0.02	0.03
3620	150.8	13045.03	24498.77	81.00	81.64	24498.13	0.17	0.00	0.05	0.04	0.13	0.00	0.01	0.04	0.42	0.00	0.01	0.02	1.30	0.00	0.01	0.01	0.10	0.00	0.01	0.06	0.32	0.00	0.01	0.01	0.32	0.00	0.01	0.01	0.42	0.00	0.02	0.02
3640	151.7	13117.10	24498.13	82.00	81.64	24498.48	0.18	0.00	0.05	0.04	0.12	0.00	0.01	0.04	0.40	0.00	0.01	0.02	1.22	0.00	0.01	0.01	0.09	0.00	0.01	0.05	0.30	0.00	0.01	0.01	0.30	0.00	0.01	0.01	0.40	0.00	0.02	0.02

Table B.2.3: River Compartment Model Output - Sediment Metal Content

Effluent D1										Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8									
Time		Flow		River		Effluent		Evap.		V out		[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]				
hr	day	km	km	km	km	m <sup>3</sup> /hr	m <sup>3</sup> /hr	m <sup>3</sup> /hr	m <sup>3</sup> /hr	m <sup>3</sup> /hr	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)	(ug)				
0	0.0	0	0	36000.0	38.00	0.0	0.0	0.0	0.0	0.0	35964.38																																
20	0.8	72.07	35964.38	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35972.72	2904.78	404.37	2.75	9.27	2156.58	178.14	0.88	7.82	7261.96	181.38	0.83	4.27	23841.23	318.36	0.86	3.01	1742.87	552.87	0.88	12.46	5937.20	178.74	0.54	3.09	6337.71	34.72	0.62	3.51	8190.41	46.49	1.28	5.47
40	1.7	144.14	35972.72	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35791.07	5632.22	786.82	5.42	18.19	4081.50	338.38	1.24	14.85	14080.55	342.61	1.63	8.38	46226.87	507.57	1.74	5.80	3379.33	1044.31	1.36	24.44	11511.92	337.83	0.87	6.86	12266.48	85.58	1.22	6.88	15866.22	87.81	2.51	10.74
60	2.5	216.21	35791.07	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35709.43	8133.13	1083.33	8.02	26.78	4982.78	479.96	1.83	22.00	20482.82	495.63	2.13	12.33	67246.71	647.56	2.57	6.89	4915.88	1481.17	1.90	35.98	14817.28	478.86	1.57	8.93	17875.91	83.03	1.60	10.14	23126.96	124.54	3.71	15.81
80	3.3	288.28	35709.43	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35627.79	10597.86	1387.35	10.51	35.95	5954.15	606.78	2.40	26.80	26494.15	613.33	3.18	16.14	83681.00	899.49	3.82	11.37	6358.80	1999.49	2.82	47.99	21059.85	804.43	2.07	11.86	23121.71	117.42	2.38	13.27	29891.43	157.19	4.86	20.09
100	4.2	360.35	35627.79	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35546.15	12655.36	1818.8	12.98	43.08	6944.13	717.89	2.86	35.33	32136.38	738.58	3.90	19.80	105511.32	1287.28	4.18	13.88	7713.21	2827.87	3.22	57.88	26275.57	718.00	2.55	14.33	30404.85	138.10	3.41	16.48	34127.11	189.21	6.48	25.30
120	5.0	432.43	35546.15	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35464.51	14675.17	1844.23	15.08	50.86	8111.63	817.02	3.50	41.23	37437.98	827.24	4.81	23.33	122308.87	1442.83	4.91	16.44	8895.10	3521.46	3.81	66.08	30098.35	815.20	3.01	18.89	32673.11	158.37	3.49	14.18	42270.62	212.01	7.10	29.91
140	5.8	504.50	35464.51	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35382.86	16695.52	2046.71	17.97	58.03	12895.61	905.98	4.32	47.89	42083.80	916.72	5.29	26.72	138245.80	1598.90	5.86	18.14	101079.31	3794.23	4.38	77.46	34876.50	903.37	3.46	19.34	37015.88	175.58	3.95	21.97	47888.04	234.94	8.18	34.28
160	6.7	576.58	35382.86	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35301.22	18834.30	2221.62	19.87	65.12	15285.74	983.95	4.52	53.50	47045.82	986.25	5.96	29.92	145693.92	1737.82	6.36	21.14	113005.58	3306.98	4.98	87.46	38406.16	961.75	3.89	21.71	41083.01	190.72	4.45	24.86	53164.06	253.33	9.16	38.44
180	7.5	648.65	35301.22	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35219.58	20586.82	2378.68	21.83	71.95	15285.71	1083.77	5.02	58.11	51472.30	1086.85	6.81	33.13	188985.11	1880.93	7.05	23.43	12353.38	3252.15	5.46	96.48	42082.50	1051.42	4.32	23.98	44821.28	242.28	4.93	27.24	56116.80	274.44	10.18	42.47
200	8.3	720.72	35219.58	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35137.94	22236.36	2518.73	24.01	78.82	18508.81	1118.54	5.50	64.51	55650.88	1129.79	7.23	36.16	212506.88	1875.73	7.71	25.43	13341.61	3443.89	5.98	105.49	45448.49	1113.34	4.73	28.17	48518.08	218.49	5.40	29.73	61072.33	289.55	11.15	46.38
220	9.2	792.79	35137.94	0.00	0.0	0.0	0.0	0.0	0.0	0.0	35056.29	23783.13	2646.26	26.83	84.84	17887.18	1171.09	5.98	69.71	60497.84	1186.65	7.84	38.07	252091.00	2087.98	8.36	27.54	14299.88	3913.95	6.48	113.99	49811.29	1186.36	5.12	32.20	51885.48	228.88	5.85	32.12	87133.30	308.88	12.08	50.09
240	10.0	864.86	35056.29	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34974.65	25235.41	2753.95	27.98	98.92	18735.38	1220.04	6.41	74.77	63098.53	1235.30	8.43	41.87	287121.56	2154.85	9.38	31.17	16141.26	3785.26	6.97	122.18	51579.85	1217.32	5.51	30.31	55528.08	238.49	6.28	34.43	61222.11	318.28	14.88	58.36
260	10.8	936.93	34974.65	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34893.01	26808.01	2858.34	28.98	98.92	18747.70	1283.08	6.84	79.52	68177.40	1279.43	9.00	44.57	318121.88	2371.53	9.93	31.01	14529.97	3889.81	7.44	130.83	54298.64	1280.81	5.88	32.28	58034.07	244.94	6.72	36.65	75381.58	327.90	13.87	57.13
280	11.7	1009.01	34893.01	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34811.37	28378.16	2939.79	31.17	102.42	20886.17	1302.37	7.26	84.15	69897.90	1318.88	9.55	47.17	328820.38	2380.85	10.19	33.24	16727.50	4018.38	7.80	137.80	58983.32	1286.46	6.24	34.14	80827.28	252.45	7.13	36.78	78965.27	337.85	14.72	60.48
300	12.5	1081.08	34811.37	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34729.73	29808.14	3017.52	33.50	107.84	22426.38	1366.81	7.67	88.61	72702.64	1353.53	10.89	49.86	338895.63	2260.78	10.76	35.24	17446.89	4125.88	8.34	144.89	59440.06	1333.82	6.59	35.95	83448.75	288.12	7.53	40.64	82088.12	348.89	15.56	68.85
320	13.3	1153.15	34729.73	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34648.08	30008.85	3086.61	36.22	113.08	24248.36	1387.42	8.06	92.80	75524.12	1384.52	11.61	52.07	347947.98	2441.81	11.32	36.70	18125.79	4209.12	8.77	151.91	61748.86	1364.36	6.98	37.09	85911.88	285.08	7.82	42.81	85273.86	354.83	16.75	66.75
340	14.2	1225.22	34648.08	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34566.44	31289.18	3148.93	36.20	118.89	25215.00	1384.02	8.46	97.03	78172.98	1412.68	11.11	54.28	329844.94	2462.09	11.85	38.33	18781.51	4304.19	9.17	159.89	63912.66	1391.51	7.26	39.38	88223.67	270.38	8.20	44.81	86274.36	361.89	17.13	69.71
360	15.0	1297.36	34566.44	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34484.80	32283.85	3202.61	38.52	122.92	26363.54	1418.81	8.82	101.00	80858.88	1436.55	11.80	58.81	348908.62	2505.52	12.38	39.90	18958.37	4378.72	9.58	161.64	65945.56	1415.64	7.58	40.97	70984.07	276.82	8.68	46.55	91072.33	389.17	17.86	72.57
380	15.8	1369.37	34484.80	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34403.16	33187.91	3258.13	40.89	127.58	27489.36	1448.58	9.18	104.62	82898.76	1459.31	12.88	62.75	372474.32	2543.52	12.88	41.41	18918.74	4474.05	9.99	171.41	67954.51	1437.08	7.89	42.53	72431.79	278.18	8.02	48.31	93708.63	373.74	18.81	75.32
400	16.7	1441.43	34403.16	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34321.52	34077.78	3313.62	43.18	132.61	28599.18	1478.50	9.51	107.57	84818.50	1479.15	13.82	67.81	395841.00	2571.38	13.81	42.88	19648.75	4564.78	10.81	187.43	69648.75	1451.38	8.41	43.43	74341.83	307.44	8.81	50.40	95491.11	389.21	19.88	80.59
420	17.5	1513.51	34321.52	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34240.87	34968.00	3332.58	45.09	138.37	29509.12	1478.38	9.88	112.64	87425.01	1484.85	12.96	82.80	398428.08	2607.25	13.85	44.28	20388.80	4558.42	10.73	183.22	71328.40	1473.08	8.48	45.45	78141.10	288.18	8.89	51.64	96557.54	400.51	20.82	85.36
440	18.3	1585.58	34240.87	0.00	0.0	0.0	0.0	0.0	0.0	0.0	34159.23	35870.90	3386.85	44.59	146.52	30227.86	1492.94	10.16	115.45	89277.16	1510.13	13.41	84.71	412022.54	2630.00	13.85	45.61	21022.54	4603.00	11.00	188.22	72881.27	1488.15	8.78	46.48	78827.43	307.62	20.07	82.95				
460	19.2	1657.66	34159.23	0.00	0.0	0.0	0.0</																																				

Table B.2.3: River Compartment Model Output - Sediment Metal Content

Flow					Effluent D1			Effluent D2			Effluent D3			Effluent D4			Effluent D5			Effluent D6			Effluent D7			Effluent D8														
Time	Distance	River	Effluent	Exp	Y <sub>out</sub>	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]	[Cu]	[Zn]	[Cd]											
hr	km		m <sup>3</sup> /hr	m <sup>3</sup> /hr		(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)	(ng)											
140	68.3	5009.90	20341.34	0.00	81.64	20526.70			47255.70	3636.85	82.81	236.86	35063.78	1611.86	18.96	193.79	118139.26	1632.14	24.94	106.82	367954.77	2646.70	26.81	76.56	26353.42	4874.89	26.82	316.89	89567.79	1608.38	16.30	76.82	106106.35	312.46	18.82	88.31	133389.96	418.28	38.44	136.24
180	69.2	5081.58	20279.70	0.00	81.64	20178.06			47271.98	3538.08	89.02	236.26	35065.87	1611.96	19.08	194.12	118176.97	1632.15	25.01	106.80	367988.43	2646.72	26.87	76.88	26363.19	4874.92	26.87	317.42	89621.08	1634.78	16.34	76.75	106136.86	312.48	18.82	88.31	133435.93	418.30	38.44	136.47
180	70.0	6054.05	20259.00	0.00	81.64	20096.42			47287.27	3538.70	83.23	236.64	35107.22	1612.00	19.05	194.43	118218.19	1632.16	25.07	106.80	368113.87	2646.74	26.87	76.88	26380.72	4874.95	26.87	317.94	89652.32	1634.78	16.34	76.75	106172.23	312.48	18.82	88.31	133477.07	418.30	38.44	136.47
1700	70.9	6126.12	20066.42	0.00	81.64	20043.28			47301.62	3538.72	83.43	237.08	35117.87	1612.01	19.10	194.73	118259.42	1632.17	25.13	106.81	368251.59	2646.76	26.89	77.12	26396.97	4874.98	26.87	318.45	89683.57	1634.78	16.34	76.75	106208.52	312.47	18.81	88.24	133515.56	418.30	38.44	136.47
1720	71.7	6198.19	20014.78	0.00	81.64	20003.13			47315.08	3538.74	83.62	237.52	35127.86	1612.02	19.14	195.02	118300.67	1632.18	25.16	106.81	368389.32	2646.78	26.89	77.35	26413.26	4875.01	26.87	318.96	89714.81	1634.78	16.34	76.75	106239.66	312.47	18.81	88.24	133557.56	418.30	38.44	136.47
1748	72.5	6270.26	20033.13	0.00	81.64	20051.48			47327.71	3538.75	83.81	237.98	35137.24	1612.02	19.19	195.30	118341.92	1632.19	25.19	106.82	368524.78	2646.79	26.93	77.52	26430.55	4875.03	26.87	319.40	89743.97	1634.78	16.34	76.75	106270.81	312.48	18.81	88.24	133599.56	418.30	38.44	136.47
1780	73.3	6342.34	20051.40	0.00	81.64	20076.85			47339.59	3538.77	86.96	238.02	35146.04	1612.03	19.23	195.57	118383.17	1632.20	25.30	106.81	368654.38	2646.79	26.96	77.25	26443.74	4875.05	26.91	319.80	89776.20	1634.78	16.34	76.75	106302.32	312.47	18.80	88.13	133628.88	418.31	38.44	136.47
1780	74.2	6414.31	20051.40	0.00	81.64	20088.21			47350.86	3538.78	84.17	238.33	35154.30	1612.04	19.27	195.82	118424.42	1632.21	25.35	106.82	368783.34	2646.80	27.04	77.35	26441.41	4875.08	26.96	320.22	89781.94	1634.78	16.34	76.75	106331.66	312.47	18.83	90.25	133658.08	418.31	38.44	136.47
1800	75.0	6486.48	20088.21	0.00	81.64	20088.57			47361.13	3538.79	84.34	238.64	35162.83	1612.04	19.31	196.07	118465.67	1632.22	25.40	106.80	368912.30	2646.81	27.10	77.45	26441.68	4875.08	26.96	320.62	89803.28	1634.78	16.34	76.75	106360.40	312.47	18.81	90.37	133687.56	418.31	38.44	136.47
1800	75.9	6558.55	20088.57	0.00	81.64	20088.57			47370.93	3538.80	84.50	238.93	35169.33	1612.05	19.34	196.31	118506.92	1632.23	25.45	106.83	369041.26	2646.82	27.15	77.56	26442.56	4875.08	26.96	321.01	89823.31	1634.78	16.34	76.75	106389.14	312.47	18.81	90.37	133715.22	418.31	38.44	136.47
1800	76.7	6630.62	20088.57	0.00	81.64	20043.28			47380.13	3538.81	84.67	239.21	35176.15	1612.05	19.38	196.56	118548.17	1632.24	25.50	106.81	369170.22	2646.83	27.20	77.64	26443.08	4875.10	26.96	321.38	89842.10	1634.78	16.34	76.75	106417.82	312.47	18.81	90.37	133742.98	418.31	38.44	136.47
1860	77.5	6702.70	20043.28	0.00	81.64	20061.64			47390.78	3538.82	84.82	239.48	35182.58	1612.05	19.42	196.81	118589.42	1632.25	25.54	106.81	369299.18	2646.83	27.25	77.81	26443.60	4875.11	26.96	321.75	89859.74	1634.78	16.34	76.75	106446.56	312.48	18.81	90.37	133770.74	418.31	38.44	136.47
1860	78.3	6774.77	20051.40	0.00	81.64	20080.08			47400.45	3538.83	84.97	239.75	35189.01	1612.06	19.46	197.07	118630.67	1632.26	25.58	106.82	369428.14	2646.84	27.30	77.94	26444.12	4875.12	26.96	322.12	89877.29	1634.78	16.34	76.75	106475.30	312.48	18.81	90.37	133798.50	418.31	38.44	136.47
1900	79.2	6846.84	20080.08	0.00	81.64	20106.35			47411.59	3538.84	85.26	240.02	35195.44	1612.06	19.49	197.18	118671.92	1632.27	25.62	106.83	369557.10	2646.85	27.35	77.97	26444.64	4875.14	26.96	322.49	89895.83	1634.78	16.34	76.75	106504.06	312.48	18.81	90.37	133826.26	418.31	38.44	136.47
1900	80.0	6918.91	20106.35	0.00	81.64	20116.71			47421.27	3538.84	85.40	240.45	35204.48	1612.06	19.55	197.58	118713.17	1632.28	25.72	106.83	369686.06	2646.85	27.44	78.04	26445.16	4875.15	26.96	322.86	89914.38	1634.78	16.34	76.75	106532.82	312.47	18.81	90.37	133854.02	418.31	38.44	136.47
1940	80.8	6990.98	20116.71	0.00	81.64	20083.07			47424.55	3538.85	85.53	240.85	35209.14	1612.06	19.59	197.75	118754.42	1632.29	25.76	106.84	369815.02	2646.86	27.48	78.11	26445.68	4875.15	26.96	323.23	89932.91	1634.78	16.34	76.75	106561.58	312.47	18.81	90.37	133881.78	418.31	38.44	136.47
1980	82.5	7135.13	20083.07	0.00	81.64	20071.79			47430.45	3538.85	85.66	240.89	35213.51	1612.07	19.61	197.92	118795.67	1632.30	25.80	106.84	369943.98	2646.86	27.52	78.18	26446.20	4875.16	26.96	323.60	89951.44	1634.78	16.34	76.75	106590.34	312.48	18.81	90.37	133909.54	418.31	38.44	136.47
2000	83.3	7207.20	20071.79	0.00	81.64	20070.14			47435.88	3538.86	85.79	241.09	35217.82	1612.07	19.64	198.08	118836.92	1632.31	25.84	106.84	370072.94	2646.87	27.57	78.25	26446.72	4875.16	26.96	323.97	89969.90	1634.78	16.34	76.75	106619.10	312.48	18.81	90.37	133937.30	418.31	38.44	136.47
2020	84.2	7279.27	20070.14	1.00	81.64	20070.50			47441.16	3538.86	85.90	241.47	35221.47	1612.07	19.68	198.25	118878.17	1632.32	25.87	106.85	370201.90	2646.87	27.60	78.31	26447.24	4875.17	26.96	324.34	89988.36	1634.78	16.34	76.75	106647.86	312.48	18.81	90.37	133965.06	418.31	38.44	136.47
2040	85.0	7351.34	20070.50	2.00	81.64	20081.86			47446.03	3538.86	86.02	241.48	35225.08	1612.07	19.69	198.41	118919.42	1632.33	25.91	106.85	370330.86	2646.87	27.64	78.37	26447.76	4875.17	26.96	324.71	89997.82	1634.78	16.34	76.75	106676.62	312.48	18.81	90.37	133993.82	418.31	38.44	136.47
2060	85.8	7423.42	20081.86	3.00	81.64	20091.22			47450.59	3538.86	86.13	241.85	35228.47	1612.07	19.72	198.58	118960.67	1632.34	25.94	106.85	370459.82	2646.87	27.67	78.43	26447.76	4875.17	26.96	325.08	90007.28	1634.78	16.34	76.75	106705.38	312.48	18.81	90.37	134022.58	418.31	38.44	136.47
2100	87.5	7495.48	20091.22	4.08	81.64	20073.58			47454.87	3538.86	86.24	241.64	35231.64	1612.07	19.74	198.70	118999.92	1632.35	25.98	106.85	370588.78	2646.87	27.71	78.49	26447.76	4875.17	26.96	325.45	90016.74	1634.78	16.34	76.75	106734.14	312.48	18.81	90.37	134051.34	418.31	38.44	136.47
2100	87.5	7567.56	20073.58	5.00	81.64	20093.93			47458.88	3538.87	86.35	242.08	35234.82	1612.07	19.77	198.84	119039.17	1632.36	26.01	106.85	370717.74	2646.87	27.74	78.54	26447.76	4875.17	26.96	325.82	90026.20	1634.78	16.34	76.75	106762.90	312.48	18.81	90.37	134080.10	418.31	38.44	136.47
2120	88.3	7639.63	20093.93	6.00	81.64	20071.79			47462.54	3538.87	86.45	242.16	35237.42	1612.07	19.79	198.97	119078.42	1632.37	26.04	106.85	370846.																			

Table B.2.3: River Compartment Model Output - Sediment Metal Content

Flows						Effluent D1				Effluent D2				Effluent D3				Effluent D4				Effluent D5				Effluent D6				Effluent D7				Effluent D8							
Time	Distance	River	Effluent	Evap	V out	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]	[Cu]	[Co]	[Zn]	[Cd]				
hr	km		m <sup>3</sup> /hr			(kg)				(kg)				(kg)				(kg)				(kg)				(kg)				(kg)				(kg)							
3280	136.7	11819.81	24852.89	64.00	81.64	24854.06				47518.48	3636.88	89.10	2457.79	35278.87	1612.06	20.40	201.95	118798.20	1832.24	26.84	113.19	300011.51	2846.88	26.83	79.77	28511.08	4975.20	22.19	330.23	97124.89	1808.48	17.53	81.93	103676.88	312.48	20.04	93.07	134131.71	418.32	41.37	145.10
3300	137.5	11891.88	24845.05	65.00	81.64	24828.41				47518.57	3636.88	89.12	2458.08	35278.94	1612.06	20.40	201.98	118798.42	1832.24	26.84	113.20	300012.26	2846.88	26.83	79.78	28511.14	4975.20	22.19	330.25	97125.08	1808.48	17.54	81.93	103676.88	312.48	20.04	93.07	134131.98	418.32	41.37	145.11
3320	138.3	11963.95	24837.21	66.00	81.64	24802.76				47518.65	3636.88	89.13	2458.26	35279.00	1612.06	20.40	201.97	118798.58	1832.24	26.85	113.21	300012.99	2846.88	26.84	79.78	28511.19	4975.20	22.19	330.27	97125.25	1808.48	17.54	81.94	103677.06	312.48	20.06	93.08	134132.20	418.32	41.38	145.12
3340	139.2	12036.02	24829.36	67.00	81.64	24777.11				47518.73	3636.88	89.15	2458.53	35279.06	1612.06	20.41	201.98	118798.74	1832.24	26.85	113.21	300013.81	2846.88	26.84	79.79	28511.24	4975.20	22.20	330.29	97125.41	1808.48	17.54	81.94	103677.24	312.48	20.05	93.08	134132.43	418.32	41.38	145.13
3360	140.0	12108.17	24821.51	68.00	81.64	24751.46				47518.81	3636.88	89.16	2458.80	35279.12	1612.06	20.41	202.00	118798.90	1832.24	26.86	113.22	300014.63	2846.88	26.85	79.79	28511.29	4975.20	22.20	330.31	97125.57	1808.48	17.55	81.95	103677.42	312.48	20.05	93.08	134132.66	418.32	41.40	145.14
3380	140.8	12180.32	24813.66	69.00	81.64	24725.81				47518.88	3636.88	89.18	2459.07	35279.18	1612.06	20.41	202.01	118799.06	1832.24	26.86	113.23	300015.45	2846.88	26.85	79.80	28511.33	4975.20	22.20	330.33	97125.71	1808.48	17.55	81.95	103677.56	312.48	20.06	93.10	134132.84	418.32	41.40	145.15
3400	141.7	12252.47	24805.81	70.00	81.64	24700.16				47518.95	3636.88	89.19	2459.34	35279.24	1612.06	20.42	202.02	118799.22	1832.24	26.86	113.23	300016.27	2846.88	26.85	79.80	28511.37	4975.20	22.21	330.35	97125.85	1808.48	17.55	81.96	103677.70	312.48	20.06	93.10	134133.03	418.32	41.41	145.15
3420	142.5	12324.61	24797.96	71.00	81.64	24674.51				47519.01	3636.88	89.20	2459.61	35279.30	1612.06	20.42	202.03	118799.38	1832.24	26.87	113.24	300017.09	2846.88	26.86	79.81	28511.41	4975.20	22.21	330.37	97126.00	1808.48	17.56	81.96	103677.84	312.48	20.06	93.10	134133.21	418.32	41.41	145.15
3440	143.3	12396.76	24790.11	72.00	81.64	24648.86				47519.07	3636.88	89.21	2459.88	35279.36	1612.06	20.42	202.04	118799.54	1832.24	26.87	113.24	300017.91	2846.88	26.86	79.81	28511.44	4975.20	22.21	330.39	97126.14	1808.48	17.56	81.97	103677.97	312.48	20.06	93.11	134133.37	418.32	41.41	145.15
3460	144.2	12468.90	24782.26	73.00	81.64	24623.21				47519.12	3636.88	89.23	2460.15	35279.43	1612.06	20.43	202.05	118799.70	1832.24	26.88	113.25	300018.73	2846.88	26.87	79.81	28511.47	4975.20	22.22	330.41	97126.28	1808.48	17.56	81.97	103678.10	312.48	20.07	93.12	134133.53	418.32	41.42	145.16
3480	145.0	12541.05	24774.41	74.00	81.64	24597.56				47519.18	3636.88	89.24	2460.42	35279.49	1612.06	20.43	202.06	118799.86	1832.24	26.88	113.26	300019.55	2846.88	26.87	79.82	28511.51	4975.20	22.22	330.42	97126.42	1808.48	17.56	81.98	103678.24	312.48	20.07	93.12	134133.67	418.32	41.43	145.16
3500	145.8	12613.20	24766.56	75.00	81.64	24571.91				47519.22	3636.88	89.25	2460.69	35279.55	1612.06	20.43	202.07	118799.99	1832.24	26.88	113.26	300020.37	2846.88	26.87	79.82	28511.53	4975.20	22.22	330.43	97126.56	1808.48	17.56	81.98	103678.38	312.48	20.07	93.13	134133.81	418.32	41.43	145.16
3520	146.7	12685.35	24758.71	76.00	81.64	24546.26				47519.27	3636.88	89.26	2460.96	35279.61	1612.06	20.43	202.08	118800.12	1832.24	26.88	113.27	300021.19	2846.88	26.88	79.83	28511.56	4975.20	22.23	330.45	97126.70	1808.48	17.57	81.98	103678.52	312.48	20.08	93.13	134133.94	418.32	41.44	145.20
3540	147.5	12757.50	24750.86	77.00	81.64	24520.61				47519.31	3636.88	89.27	2461.23	35279.67	1612.06	20.44	202.09	118800.26	1832.24	26.88	113.27	300022.01	2846.88	26.88	79.83	28511.58	4975.20	22.23	330.46	97126.84	1808.48	17.57	81.99	103678.66	312.48	20.08	93.13	134134.08	418.32	41.45	145.20
3560	148.3	12829.65	24743.01	78.00	81.64	24495.06				47519.35	3636.88	89.28	2461.50	35279.73	1612.06	20.44	202.10	118800.39	1832.24	26.89	113.27	300022.83	2846.88	26.89	79.83	28511.61	4975.20	22.23	330.48	97126.98	1808.48	17.57	81.99	103678.80	312.48	20.08	93.14	134134.18	418.32	41.45	145.21
3580	149.2	12901.80	24735.21	79.00	81.64	24469.51				47519.39	3636.88	89.29	2461.77	35279.79	1612.06	20.44	202.10	118800.52	1832.24	26.90	113.28	300023.65	2846.88	26.89	79.83	28511.64	4975.20	22.23	330.49	97127.12	1808.48	17.57	81.99	103678.94	312.48	20.08	93.14	134134.28	418.32	41.45	145.21
3600	150.0	12974.00	24727.41	80.00	81.64	24444.06				47519.43	3636.88	89.30	2462.04	35279.85	1612.06	20.44	202.11	118800.65	1832.24	26.90	113.28	300024.47	2846.88	26.89	79.84	28511.66	4975.20	22.24	330.51	97127.26	1808.48	17.57	82.00	103679.08	312.48	20.08	93.15	134134.40	418.32	41.46	145.22
3620	150.8	13046.15	24719.61	81.00	81.64	24418.51				47519.47	3636.88	89.31	2462.31	35279.91	1612.06	20.44	202.12	118800.78	1832.24	26.90	113.29	300025.29	2846.88	26.89	79.84	28511.68	4975.20	22.24	330.51	97127.40	1808.48	17.58	82.00	103679.22	312.48	20.09	93.15	134134.57	418.32	41.47	145.23
3640	151.7	13118.30	24711.81	82.00	81.64	24393.06				47519.49	3636.88	89.32	2462.58	35279.97	1612.06	20.45	202.13	118800.91	1832.24	26.91	113.29	300026.11	2846.88	26.90	79.85	28511.70	4975.20	22.24	330.52	97127.54	1808.48	17.58	82.00	103679.36	312.48	20.09	93.15	134134.68	418.32	41.47	145.23
3660	152.5	13190.45	24704.01	83.00	81.64	24367.51				47519.52	3636.88	89.33	2462.85	35279.98	1612.06	20.45	202.13	118801.04	1832.24	26.91	113.30	300026.93	2846.88	26.90	79.85	28511.71	4975.20	22.24	330.54	97127.68	1808.48	17.58	82.01	103679.50	312.48	20.09	93.16	134134.78	418.32	41.48	145.24
3680	153.3	13262.60	24696.21	84.00	81.64	24342.06				47519.55	3636.88	89.34	2463.12	35279.99	1612.06	20.45	202.14	118801.17	1832.24	26.91	113.30	300027.75	2846.88	26.90	79.85	28511.73	4975.20	22.25	330.55	97127.82	1808.48	17.58	82.01	103679.64	312.48	20.09	93.16	134134.88	418.32	41.48	145.24
3700	154.2	13334.75	24688.41	85.00	81.64	24316.51				47519.58	3636.88	89.35	2463.39	35279.99	1612.06	20.45	202.15	118801.30	1832.24	26.91	113.30	300028.57	2846.88	26.91	79.85	28511.75	4975.20	22.25	330.56	97127.96	1808.48	17.58	82.01	103679.78	312.48	20.09	93.16	134134.98	418.32	41.48	145.24
3720	155.0	13406.90	24680.61	86.00	81.64	24291.06				47519.60	3636.88	89.36	2463.66	35279.99	1612.06	20.46	202.15	118801.43	1832.24	26.91	113.31	300029.39	2846.88	26.91	79.85	28511.76	4975.20	22.25	330.57	97128.10	1808.48	17.58	82.01	103679.92	312.48	20.10	93.16	134135.08	418.32	41.48	145.24