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Sustainable Water Quality Monitoring for Developing Countries in the Context of Mining

Monitoring systems and modelling

Nhantumbo, Clemencio

2017

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Citation for published version (APA):

Nhantumbo, C. (2017). *Sustainable Water Quality Monitoring for Developing Countries in the Context of Mining: Monitoring systems and modelling*. (1st ed.). Water Resources Engineering, Lund University.

Total number of authors:

1

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Sustainable Water Quality Monitoring for Developing Countries in the Context of Mining

Sustainable Water Quality Monitoring for Developing Countries in the Context of Mining

Monitoring systems and modelling

Clemêncio M. Carlos Nhantumbo



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DOCTORAL DISSERTATION

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To be defended at the Faculty of Engineering, V-building, John Ericssons väg 1,
Lund, room V:B on June 1st, 2017 at 10:15 a.m.

Faculty opponent
Prof. Björn Klöve

Organization LUND UNIVERSITY Water Resources Engineering Box 118 SE-22100 Lund, Sweden Author Clemencio Nhandumbo		Document name: DOCTORAL THESIS
		Date of issue: 2017-06-01
		Sponsoring organization: Swedish International Development Cooperation (SIDA) and Lars Erik Lundberg Scholarship Foundation
Title and subtitle: Sustainable Water Quality Monitoring for Developing Countries in the Context of Mining - Monitoring systems and modelling		
Abstract Mining, seen as a source of revenue in most developing countries, threatens seriously the environment. Mining impacts the water quality and one of the main problems of mining is acid mine drainage. Low pH and high concentration of heavy metals characterize acid mine drainage. When a stream is impacted by acid mine drainage both human activities and the ecological system are seriously affected. In Mozambique coal mining is growing faster since 2010 while water quality monitoring programs are not well established and improvements are limited due to lack of skilled people and financial resources. The major coal reserves of Mozambique are located in the riparian area of Zambezi River Basin which is the largest river basin in Southern Africa with 11% of its catchment area in Mozambique. The Zambezi river basin in Mozambique has a high potential for development of human activities and its environment is rich and diversified. There are water quality monitoring systems already developed and successfully implemented in developed countries. However, these systems are not sustainable for developing countries due to lack of resources. A water quality monitoring system that (1) produces consistent and comparable water quality information; (2) provides feedback to outcomes and goals of the government; and (3) promotes continuous improvement of the water quality, in the context of mining development and under the constraint of lack of human and financial resources, is proposed for the Zambezi River Basin in Mozambique. The system includes two alternative monitoring procedures. It is concluded that the best way forward is to implement the first procedure which improves the current situation by using web-based data sharing and slowly move to the second procedure which is centralized and with one company doing water quality monitoring for the entire river basin in Mozambique. Modelling is an alternative solution for reducing the cost of monitoring by: (1) estimating difficult and costly to measure parameters based on others which are easily obtained and (2) simulating contamination and reclamation of already impacted streams thus shifting usage of resources to monitor water quality changes in more vulnerable areas. Existing surface water quality models have limitations in simulating contamination of streams by acidic discharges. OTIS and PHREEQ C are used for simulating mixing and transport of non-conservative pollutants but they fail when the task is to simulate pH in streams which are influenced by equilibrium reactions between the alkalinity species interacting with the surrounding environment. Within the scope of this work two models were developed, model (I) for estimating the concentration of inorganic ions in surface water, and model (II) for simulating pH and alkalinity in streams impacted by acidic discharges. The model (I) estimates the concentration of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) together with the maximum possible concentrations of minor ions and heavy metals (Fe^{2+} , Mn^{2+} , Cd^{2+} , Cu^{2+} , Al^{3+} , Pd^{2+} and Zn^{2+}) based on pH, alkalinity and temperature. The model (II) was developed and tested to simulate pH and alkalinity in the near field, mixing zone considering only the effect of carbonaceous alkalinity. Finally, the model (II) was extended to include the effect of iron (III) in the near field and a modelling methodology is proposed for simulating pH and alkalinity in the far field. The modelling methodology proposed is based on already demonstrated valid principles and the models results while not tested using laboratory or field data are as expected. The modelling methodology can be used for simulating processes in streams. For real cases calibration will be necessary by adjusting parameters such as the dispersion and mass transfer coefficients.		
Key words: Water Quality, Monitoring systems, Modelling, pH and alkalinity		
Supplementary bibliographical information		Language: English
ISSN and key title: 1101-9824		ISBN (print) 978-91-7753-250-7 ISBN (pdf) 978-91-7753-251-4
Recipient's notes	Number of pages	
	Security classification	

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Monitoring systems and modelling

Clemêncio M. Carlos Nhantumbo



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Faculty of Engineering, Department of Building & Environmental Technology
Division of Water Resources Engineering

ISBN (print) 978-91-7753-250-7

ISBN (pdf) 978-91-7753-251-4

ISSN 1101-9824

REPORT 1070

Printed in Sweden by Media-Tryck, Lund University
Lund 2016



Dedication

I dedicate my thesis to my children Carla, Clemêncio and Kyara.

In your weakness you have possibilities, use them wisely!

Acknowledgement

I thank my main supervisor Rolf Larsson for patient and close assistance for both academic and social issues during my studies. I am grateful to my co-supervisors, Magnus Larson and Dinis Juízo for encouraging and assisting me during my studies. I express great respect to Kenneth M Persson for encouraging and supporting me with chemistry in my work. I extend my gratitude to the assistance given by head of division Hans Hanson and the administrative personnel.

I acknowledge the support by the Swedish International Development Agency (SIDA) under the agreement EMU-SIDA 2011–2015 and a monthly stipend given by the Lars Erik Lundberg Scholarship Foundation that allowed me to prolongate my staying in Sweden during the last two years of my studies. I also thank Carlos Lucas the Head of Cooperation Department and Nelson Matsinhe, the coordinator of Integrated Water Resources Management under the agreement EMU-SIDA 2011-2015 at Eduardo Mondlane University (EMU) for their patient assistance.

I thank my parents Ana and Carlos for giving me life and basic education that allowed me to accept challenges in life and wisdom to turn them into achievements. I thank my wife, Carla for giving me the reason to do everything in my life, my children Kyara, Carla and Clemêncio Júnior. I thank my colleagues and all people that supported me with my work and social life during my doctoral studies. Finally, I express my gratitude to creator of life, I was taught to call him God, for giving me opportunity to be part of his amazing creation.

Popular summary

Mining is a source of revenue and it is now common in most developing countries. However, it might cause severe impacts to the environment and most of them are irreversible. Mining usually affects the rivers, lagoons and aquifers making its water inappropriate for human activities and living species. In some cases, the impacts of mining to the water resources come along time after the mining has ceased. When mining has ceased, the mining areas often become completely inappropriate for all kinds of live. Reclamation of areas impacted by mining is expensive and it takes a long time to get satisfactory results. The way mining is being done in developing countries, no money will be left to manage environmental problems after mining closure which makes the situation even worse.

In Mozambique, mining is developing fast since 2010. Huge reserves of coal were recently discovered in Tete province in the riparian areas of Zambezi River Basin. The Zambezi River Basin is the largest river basin in Southern Africa with rich and diversified environment and high potential for development of human activities such as agriculture, navigation, hydropower production and recreation. Mining threatens the environment in the riparian area of the river and the water quality is one of the major issues.

To allow actions protection of water resources, water quality monitoring programs are essential for understand the water quality changes while they are not well established in most developing countries. There are water quality monitoring systems developed and implemented successfully mostly in developed countries. Lack of skilled people and financial resources limits the implementation of water quality monitoring programs in developing countries. Improved water quality monitoring system that considers the lack of resources is necessary for developing countries in the context of mining development.

In this thesis, a water quality monitoring system, that takes into consideration the lack of skilled people and financial resources that can be used for developed countries in the context of mining development is proposed for Zambezi River Basin in Mozambique. The system values the outcomes and goals of the government aiming to guarantee financial support and the generation of good water quality information. The system considers first to improve data sharing within the entities doing water quality monitoring in the river basin and slowly move to a centralized approach, where one company does the water quality monitoring for the entire river basin. The centralized system will ensure consistence and comparability of the water quality data, while reducing the overall monitoring cost. However, it is expected to

be a challenge to convince all stakeholders, especially the coal mines to have the same company doing monitoring.

Models are proposed to be used for reducing the cost of water quality monitoring programs; either by (1) reducing the cost of sampling and analysis by estimating difficult and costly to measure parameters using others that are easy to measure at low cost; and (2) allocating the resources in areas where there is high risk of pollution identified by simulating acidification and reclamation of streams already impacted by acidic discharge. The last point is important for developing countries because the resources are limited.

Abstract

Mining, seen as a source of revenue in most developing countries, threatens seriously the environment. Mining impacts the water quality and one of the main problems of mining is acid mine drainage. Low pH and high concentration of heavy metals characterize acid mine drainage. When a stream is impacted by acid mine drainage both human activities and the ecological system are seriously affected.

In Mozambique coal mining is growing faster since 2010 while water quality monitoring programs are not well established and improvements are limited due to lack of skilled people and financial resources. The major coal reserves of Mozambique are located in the riparian area of Zambezi River Basin which is the largest river basin in Southern Africa with 11% of its catchment area in Mozambique. The Zambezi river basin in Mozambique has a high potential for development of human activities and its environment is rich and diversified.

There are water quality monitoring systems already developed and successfully implemented in developed countries. However, these systems are not sustainable for developing countries due to lack of resources. A water quality monitoring system that (1) produces consistent and comparable water quality information; (2) provides feedback to outcomes and goals of the government; and (3) promotes continuous improvement of the water quality, in the context of mining development and under the constraint of lack of human and financial resources, is proposed for the Zambezi River Basin in Mozambique. The system includes two alternative monitoring procedures. It is concluded that the best way forward is to implement the first procedure which improves the current situation by using web-based data sharing and slowly move to the second procedure which is centralized and with one company doing water quality monitoring for the entire river basin in Mozambique.

Modelling is an alternative solution for reducing the cost of monitoring by: (1) estimating difficult and costly to measure parameters based on others which are easily obtained and (2) simulating contamination and reclamation of already impacted streams thus shifting usage of resources to monitor water quality changes in more vulnerable areas. Existing surface water quality models have limitations in simulating contamination of streams by acidic discharges. OTIS and PHREEQ C are used for simulating mixing and transport of non-conservative pollutants but they fail when the task is to simulate pH in streams which are influenced by equilibrium reactions between the alkalinity species interacting with the surrounding environment.

Within the scope of this work two models were developed, model (I) for estimating the concentration of inorganic ions in surface water, and model (II) for simulating pH and alkalinity in streams impacted by acidic discharges. The model (I) estimates the concentration of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) together with the maximum possible concentrations of minor ions and heavy metals (Fe^{2+} , Mn^{2+} , Cd^{2+} , Cu^{2+} , Al^{3+} , Pd^{2+} and Zn^{2+}) based on pH, alkalinity and temperature. The model (II) was developed and tested to simulate pH and alkalinity in the near field, mixing zone considering only the effect of carbonaceous alkalinity.

Finally, the model (II) was extended to include the effect of iron (III) in the near field and a modelling methodology is proposed for simulating pH and alkalinity in the far field. The modelling methodology proposed is based on already demonstrated valid principles and the models results while not tested using laboratory or field data are as expected. The modelling methodology can be used for simulating processes in streams. For real cases calibration will be necessary by adjusting parameters such as the dispersion and mass transfer coefficients.

Papers

Appended papers

- I. Nhantumbo, C., Larsson, R., Juizo, D. & Larson, M., 2015. *Key issues for water quality monitoring in the Zambezi River Basin in Mozambique in the context of mining development*. Journal of Water Resources and Protection – [published]; DOI: [10.4236/jwarp.2015.75035](https://doi.org/10.4236/jwarp.2015.75035)
- II. Nhantumbo, C., Larsson, R., Larson, M., Juizo, D. & Persson, K., 2015. *A simplified model to estimate the concentration of inorganic ions and heavy metals in rivers*. Water Journal – [published]. DOI [10.3390/w8100453](https://doi.org/10.3390/w8100453);
- III. Nhantumbo, C., Carvalho, F., Uvo, C., Larson, M., & Larsson, R., 2017. *Applicability of a processes-based model and artificial neural networks to estimate the concentration of major ions in rivers*. Journal of Geochemical Exploration [submitted];
- IV. Nhantumbo, C., Larsson, R., Larson, M., Juizo, D. & Persson, K., 2017. *Simplified model to simulate pH and alkalinity in the mixing zone of surface water and acidic discharge (pH-mixing model)*. Mine Water and Environment – Submitted [under-review]
- V. Nhantumbo, C., Larsson, R., Larson, M., Juizo, D. & Persson, K., 2017. *Modelling pH and alkalinity in streams impacted by acidic discharges*. Journal of Hydrology [submitted].

Author's contribution to appended papers

- I. The author did the literature review, study visits to Zambezi River Basin, mining companies and government organization in Mozambique to collect information about mining activity and water quality monitoring in Zambezi River Basin. The author conducted two seminars together with co-authors in Maputo and Tete in Mozambique to discuss the water quality monitoring system and procedures proposed with relevant stakeholders. The author wrote the first version of the paper and participated in editing of the paper.

- II. The author developed the model and wrote the first draft of the paper with technical support of the co-authors. The author also participated in editing of the paper.
- III. The author did the comparative analysis of the physical processes based model and the artificial neural networks model and wrote the first draft of the paper. Co-authors supported in analysing data and editing of the paper.
- IV. The author with support of the co-authors developed the model and did laboratory experiments to generate data to test the model and wrote the first draft of the paper. The author also worked together with the co-authors in editing of the paper.
- V. The author developed the model, did the analysis of the results, and wrote the first draft of the paper with support of the co-authors. The author also worked with editing of the paper.

Other publications

- I. Nhantumbo, C., Larsson, R., Larson, M., Juizo, D. & Persson, K., 2015. *Applicability of water quality monitoring systems and models in developing countries in the context of mining development*. 5th International Conference on Environmental Science and Development. [published]. DOI: IJMAS-IRAJ-DOI-3873.
- II. Nhantumbo, C., Larsson, R., Larson, M., Juizo, D. & Persson, K., *Modelling pH and alkalinity in rivers impacted by acid mine drainage*. IMWA conference 2016 – [published].
https://www.imwa.info/docs/imwa_2016/IMWA2016_Nhantumbo_167.pdf;

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1.Introduction

1.1 Background

Mining has been impacting the water quality of rivers worldwide. Cases of mining impacting water resources have been reported in several countries such as USA, Brazil, Australia, Spain, South Africa, and China (Anawar, 2015; DPLF, 2014; ICMM, 2012; Ochieng, Seanego, & Nkwonta, 2010). The main issue of mining impacting water resources is acid mine drainage (AMD) (Anawar, 2015; Ochieng, Seanego, & Nkwonta, 2010). The impact of AMD to the environment can be over a long period such as for Rio Tinto in Spain or severe as the Iron Mountain in California (Olías & Nieto, 2015; Nordstrom, Alpers, Ptacek, & Blowes, 2000) . Water quality monitoring is essential, when water is impacted or at risk of being impacted, for allowing adoption of management solutions to protect the environment before severe damages occur.

Mining is now common in most developing countries while water quality monitoring programs are not well established (Paper I). In Mozambique coal production was expected to grow from about 0.036 million tons in 2010 to 20 million tons in 2015 (Paper I). The largest coal mining area in Mozambique is located in Zambezi River Basin which is the largest river basin in Southern Africa and has about 11% of its total area in Mozambique (Paper I). Monitoring programs in developing countries are limited regarding the number of parameters monitored and the volume of samples analyzed. Although efforts are made, lack of human and financial resources limit improvements (Paper I). Poor legislation is also limiting water quality monitoring in developing countries (Pondja, Persson, & Matsinhe, 2016).

A water quality monitoring system improved and supported by models are an alternative solution (Paper I, Paper II). Water quality monitoring systems and models are used mostly in developed countries. The most well-known water quality monitoring systems are (1) Result-Based Monitoring and Evaluation, (2) Framework for Water Quality Monitoring, and (3) Monitoring System adopted by the European Union (EU) under EU Water Framework Directive (Paper I). However, these systems were not developed to be used for cases where there is mining development with limited resources to do water quality monitoring (Paper

D). There are also models that can be used to support water quality monitoring such as Streeter–Phelps, the QUAL, WASP, QUASAR, MIKE, BASIN, EFDC, and PHREEQ C (Wang, Li, Jia, Qi, & Ding, 2013). However, none of these models were developed specifically to deal with water quality evolution in rivers affected by mining. The models also require a lot of input data to perform simulations, while such data are not readily available in most developing countries (Paper II).

1.2 Objectives

The main objective of this thesis is to suggest improved water quality monitoring system supported by models. The system is to be used for monitoring water quality in the context of mining in developing countries where human and financial resources are limited.

To fulfil the main objective the following specific objectives were formulated:

- Review available water quality monitoring systems and suggest one for Zambezi River Basin based on the existing conditions;
- Evaluate the applicability of available surface water quality models in the context of mining development;
- Develop a model for reducing sampling and analysis, thus reducing the cost of water quality monitoring programs;
- Develop a model for simulating contamination of streams due to acidic discharge.

Although, improved water quality monitoring systems are of interest for most developing countries. The Zambezi River Basin was selected as study area to make the results of the study more specific. Still, data from Swedish rivers was used to test the developed model due to lack of data in Zambezi River Basin and other rivers in developing countries.

1.3 Methods

The thesis was based on literature reviews, site visits, laboratory experiments and developing computer model algorithms using Python, Fortran and MATLAB. Literature reviews conducted were focused on the available water quality monitoring systems, and models that can be used in developing countries in the context of mining development as well as for understanding the main problems of mining and theories used for modelling. Site visits were conducted to (i) an area already impacted by coal mining, Criciúma in Brazil, to understand the common problems of mining as well as, (ii) to the coal mining area, Zambezi River Basin

and the institutions responsible for doing water quality monitoring in Mozambique, to understand the main problems of water quality monitoring. Laboratory experiments were performed to generate data to test the model for simulating pH and alkalinity at the mixing zone. Finally, the models were converted into three computer algorithms, (1) for estimating inorganic ions in water, (2) for simulating pH and alkalinity in the near field mixing zone when acidic water is discharged into a stream, and (3) for simulating pH and alkalinity downstream the mixing zone.

1.4 Limitations

Lack of data made it impossible to test the models for rivers in developing countries where the models are expected to be used. Data from Swedish rivers was used to test model 1, while laboratory data was used for testing model 2 for simulating pH and alkalinity in the mixing zone. The model 2 which can be used to get a first estimate of pH and alkalinity in the mixing zone still needs some improvement for simulating contamination by acid mine drainage. An extension of the model to include more alkalinity species is also necessary,

Model 2 is further extended to simulate pH and alkalinity in the near field mixing zone by including iron as well as for simulating the process downstream of the mixing zone. The model was developed based on already validated theories and concepts. However, due to the complexity of the model and the limited time for concluding this study it was not possible to gather data to test the extended model.

2. Study area

The riparian area of Zambezi River Basin in Tete province was selected as study area. This area was selected because it has the largest coal reserves of Mozambique and coal mining is developing faster since 2010 while a water quality monitoring program is not well established. The region has rich biodiversity and has high potential for development of human activities such as agriculture and hydropower production. An improved water quality monitoring program that allows understanding of water quality changes is necessary for sustainable management of water resources.

2.1 Zambezi River Basin

The Zambezi River Basin (ZRB) is the largest river basin in Southern Africa with about 1 370 000 km² and average discharge at the outlet of 4100 m³/s (World Bank, 2009). Eleven percent (11%) of total area of ZRB is in Mozambique. ZRB sustains life of about 30 million people and keeps the natural environment rich and diversified. The river is essential for the economy of its riparian countries which include Angola, Botswana, Malawi, Mozambique, Namibia, Tanzania, Zambia, and Zimbabwe, see Figure 1 (World Bank, 2009).

The average precipitation in ZRB is 950 mm/year. Due to uneven rainfall distribution, the north part of the river basin contributes with more runoff compared to the south part. The highest precipitation, about 2400 mm/year has been observed in the northeast part of the basin, and the lowest, about 500 mm/year in the southeast part. The main stream of ZRB crosses the Mozambican border with an average flow of about 2300 m³/s. On its way through Mozambique it receives another 1800 m³/s, about 70% out of which comes from the mining area (Paper I).

Twelve dams and almost 53 new projects of dams were being analysed until 2008. The total installed capacity for energy production in Zambezi River is approximately 5000 MW. The largest hydroelectric power plant is Cahora-Bassa dam (2075 MW), which is located in Tete province in Mozambique (World Bank, 2009). Zimbabwe had the largest irrigated area among the riparian countries with 108 717 ha compared to Mozambique, which only has 8 436 ha. However, studies show that Mozambique has higher potential for irrigation compared to all other

riparian countries with about 600 000 ha (World Bank, 2009). Ninety percent (90%) of urban and fifteen percent (15%) of rural domestic water supply in the ZRB is from surface water, whereas the remaining water supply is from groundwater sources (SADC-WD/Zambezi River Authority, 2007).

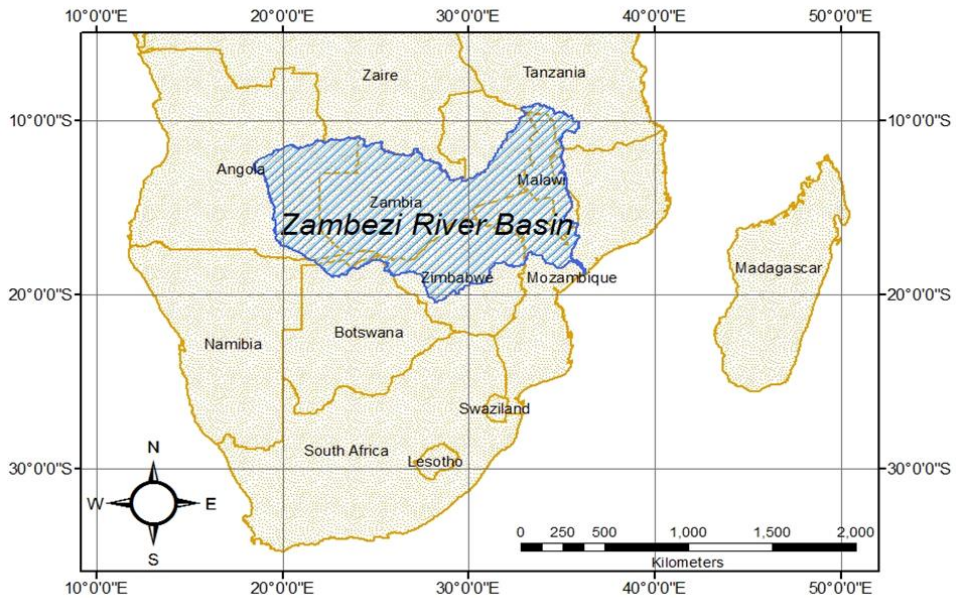


Figure 1 Zambezi River Basin (Paper I)

2.2 Coal mining

Coal mining in Mozambique started during the colonial period in 1920 by Portuguese companies (Alexandre, 2012). The highest production before 2004, about 575 000 tons/year was reached in 1981 (Alexandre, 2012). In 2004, the Mozambican government launched an international contest for the development of the Moatize Coal Reserve that was won by Companhia do Vale do Rio Doce (Alexandre, 2012). In 2014 there were more than 60 licenses and 40 requests for licenses for coal mining in Mozambique that are owned by around 30 companies, **Figure 2**. There were three companies extracting coal at the end of 2011, all of which were located in Moatize. Until 2012 seven companies were extracting coal in

Tete: Vale Moçambique, Rio tinto, Minas de Moatize, Jindal in Changara district, ENRC, Ncondedzi Coal Company, and Minas Revúbue (Paper I).

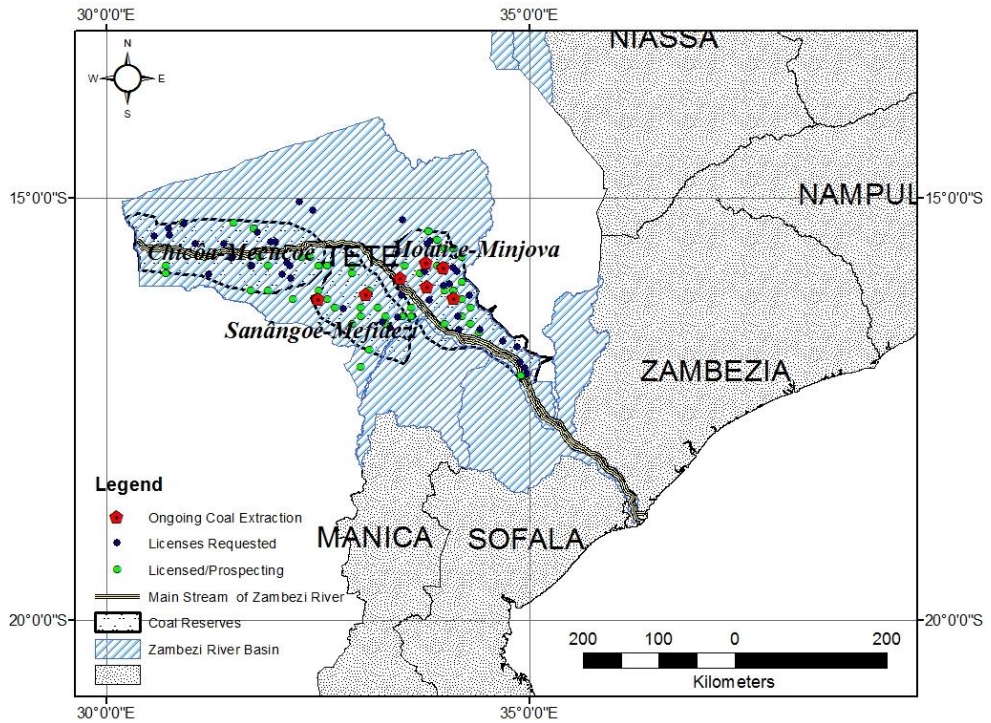


Figure 2 Coal mining in Zambezi River Basin in Mozambique (paper I)

The ministry of Mineral Resources (MIREM) has produced projections of coal production in Mozambique that show a growth of coal production from 2.9 million of tons in 2011 to 39.0 million of tons in 2019. After this peak the production would reduce to 6.7 million of tons until 2028. However, coal production in Mozambique reduced already in 2015 due to lowering of prices of coking coal in the international market. The coking coal cost was less than 100 USD per tonne after 2015. However, since November 2016 the price of coking coal in the international market rose to 260-270 USD/tonne, and as a result the coal production in Mozambique is increasing again (Scala, 2017).

2.3 Water Quality Monitoring in Zambezi River Basin

A river basin organization, Zambezi Watershed Commission (ZAMCOM) was created in 1995 and came into force in 1998. The organization was created to promote equitable and reasonable utilization of the water resources of the Zambezi watershed as well as efficient sustainable management for the river basin. Unfortunately, lack of resources and low data availability limit the implementation of sustainable, integrated water resources management.

ARA – Zambeze is the regional administration of water responsible for the management of Zambezi River Basin in Mozambique (Paper I). Three types of monitoring are done in the Zambezi River Basin: Surveillance, Operational, and Investigative Monitoring. Surveillance Monitoring is done by ARA-Zambeze, and includes only the basic parameters: temperature, pH, electric conductivity, total dissolved solids, dissolved oxygen, ortho redox phosphate, salinity, turbidity, color, smell, chlorates, total coliforms, and fecal coliforms (ARA-Zambeze, 2012). Operational monitoring is done by the companies using and/or affecting the water of the river. Finally, investigative monitoring is performed by the Institute of Fish Investigation of Songo and other research institutions (Paper I). However, the lack of resources limits the water quality monitoring performed in ZRB. Thereby is not allowing understanding of water quality changes to protect the water resources (Paper I). Understanding water quality changes gets even more important due to mining development within the river basin in Mozambique.

Industries including mining companies, that could impact the environment during their activities have obligation under Mozambican legislation of doing environmental impacts assessment and submit the reports to the Ministry of Land, Environment, and Rural Development before starting their activities. Additionally, industries which have high probability of impacting water resources have obligation of doing water quality monitoring in their area of influence and submit periodical physical reports to the river basin organization. For the case of coal mines with their activities based in the riparian area of Zambezi River Basin in Mozambique, the reports are submitted to ARA-Zambeze. However, the capability of ARA-Zambeze in doing operative oversight for the water quality monitoring done by the mining companies is limited and there is no way of making sure that the water quality monitoring information in the submitted reports is accurate.

3. Water Quality Monitoring Systems

As stated before, a water quality monitoring system for the Zambezi River Basin that takes into consideration the lack of human and financial resources in the context of mining development is to be proposed. The system should be based on available water quality monitoring systems and the actual conditions in Zambezi River Basin as described in chapter 2.

3.1 Review of water quality monitoring systems

A variety of water quality monitoring systems have been developed. As mentioned in the introduction, the most well-known systems are (1) Result-Based Monitoring and Evaluation, (2) Framework for Water Quality Monitoring, and (3) Monitoring System adopted by the European Union (EU) under the EU Water Framework Directive. These systems have differences and similarities depending on the objective for which they were developed.

i) Result-Based Monitoring and Evaluation (World Bank)

The World Bank has adopted the Result-Based Monitoring and Evaluation System (RMES) for integrated water resources management (IWRM Plan Joint Venture Namibia, 2010). RMES is an improved version of Implementation-Focused Monitoring and Evaluation, designed to address the “did they do it?” question. The main weakness of the Implementation-Focus Monitoring and Evaluation is that it does not provide the policymakers with information on success or failure of the project, program, or policy (Kusek & Rist, 2004).

RMES was designed to answer the “so what?” question, which it does by providing feedback on actual outcomes related to the goals of the government (Kusek & Rist, 2004). The system also checks if the water quality is being protected with implemented actions. The system scheme is presented as a table and has 10 steps, see figure 3.

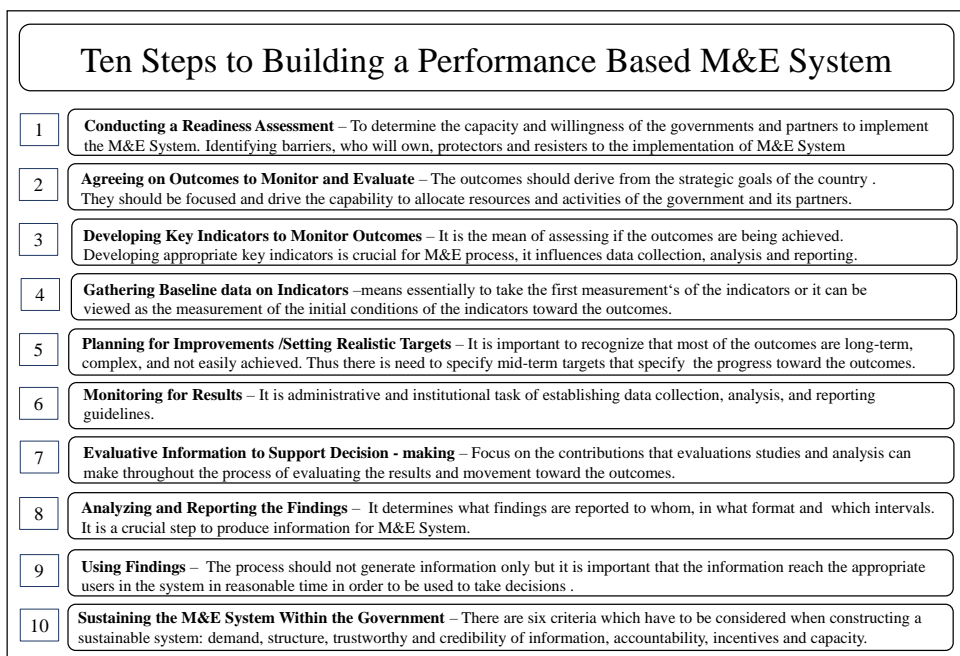


Figure 3 Ten Steps for building a result-based monitoring and evaluation system (RMES) adapted from: (Kusek & Rist, 2004) and (IWRM Plan Joint Venture Namibia, 2010) (Paper I)

Although monitoring objectives are not explicitly defined, RMES includes three issues which are not considered in the other monitoring systems: 1) selecting the key indicators that determine the willingness of the different stakeholders to cooperate with the monitoring; 2) defining the monitoring outcomes; and 3) sustaining the system within the government. This system was designed to ensure that the government goals are satisfied intending to guarantee support for the monitoring program.

The Ministry of Agriculture, Water and Forest of Namibia proposed the use of RMES during the implementation of Integrated Water Resources Management (IWRM) (IWRM Plan Joint Venture Namibia, 2010). In the context of implementing IWRM the Namibian government discussed a funding allocation procedure for involving all water users. This brings up the fourth principle of the Dublin Statements which considers water as an economic good and states that the users should pay for the use of water to guarantee availability, management, and conservation of the resource. This system was also implemented in some developed countries, such as Australia, Canada, Netherlands, and United States (Kusek & Rist, 2004).

ii) Framework for Water Quality Monitoring (US-NWQMC)

The Framework for Water Quality Monitoring (FWQM) was developed and implemented in the USA. This system was developed to enhance production of consistent and comparable water quality information by (1) analyzing the characteristics and trends of water quality; (2) identifying emerging water quality issues; and (3) checking the compliance with regulations to support fair and equitable water resources management (AWRA, 2004; Peter & Ward, 2004). A graphical representation of FWQM was proposed by the National Water Quality Monitoring Council (NWQMC), see Figure 4a.

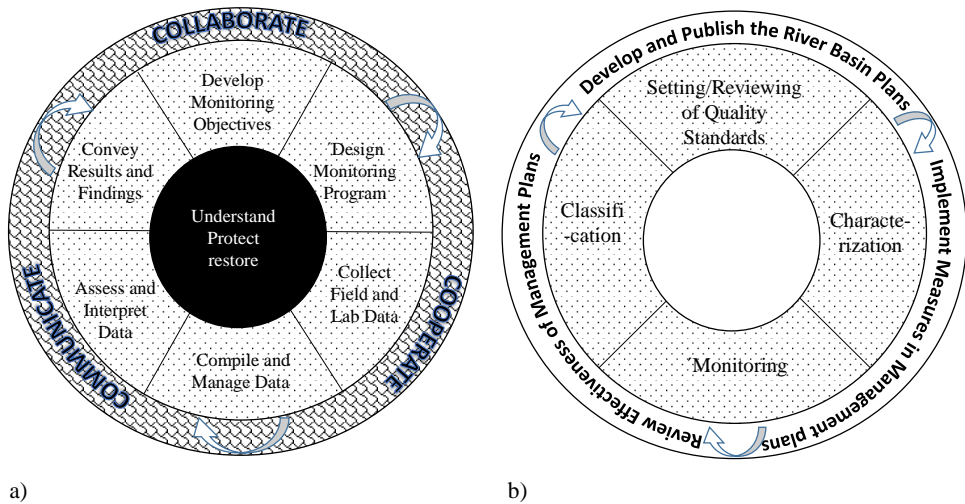


Figure 4 a) Framework for water quality monitoring (FWQM) adapted from NWQMC (AWRA, 2004). b) River Basin Management Planning Cycle adopted by European Union through EU-WFD. (adapted from Paper I)

The system has a cyclic approach with six elements, Figure 4a: 1) develop monitoring objectives; 2) design monitoring program; 3) collect field and laboratory data; 4) compile and manage data; 5) assess and interpret data; and 6) convey results and findings. Additionally, four issues must be considered when implementing the FWQM: identify data users; engage monitoring partners; evaluate the monitoring program; and use information technology to connect the framework elements (Peter & Ward, 2004). The system also values communication, collaboration and cooperation as means for meeting the monitoring objectives which are typically defined to answer the following questions: (1) Is the water acceptable as potable water or for swimming and other aquatic uses or habits?; (2) Is the water quality getting better or worse?; (3) Is the water quality changing due to certain water uses or management?; (4) Are the water quality requirements being met? and (5) How

does the water quality of a certain water body compare with other water bodies? (AWRA, 2004; Spooner & Mallard, 2004).

iii) *Water Resources Monitoring System Adopted under the EU Water Framework Directive*

The European Union through the European Union Water Framework Directive (EU-WFD) adopted the River Basin Management Planning Cycle, Figure 4b. This cycle includes two cycles presented in the inner and outer rings of a circle. The outer ring describes the process which has to be followed for implementing management options and the inner ring describes continuous investigation of water quality changes. The outer ring has three steps for implementing management options: 1) Develop and Publish the River Basin Plans; 2) Implement Measures in Management plans; and 3) Review Effectiveness of Management Plans. The inner ring has three steps as well: 1) Setting/Reviewing of Quality Standards; 2) Characterization; Monitoring; and 3) Classification. The inner ring aims to guarantee that the water quality changes are understood and the outer ring aims to guarantee that the management options are continuously being implemented and improved based on the results of previously implemented management options and water quality changes obtained from water quality monitoring.

The EU-WFD distinguishes three types of water quality monitoring programs: surveillance, operational and investigative monitoring. Surveillance monitoring gives the overall water quality status within the catchment. Operational monitoring is required where pollution or other types of impacts on ecological status is apparent. Investigative monitoring is required when the surveillance monitoring shows that the objectives are not being met and when the operational monitoring is not yet established.

3.2 Water Quality Monitoring System for Zambezi River Basin

Water quality monitoring systems have been implemented successfully in developed countries. The main reason for failure of water quality monitoring programs in developing countries is lack of skilled people and financial resources. In developing countries, few activities are fully funded compared to the ones that are proposed or necessary. Immediate education and health problems such as reducing the level of illiteracy as well as fighting epidemic diseases have priority compared to water quality monitoring. Thus, it is important to show that water quality monitoring is a key issue to guarantee continuous access to basic needs such

as potable water and productive agricultural land. Focusing on the government goals and outcomes is a key issue for getting support for water quality monitoring programs as suggested in RMES. However, it is important to have a system that guarantees production of consistent and comparable water quality data as well as continuous improvement of the system using a cyclic view as the FWQM and EU-WFD.

A system that combines the principles of FWQM, RMES and EU-WFD is proposed for ZRB, Figure 5 (Paper I). The system is proposed to produce consistent and comparable water quality information; providing feedback to outcomes and goals of the government; while guaranteeing continuous improvement of the system, in the context of mining development and under the constraint of lack of human and financial resources. The system has two levels, the *higher level* and the *operational level*. At *higher level* the monitoring system starts by reviewing the government goals as defined by national legislation and ends reviewing if the government goals and outcomes are satisfied. At *operational level* the monitoring system starts by selecting the target pollution sources to guarantee that more resources are used where the likelihood of having water contamination is higher and ends by using the findings for defining water protection measures.

Two alternative water quality monitoring procedures are proposed to operationalize the monitoring system where each stakeholder has its duty clearly defined, Figure 6 and 7 (Paper I). The first monitoring procedure is based on an improved data sharing system, where companies doing water quality monitoring for different reasons in the river basin as well as the government organizations have a common web-based water quality database. The water quality database should allow for doing overall water quality change analyses in the river basin as well as water quality trend analyses. The second water quality monitoring procedure, is based on having one single consulting company responsible for doing water quality monitoring for the entire river basin. The companies, and the government organizations should pay the company for water quality monitoring according to their interests. The latter procedure has advantages compared to the first procedure such as: (1) making sure that all water samples are analyzed using the same methods allowing comparability and more accurate trend analysis; (2) reducing the water quality monitoring cost by reducing the number of samples analyzed by the same equipment. However, the second procedure has challenges, such as: (1) convincing all stakeholders to accept having the same company doing water quality monitoring in their area of influence; (2) ARA-Zambeze has to guarantee that the consulting company is producing good water quality monitoring data by doing operational oversighting.

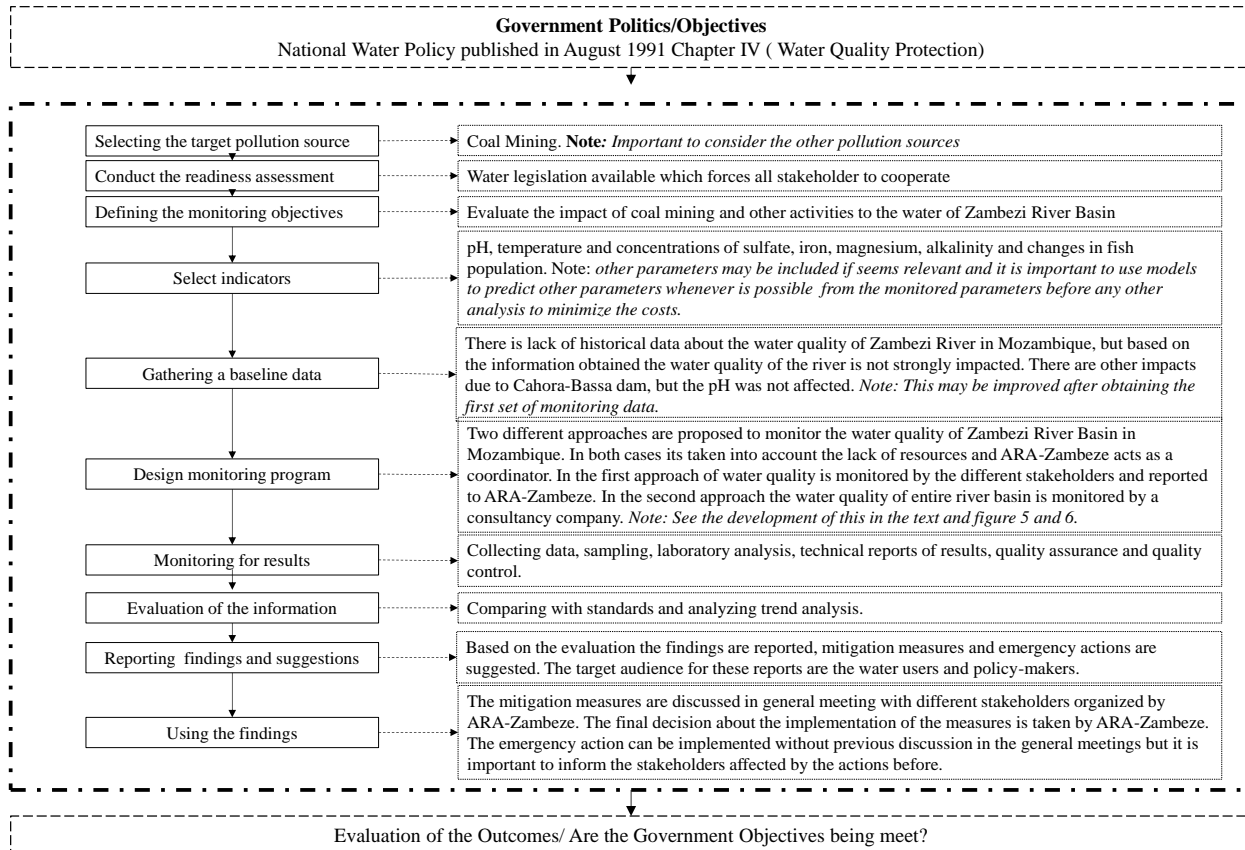


Figure 5 Water quality monitoring system proposed for Zambezi River Basin (Paper I)

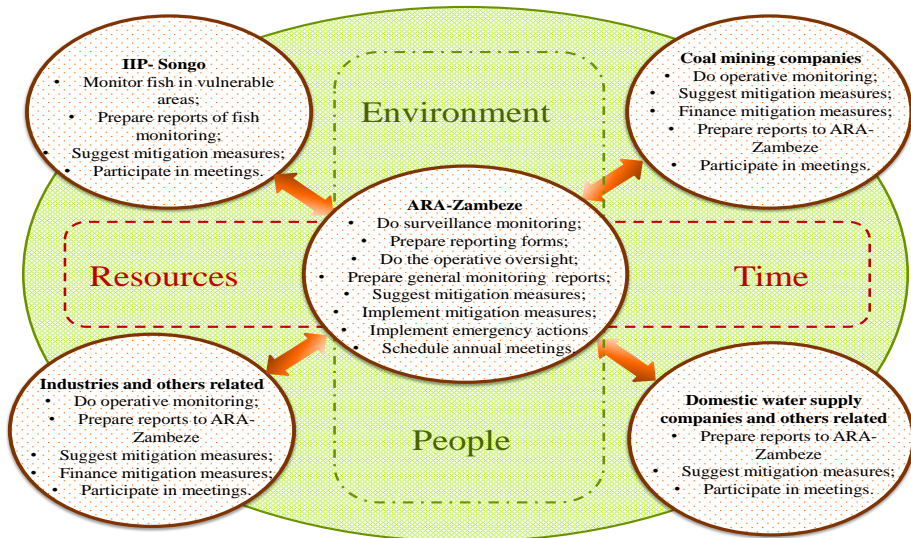


Figure 6 First suggested procedure for water quality monitoring for Zambezi River Basin. Improved data sharing system (Paper I).

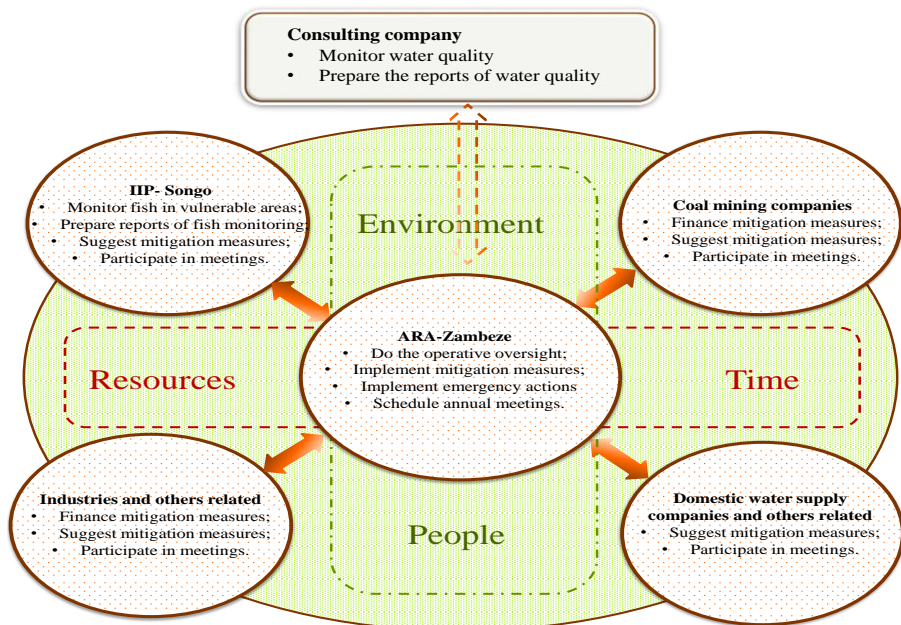


Figure 7 Second suggested procedure for water quality monitoring for Zambezi River Basin. All monitoring performed by one consulting company (Paper I)

As mentioned before the water quality monitoring system is proposed aiming to guarantee that the government goals and outcomes are satisfied; the water quality information generated is consistent and comparable; and the system still yields satisfactory water quality data even though there is a lack of resources. The *higher level* aims to guarantee that the government goals are satisfied, thus ensuring continuous support for the water quality monitoring system. The *operational level* aims to guarantee generation of consistent and comparable water quality data with continuous improvement of the water quality monitoring system. Finally, the proposed procedures aim to generate sufficient water quality information even though there is a lack of resources, through efficient data sharing within the stakeholders (first procedure, figure 6) and centralizing the water quality monitoring (second procedure, figure 7). The other tool which is expected to be used for reducing the water quality monitoring cost are models, discussed in chapter 4.

4. Use of Models for Water Quality Monitoring

Models can be used together with improved water quality monitoring systems for reducing the need for skilled people and financial resources. Models can be used for: (1) estimating water quality parameters based on the ones that are easy to measure, thus reducing the cost of sampling and analysis needed for water quality monitoring (Paper II); and (2) simulating different scenarios of pollution allowing for properly planning of water quality monitoring and reclamation of impacted streams (Paper IV). Simulating contamination of streams due to available sources of pollution as well as simulating reclamation of streams allows allocating resources in areas with high risk of pollution. Proper allocation of resources is important particularly when they are limited.

Mining activity typically impacts water quality by: (1) increasing turbidity and total solids concentration; (2) lowering pH, thus affecting the solubility of minerals in the stream bed and increasing the concentration of heavy metals, known as acid mine drainage (AMD); and (3) causing precipitation of minerals such as iron hydroxide that coat the stream bed (Paper II). AMD is one of the major issues of mining. Monitoring and understanding pH changes in water is crucial when there is mining (Paper II). Thus, it is important (1) to have models that can simulate pH change in streams impacted by acidic discharge; and (2) to have a model that estimate other parameters based on pH to be used in streams impacted by acidic discharges since pH influence several water quality parameters.

Surface water quality models such as Streeter-Phelps, QUAL, WASP, QUASAR, MIKE, BASIN Model, EFDC, OTIS and PHREEQ C can be used for simulating processes in streams (Walton-Day, Paschke, Runkel, & Kimball, 2007; Wang, Li, Jia, Qi, & Ding, 2013). Some of these models cannot simulate pH such as the Streeter-Phelps model which was developed to simulate oxygen balance as a first order biological oxygen demand decay (Rinaldi & Soncini-Sessa, 1977). While models such as OTIS and PHREEQ C can be used to simulate mixing and transport of non-conservative pollutants (Parkhurst & Appelo, 2013; Walton-Day, Paschke, Runkel, & Kimball, 2007), PHREEQ C is also used to simulate speciation of water, estimating concentration of soluble ions based on mineralogy (Parkhurst & Appelo, 2013).

When using PHREEQ C for simulating either speciation or mixing in streams it is assumed that there is equilibrium of water with stream bed minerals such as calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$) and/or gypsum ($CaSO_4 \cdot 2H_2O$) as well as with CO_2 in the atmosphere (Parkhurst & Appelo, 2013). When acidic water is discharged into a stream the equilibrium of alkalinity species (H^+ , OH^- , CO_3^{2-} , HCO_3^- , and H_2CO_3) within the water column is reached in shorter time compared to the time necessary to reach equilibrium with stream bed minerals and CO_2 in the atmosphere at the lower and upper boundaries respectively. Lower values of pH and different concentrations of dissolved ions might characterize the mixing zone compared to the one estimated using equilibrium with stream bed minerals and CO_2 in the atmosphere. When using OTIS to simulate mixing, only the dilution effect is considered, while equilibrium between the alkalinity species cannot be simulated (Walton-Day, Paschke, Runkel, & Kimball, 2007).

Two models are proposed, the first model (Model 1) to estimate the concentration of major ions based on pH, alkalinity and temperature; and the second model (Model 2) to simulate pH and alkalinity in the mixing zone as well as the reactional transport process downstream the mixing zone in streams impacted by acidic discharges, Figure 8. The models can be used separately, but they can also be combined to get a water quality model that simulates pH and alkalinity in streams impacted by acidic discharges as well as getting speciation in terms of inorganic ions.

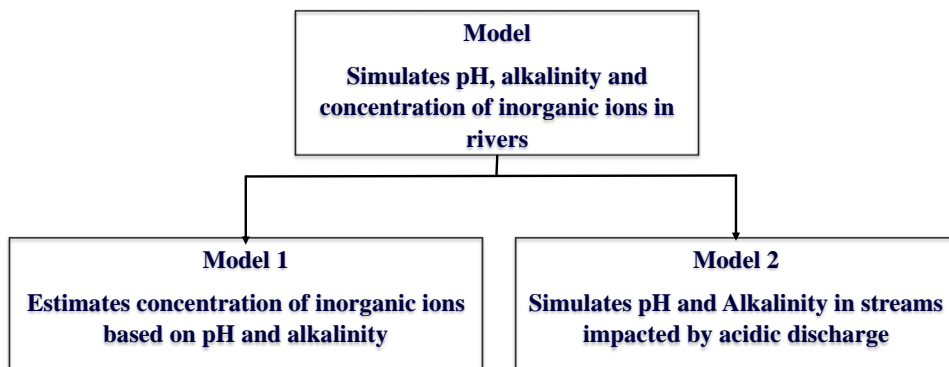


Figure 8 Modelling strategy. The model has two components, model 1 which estimates the concentration of major ions based on pH, alkalinity and temperature and model 2 which estimates pH and alkalinity in the near field, mixing zone and further downstream in the far field.

4.1 Theory

For the modelling, the following concepts and theories were used: carbonic acid and iron hydroxide (III) dissociation, total alkalinity, protolithic theory of water; major ions, solubility, conductivity, and mass flux. The main idea behind the modelling is to combine existing theories and concepts to develop water quality models that can be used for minimizing the water quality monitoring costs in streams impacted by acidic discharges.

i) Carbonic acid equilibrium

Carbonate equilibrium defined by reactions equations 1, 1a, 2 and 2a relates pH with concentration of carbonate alkalinity species in water. Equilibrium constants can be estimated using temperature dependent correlations (Appelo & Postma, 1999).



$$K_{a1} = \frac{[H^+] \times [HCO_3^-]}{[H_2CO_3]} \quad (1a)$$



$$K_{a2} = \frac{[H^+] \times [CO_3^{2-}]}{[HCO_3^-]} \quad (2a)$$

The sum of concentration of all inorganic carbon species is called total inorganic carbon (TIC). TIC is conservative with respect to mixing and is calculated using equation 3.

$$TIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (3)$$

The concentration of each inorganic specie is calculated using equations (4)-(6). The values of the constants, $\alpha_{H_2CO_3}$, $\alpha_{HCO_3^-}$, and $\alpha_{CO_3^{2-}}$ represent the contribution of each carbonate specie to the TIC and the sum of their values is therefore equal one.

$$[H_2CO_3] = \alpha_{H_2CO_3} \cdot TIC \quad (4)$$

$$[HCO_3^-] = \alpha_{HCO_3^-} \cdot TIC \quad (5)$$

$$[CO_3^{2-}] = \alpha_{CO_3^{2-}} \cdot TIC \quad (6)$$

The constants $\alpha_{H_2CO_3}$, $\alpha_{HCO_3^-}$, and $\alpha_{CO_3^{2-}}$ are calculated as functions of the concentration of hydrogen ions and equilibrium constants, equations (7)-(9). These equations are obtained combining equations 1a, 2a, 3 and (4)-(6).

$$\alpha_{H_2CO_3} = \frac{[H^+]^2}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2}} \quad (7)$$

$$\alpha_{HCO_3^-} = \frac{K_{a1} \cdot [H^+]}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2}} \quad (8)$$

$$\alpha_{CO_3^{2-}} = \frac{K_{a1} \cdot K_{a2}}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2}} \quad (9)$$

ii) *Iron hydroxide (III) equilibrium*

Using the analogy with carbonic acid equilibrium, iron hydroxide (III) equilibrium is described by equations (10)-(12). The equilibrium constants are calculated using equations (10a)-(12a). The values of constants are available in the literature for 25°C (Appelo & Postma, 1999).



$$K_1 = \frac{[Fe(OH)_2^+] \cdot [OH^-]}{[Fe(OH)_3]} \quad (10a)$$



$$K_2 = \frac{[Fe(OH)^{2+}] \cdot [OH^-]}{[Fe(OH)_2^+]} \quad (11a)$$



$$K_3 = \frac{[Fe^{3+}] \cdot [OH^-]}{[Fe(OH)^{2+}]} \quad (12a)$$

The sum of concentration of all iron species (III) is called total iron (III). Like TIC, total iron (III) (*TFe*) is also conservative with respect to mixing. Total iron (III) is calculated using equation 13.

$$TFe = [Fe(OH)_3] + [Fe(OH)_2^+] + [Fe(OH)^{2+}] + [Fe^{3+}] \quad (13)$$

The concentration of each iron specie can be calculated using equations (14)-(16). The values of constants, $\beta_{Fe(OH)_3}$, $\beta_{Fe(OH)_2^+}$, $\beta_{Fe(OH)^{2+}}$, and $\beta_{Fe^{3+}}$ represent the contribution of each iron (III) specie to the total iron (III) and the sum of their values is therefore equal one.

$$[Fe(OH)_3] = \beta_{Fe(OH)_3} \cdot TFe \quad (14)$$

$$[Fe(OH)_2^+] = \beta_{Fe(OH)_2^+} \cdot TFe \quad (15)$$

$$[Fe(OH)^{2+}] = \beta_{Fe(OH)^{2+}} \cdot TFe \quad (16)$$

$$[Fe^{3+}] = \beta_{Fe^{3+}} \cdot TFe \quad (17)$$

The constants $\beta_{Fe(OH)_3}$, $\beta_{Fe(OH)_2^+}$, $\beta_{Fe(OH)^{2+}}$, and $\beta_{Fe^{3+}}$ are calculated as a function of concentration of hydroxide ions and equilibrium constants, equations (18)-(21). This equations are obtained combining equations 10a, 11a, 12a, 13 and (14)-(17).

$$\beta_{Fe(OH)_3} = \frac{[OH^-]^3}{[OH^-]^3 + K_1[OH^-]^2 + K_1K_2[OH^-] + K_1K_2K_3} \quad (18)$$

$$\beta_{Fe(OH)_2^+} = \frac{K_1[OH^-]^2}{[OH^-]^3 + K_1[OH^-]^2 + K_1K_2[OH^-] + K_1K_2K_3} \quad (19)$$

$$\beta_{Fe(OH)^{2+}} = \frac{K_1K_2[OH^-]}{[OH^-]^3 + K_1[OH^-]^2 + K_1K_2[OH^-] + K_1K_2K_3} \quad (20)$$

$$\beta_{Fe^{3+}} = \frac{K_1K_2K_3}{[OH^-]^3 + K_1[OH^-]^2 + K_1K_2[OH^-] + K_1K_2K_3} \quad (21)$$

iii) Protolithic water theory

The dissociation constant of water determines the relationship between molar concentration of H^+ and OH^- in water at a specific temperature. Equations 22 and 23 show the chemical and mathematical interpretation of protolithic theory of water. For convenience, the concentration of H^+ is usually expressed in terms of pH,

equation 24. The dissociation constant of water are estimated using the temperature-dependent empirical equation (Appelo & Postma, 1999).



$$K_w = [H^+] \cdot [OH^-] \quad (23)$$

$$pH = -\log_{10}([H^+]) \quad (24)$$

iv) Total alkalinity

Alkalinity is defined as the ability of water to neutralize acids. It expresses the excess of proton donors over the proton acceptors (Wolf-Gladrow, Zeebe, Klaas, Körtzinger, & Dickson, 2007). Alkalinity also reflects the excess of chemical bases of the solution relative to an arbitrarily specified zero level, or equivalent point (Munhoven, 2013). Total alkalinity (TA) can be determined with higher accuracy using complex equations, such as equation 25.

Ideally, the TA represents the amount of bases contained in a sample of the natural water that will accept a proton when a sample is titrated with a strong acid to the carbonic acid end point. The carbonic acid end point is the point where the hydrogen protons H^+ become more abundant than hydrogen carbonate ions HCO_3^- . The carbonic acid end point is close to a pH equal 4.3. AMD samples may present negative alkalinity, meaning that a strong base instead of a strong acid must be added to reach the carbonic acid end point (Munhoven, 2013).

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [H_3SiO_4^-] + [NH_3] + [HS^-] + 2[S^{2-}] + \dots - ([H^+] + [HSO_4^-] + [HF] + [H_3PO_4] + \dots) \quad (25)$$

The alkalinity as defined above is a conservative quantity with respect to mixing in water, and with respect to changes in temperature and pressure (Wolf-Gladrow, Zeebe, Klaas, Körtzinger, & Dickson, 2007). Normally, in natural waters the carbonate alkalinity is the most important part of the TA. Equation 25 can therefore be reduced to equation 25a.

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \quad (25a)$$

Equation 26 expresses total alkalinity as function of concentration of hydrogen protons. The equation is obtained combining equations (3)-(9), 23, and 25a.

$$TA = \frac{K_{a1} \cdot [H^+] + 2K_{a1} \cdot K_{a2}}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2}} \cdot TIC + \frac{K_w}{[H^+]} - [H^+] \quad (26)$$

The other common concept of alkalinity states that total alkalinity is the ability of water in capturing hydrogen protons, if only carbonic acid and iron hydroxide reactions have significant influence on pH and alkalinity. Based on this presumption the TA is calculated using equation 27 (Paper V).

$$TA = [HCO_3^-] + [CO_3^{2-}] + [Fe(OH)_3] + [Fe(OH)_2^+] + [Fe(OH)^{2+}] + [OH^-] - [H^+] \quad (27)$$

Equation 27 also can be written as a function of concentration of hydrogen protons, equation 28. This is accomplished combining equations (3)-(9), (13)-(21), 23 and 27.

$$TA = \frac{k_{a1} \cdot [H^+] + 2 \cdot k_{a1} \cdot k_{a2}}{[H^+]^2 + k_{a1} \cdot [H^+] + k_{a1} \cdot k_{a2}} + \frac{3 \frac{K_w^3}{[H^+]^3} + 2K_1 \frac{K_w^2}{[H^+]^2} + K_1 K_2 \frac{K_w}{[H^+]}}{\frac{K_w^3}{[H^+]^3} + K_1 \frac{K_w^2}{[H^+]^2} + K_1 K_2 \frac{K_w}{[H^+]}} + K_1 K_2 K_3 \quad (28)$$

$$+ \frac{K_w}{[H^+]} - [H^+]$$

v) **Major ions**

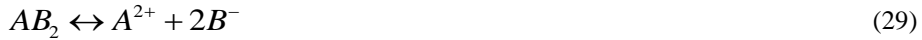
Major ions are the ions that usually appear in significantly larger concentrations than other ions. In river water these ions are: Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^- (Murray, 2004). Average concentrations of these ions per continent were estimated and made available (Livingstone, 1963).

The average concentrations of major ions were converted to eq/l and further, the concentrations in eq/l were converted to relative concentration of major ions in percentage, table 1. Relative concentration of major ions is the percentage of each ion in relation to the total concentration of positive ions in case of positive ion, and in relation to total concentration of negative ions in case of negative ion (Paper II).

It was demonstrated that the relative concentration of major ions does not change considerably over time (Paper II). This was confirmed by evaluating the trends using the Man–Kendell test together with linear regression. Using Man–Kendell test and a significance level of 0.05 it was found that, there is sufficient evidence to conclude that there is no trend. The linear regression showed that the changes in relative concentrations during a period of 10 years did not exceed 10% (Paper II).

vi) Solubility

The solubility of minerals determined by solubility constants is illustrated using a hypothetical mineral (AB_2). Equations 29 and 30 are the chemical reaction of dissolution and the solubility constant of the hypothetical mineral, respectively (Appelo & Postma, 1999). Based on the solubility of the mineral, three different dissolution states are defined. i) Non-saturated condition, when more solute can be added to the solvent (water) without forming precipitate. ii) Saturated condition, is the limit condition at which precipitate is immediately formed in case of addition of a small amount of solute. iii) Super-saturated condition, when there is a precipitate of mineral which cannot be dissolved in the solution.



$$K_{AB_2} = [A^{2+}] \cdot [B^-]^2 = 10^{-b} \quad (30)$$

vii) Conductivity

The conductivity of a water sample is determined by the contribution of each dissolved solute as well as the interaction between them (Pawlowicz, 2008). The interaction between the ions have a significant contribution only if the concentration of total dissolved solids increase to high levels (Pawlowicz, 2008). For dilute solutions, the conductivity factor per ion can be determined and used to estimate total conductivity, equation 31 (Tolgyessy, 1993). Conductivity factors of major ions are given in table 2.

$$EC_{estimated} = \sum_{i=1}^n f_i \cdot C_i \quad (31)$$

Table 1 Average relative concentration of major ions as a percentage (%). The values in the table represent the average value per continent and its variability around average value. In some cases the average concentration of certain ion is low and its variability include negative values. Note that, negative values of concentration are not possible. Consider only the positive part of the variability range (Murray, 2004) (Paper II).

Ions (%)	North America	South America	Europe	Asia	Africa	Australia	World
NO₃⁻	0.9 ± 5.5	1.5 ± 2.4	2.6 ± 6.2	0.7 ± 1.3	1.0 ± 7.8	0.1 ± 5.0	1.1 ± 4.7
Cl⁻	12.7 ± 27.6	18.2 ± 24.9	8.4 ± 25.2	14.2 ± 22.2	25.4 ± 20.5	33.0 ± 32.4	15.4 ± 25.5
SO₄²⁻	23.5 ± 31.7	13.2 ± 19.1	21.6 ± 25.6	10.1 ± 20.5	21.0 ± 19.6	6.3 ± 7.9	16.4 ± 20.3
HCO₃⁻	62.9 ± 38.6	67.1 ± 28.1	67.4 ± 32.7	75.0 ± 32.6	52.6 ± 29.2	60.6 ± 30.2	67.1 ± 31.9
Sum	100	100	100	100	100	100	100
K⁺	1.9 ± 3.2	7.2 ± 5.5	1.9 ± 9.1	0.0 ± 3.9	6.2 ± 12.7	6.2 ± 5.8	4.1 ± 6.8
Na⁺	20.7 ± 22.6	24.5 ± 30.7	10.2 ± 24.0	33.7 ± 17.6	21.7 ± 26.1	21.7 ± 17.5	19.2 ± 31.1
Mg²⁺	22.0 ± 10.9	17.6 ± 11.4	20.3 ± 31.9	22.3 ± 11.7	38.7 ± 17.9	38.7 ± 13.7	24.0 ± 16.3
Ca²⁺	55.4 ± 20.0	50.7 ± 28.3	67.6 ± 34.3	44.0 ± 20.6	33.5 ± 21.6	33.5 ± 14.2	52.6 ± 23.2
Sum	100	100	100	100	100	100	100

Table 2 Conductivity factors of ions at low concentration (Tolgyessy, 1993) (Paper II)

Ions	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	HCO ₃ ⁻	CO ₃ ²⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
Conductivity factor f_i (µS/cm per mg /L)	2.60	3.82	1.84	2.13	0.715	2.82	2.14	1.15	1.54

4.2 Model 1- Estimating inorganic ions in surface water

None of the models mentioned in the introduction to this chapter were developed to deal with water quality in waters affected by acid mine drainage. It would be useful to have a model based on pH to estimate the concentration of ions in water since pH influences the solubility of minerals in water (Appelo & Postma, 1999). There are relatively few studies about concentration changes of major ions (MI) in rivers compared to minor ions and heavy metals. A thorough search of the literature did not reveal any studies that include models to estimate the concentrations of MI in rivers. An interesting but rather old inventory of the concentrations of MI in rivers and lakes all over the world was carried out in the context of salt discharge to the oceans (Livingstone, 1963). The study resulted in an estimate of the total amount of salts discharged to the oceans by rivers and the average concentrations of MI in rivers per continent (Clarke, 1924; Conway, Mean geochemical data in relation to ocean evolution, 1942; Conway, The Chemical Evolution of the Ocean, 1943; Livingstone, 1963) . It was also demonstrated that pH combined with electrical conductivity and concentration of sulphate ions can be used to estimate concentration of metals in AMD using statistical methods (Valente, Ferreira, Grande, Torre, & Borrego, 2013). There is a possibility of developing a model that can be used to estimate the concentration of major ions in water combining theoretical concepts and relationships already studied (Paper II). Model 1 is a process based model developed to estimate the concentration of major ions using pH alkalinity and temperature.

4.2.1 Modelling methodology

Theoretical concepts and relationships as well as statistics are combined to develop a model that estimates concentration of major ions using pH, alkalinity and temperature. Theoretical concepts and relationships that were used include: (i) carbonate equilibrium; (ii) total alkalinity; (iii) statistics of MI; (iv) solubility of minerals; and (v) conductivity as function of major ions in water (Paper II).

Concentration of H^+ , OH^- , H^+ , CO_3^{2-} , HCO_3^- and H_2CO_3 is estimated by the model using pH, alkalinity, and temperature. Further, concentration of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , and NO_3^-) are estimated based on concentration of HCO_3^- and relative concentrations of major ions in the base month (base month - the month in which the data to calibrate the model is collected and the first

estimation is done). The model has two options to perform simulations, *the customized* and *generalized methods*, distinguished by the data used to calibrate the model (Paper II). The *customized method* uses the river specific relative concentration of major ions of the base month to calibrate the model while *generalized method* uses default relative concentrations of major ions per region (Africa, North America, South America, Europe, Asia, Australia, or the “world”), table 1. The option “world” can be used for any region and it is possible to get an idea of which option (regional or world) is giving the better estimates by comparing the difference between estimated and measured electric conductivity (DiffEC). The model also estimates the total hardness as the sum of the concentrations of Mg^{2+} and Ca^{2+} .

The third part of the model uses equilibrium equations to estimate the concentrations of iron, manganese, and some heavy metals (Paper II). The main purpose of estimating heavy metals is to get maximum possible concentrations to use as an indication to decide whether there is a need for taking field samples for more accurate analyses. The algorithm of the model is shown in Figure 9.

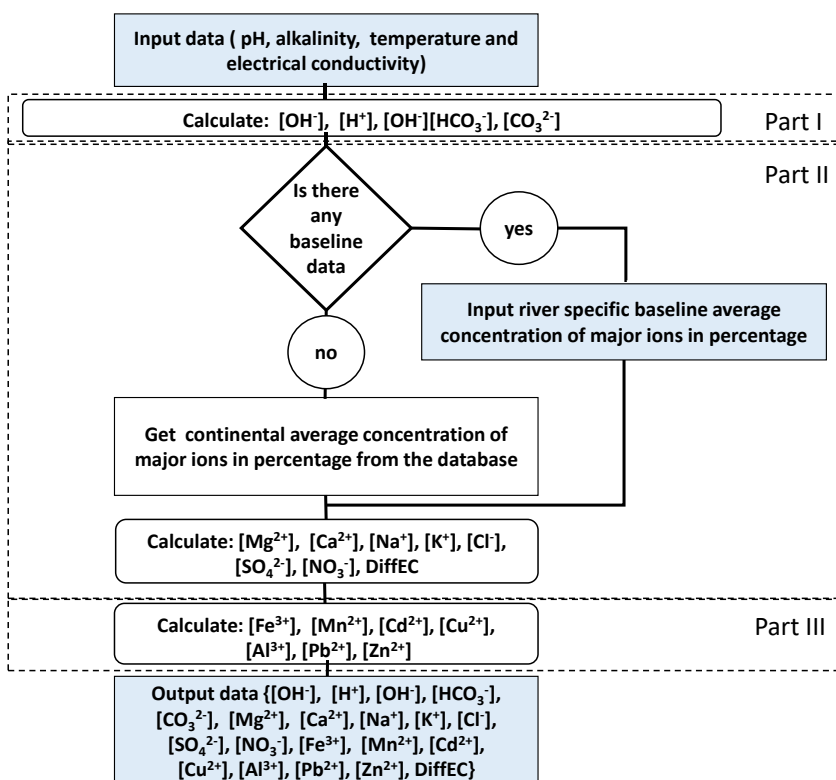


Figure 9 Algorithm of model 1. (adapted from Paper II).

4.2.2 Evaluation of performance of model 1

Two parameters were used to evaluate the model performance, the *difference between the measured and estimated electric conductivity as a percentage (DiffEC)* and the *Root mean square error (RMSE)*. DiffEC is used internally, within the model to evaluate the modelled results while RMSE is used as an external tool to evaluate the model performance in this study. The correlation coefficient R is also used to compare the process based model suggested here with artificial neural networks based model.

i) *Difference between the measured and estimated electric conductivity as a percentage DiffEC*

A parameter to evaluate the estimated concentration of ions is included in the model. The parameter is the difference between the measured and estimated electric conductivity in percentage DiffEC, equation 32.

$$DiffEC(\%) = \frac{EC_{measured} - EC_{estimated}}{EC_{measured}} \times 100\% \quad (32)$$

Ideally, if all ions were included in the model, this value should be zero; however, the model estimates the electric conductivity using only the major ions. The value should therefore always be higher than zero, since some ions are left out in the model. Sometimes the model may get DiffEC less than zero, implying that it is underestimating the concentrations of ions with low electric conductivity factors (bicarbonate, sulphate, nitrate, or potassium) or overestimating the ions with high electric conductivity factors (magnesium, calcium, chlorine or sodium), table 2. Even if the concentrations of ions with high electric conductivity are overestimated, the DiffEC may still be positive when the concentration of the ions not considered by the model is high.

When there is baseline data, the customized method is favourable to estimate the concentrations of ions because it uses site specific data for calibration. The value of DiffEC for the base month (or the month in which data was collected to calibrate the model) should be higher than zero. The value of DiffEC for the base month shows the relationship between the major ions and the ions not considered by the model.

ii) *Root mean square error (RMSE)*

Root mean square error was used to compare the modelled and measured value of concentration of major ions, equation 33. RMSE relative to the minimum

[RMSE_{min} (%)] and maximum [RMSE_{max} (%)] measured value as a percentage were also used to quantify the error of estimates, equations 34 and 35, respectively.

$$RMSE = \sqrt{\sum_{i=1}^n (C_{meas}^i - C_{calc}^i)^2 / n} \quad (33)$$

where, C_{meas} is the measured concentration of ions, C_{calc} is the modelled value of the concentration and n is the number of samples used to evaluate the model.

$$RMSE \min(\%) = \frac{RMSE}{C_{meas, \min}} \times 100 \quad (34)$$

$$RMSE \max(\%) = \frac{RMSE}{C_{meas, \max}} \times 100 \quad (35)$$

4.2.3 Results and discussion

Data from four stations in Swedish Rivers was used to test the model. The rivers stations are: Skellefte älv, (Slagnäs), Vindelälven, (Maltbrännan), V. Dalälven, (Mockfjärd), and Klarälven, (Edsforsen). The selection of the Swedish rivers was justified by the availability of comprehensive data covering a long period of time. Although the focus of the present study was to develop a method to be applicable in developing countries, the governing laws for equilibrium concentration are universal and not site specific, which implies that a comprehensive data set from any river is suitable for testing the model.

Both modelling methods were tested, the generalized and the customized method. As stated before, the generalized method uses continental averages, default data, to calibrate the model when river specific data is not available. The customized method uses a single measurement of relative concentrations of major ions in the base month or an average of one year of measurements of relative concentration of major ions to calibrate the model.

The values of RMSE for the customized method are between 0 and 67%, but about 80% of the RMSE values are below 15%, for the four stations used in the model validation (Paper II). For the generalized method, the corresponding RMSE (%) values are between 0 and 101% and about 80% of the RMSE values are below 50% (Paper II). The analysis of RMSE was carried out excluding nitrate because its estimates exhibit larger errors, RMSE higher than 150%. The RMSE analysis demonstrate that the customized method gives better results than the generalized

method, as expected. The model works better to estimate the concentrations of ions with relatively higher concentrations. For nitrate, which, in general, has lower concentrations at all four monitoring stations compared to the other ions, the modelled concentration values are quite different from the measured values. The other reason why the model does not work well for nitrate is that nitrogen in surface water is governed by many factors and the pH, alkalinity and temperature are not enough to capture completely the effect of those factors. The factors include the increasing concentration of nitrogen in river in later autumn, reaching its peak in spring that is explained by the increasing losses from soils and low biological activity in rivers (Laznik, Stalnacke, & Grimvall, 1999). The lower concentration of nitrogen in summer and earlier autumn is caused by consumption by phytoplankton; nitrogen uptake by crops and other biota; and denitrification processes in soil and groundwater (Laznik, Stalnacke, & Grimvall, 1999).

The values of DiffEC for the generalized method varied between -15% and $+40\%$, but for the customized method it did not go beyond $\pm 20\%$ in relation to the baseline value at all four stations used to test the model. Therefore, it is recommended that when doing estimates using the generalized method, the values of DiffEC should be between -15% to $+40\%$ and when using the customized method, it is recommended that the values of DiffEC do not go beyond $\pm 20\%$ from the baseline value (Paper II). Employing the suggested limits on DiffEC there is an 80% probability of having an RMSE (%) below 15% using the customized method and below 50% using the generalized method (Paper II). If the value of DiffEC goes beyond the suggested limits, the first option is to gather data from the river of interest to recalibrate the model; such deviations might be caused by disturbances to the river system from pollution discharge due to mining or other activities. If the value of DiffEC still remains out of the normal range, the model is not recommended for the specific river; the reason could be that significant amounts of ions, other than the major ions considered in the present model, cause considerable variability in the relative concentrations of ions.

4.2.4 Comparing the model with Artificial Neural Networks

Traditional statistical and neural networks models can also be used to estimate concentration of ions in water. It is relevant to know the advantages of using statistical models compared to physical processes based model (PPBM) suggested here. It has been shown that under favourable conditions artificial intelligence models such as artificial neural networks (ANN) perform better than traditional statistical regression analysis (Paliwal & Kumar, 2009). The same data from four Swedish Rivers was used to test the performance of ANN and PPBM; the values of RMSE and correlation coefficient (R) were used to compare the results obtained from the models.

Monthly data from 2001 to 2011 was used to develop and test the ANN model. The data were divided into two parts; 60% to develop the model and 40% for testing it. Using this division, 72 data samples were used for developing the model and 48 for the testing. The same data with 48 samples used to test the ANN model was used to test the PPBM. Only the customized method, the most accurate one, in PPBM was used and an average of two samples were used for calibration.

The model provided good estimates for all ions using both models in Skellefte älv, at the Slagnäs station, except for nitrate (NO_3^-), see figures 10 and 11 (Paper III). Similar results were obtained at the other three stations modelled. For ANN, the RMSE (%) for all stations vary from 4 to 38 %, excluding nitrate, while the values associated with nitrate are high, reaching values around 1000 (Paper III). For PPBM the RMSE values for all stations vary from 4 to 71 %, excluding nitrate, while the values associated with nitrate are high, reaching around 3000 (Paper III).

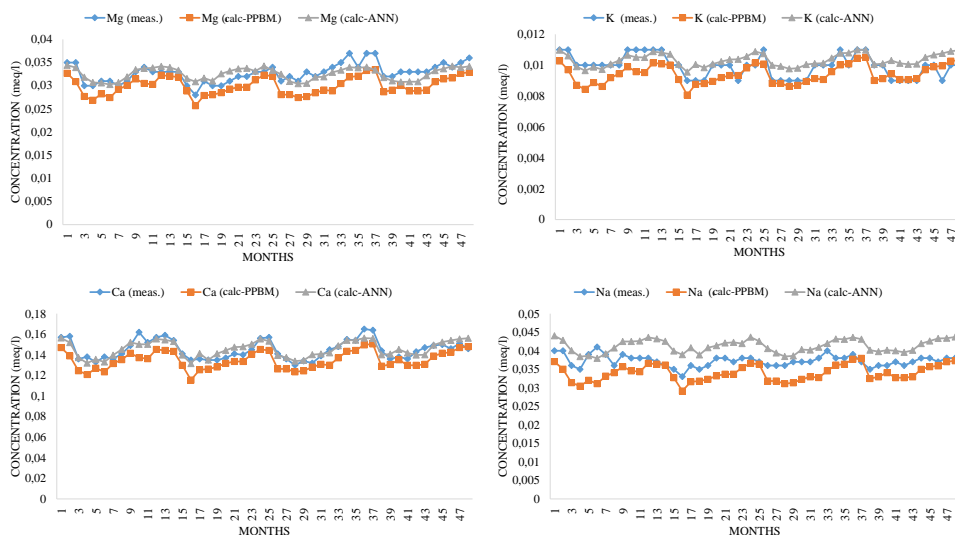


Figure 10 Concentration of positive ions in Skellefte älv at (Slagnäs station) [measured (meas.), estimated using physical processes based model (calc-PPBM.) and estimated using artificial neural networks (calc-ANN)] (Paper III)

The values of R show that the estimated and the measured values are well correlated when using ANN, varying from 0.42 to 1.0, and the p-values associated with the correlation coefficient are smaller than 0.05, implying that all correlation coefficients are significant. While for PPBM the values of the correlation coefficient are occasionally low, varying from 0.17 to 1.0 and the p-values associated with the correlation coefficient are occasionally higher than 0.05.

An additional parameter to evaluate the quality of estimated values is available in PPBM, the DiffEC. The values of DiffEC in the Skellefte älv at Slagnäs and

Vindelälven at Maltbrännan have a span of 13 and 34, respectively, and the estimated values are better compared to Klarälven at Edsforsten and V. Dalälven at Mockfjärd stations which have a span of 56 and 57, respectively (Paper III). As stated previously, it is recommended that the values of DiffEC do not go beyond $\pm 20\%$ from the baseline value (Paper II). The PPBM should have been recalibrated when the results started to exhibit value of DiffEC outside the recommended range. However, the model was not recalibrated since the task was to compare the models performance for the same conditions and data.

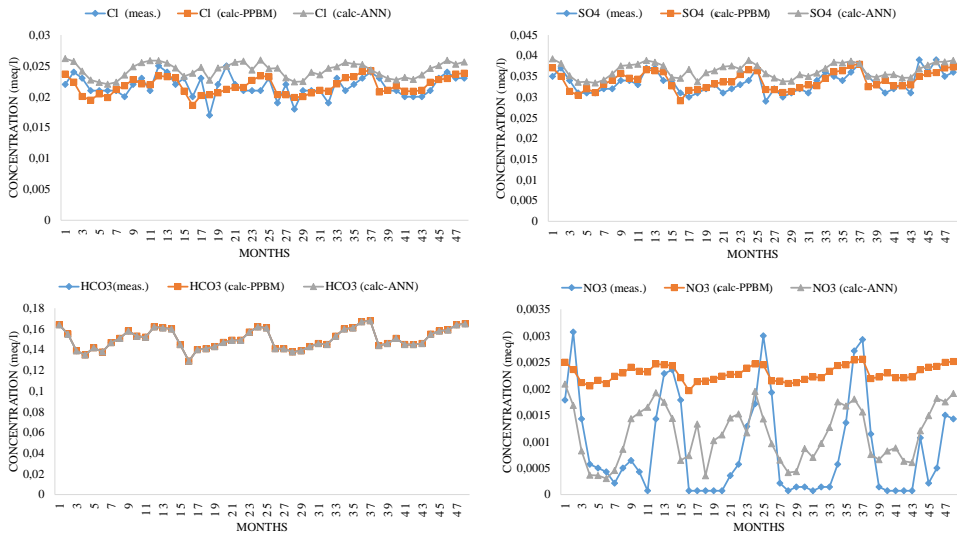


Figure 11 Concentration of negative ions in Skellefte älv at (Slagnäs station) [measured (meas.), estimated using physical process based model (calc-PPBM.) and estimated using artificial neural networks (calc-ANN)] (Paper III)

When there is enough historical data it is recommended to use the ANN model combined with PPBM. This is because even if the ANN model gives better results there is no way to check the accuracy of the estimates, whereas the PPBM can rely on DiffEC for this purpose. The PPBM might be the only option when there are no historical data to develop the ANN model; also, the PPBM is still able to provide information about the quality of the estimates through the value of DiffEC. This favours the application of PPBM in developing countries where there is limited historical data due to poor monitoring programs resulting from lack of resources.

4.3 Model 2 - pH and alkalinity in streams

Because of rivers impacted by acidification (Anawar, 2015; DPLF, 2014; ICM, 2012; Ochieng, Seanego, & Nkwonta, 2010), the poor water quality monitoring programs in developing countries (Paper I), and the lack of appropriate and simple models to simulate acidification (Paper II) it is relevant to develop a new model that simulates water quality changes in rivers impacted by acidic discharge. Contamination of rivers by acidic discharges includes two stages: (1) near field where the mixing of acidic discharge with the stream water takes place, the region ends when the homogeneity in the cross-sectional area of stream and equilibrium between alkalinity species are reached; and (2) far field, the region starts where the near field ends until the pH and alkalinity in the stream remains almost constant, figure 12.

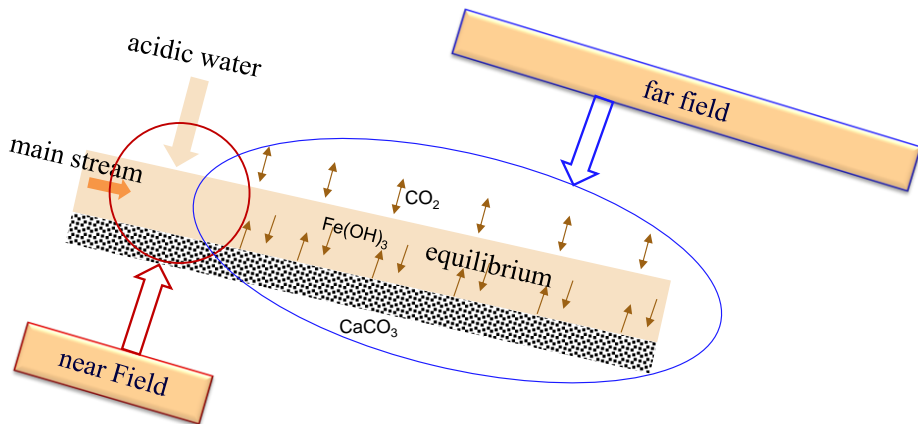


Figure 12 A conceptual model of a main stream affected by a release of acidic water. Two regions are identified: (1) near field where intense mixing of acidic discharge and stream water takes place and (2) far field where mixing in the cross section is complete and concentration vary due to advection-dispersion and processes at the upper and lower boundaries (Paper V).

The near field and far field are modelled separately. In chapter 4.3.1 a model which simulates pH and alkalinity in the mixing zone is presented. The model is developed considering only carbonaceous alkalinity to allow easy demonstration of the modelling approach and it was tested using laboratory experiments.

A complete modelling methodology for simulating pH and alkalinity in streams is presented in chapter 4.3.2. However, the main purpose of this chapter is to present a model for simulating pH and alkalinity in the far field an extension of a model to estimate pH and alkalinity at the near field is demonstrated by including the effect of iron (III). The model was not tested with measured data. However, a discussion

about the validity of the model concepts used and quality of the model results is presented based on a simulation of a hypothetical case.

4.3.1 Simulating pH and alkalinity in the mixing zone

A simple and easy-to-use physical process based model that simulates pH and alkalinity in the near field, mixing zone is proposed. A model that considers equilibrium between the alkalinity species in water but does not consider equilibrium with CO_2 in the atmosphere and stream bed minerals at the mixing zone is developed to overcome the limitations of available models in simulating acidification of streams.

For modelling purpose, complete and instantaneous mixing is assumed, that is, a completely stirred (CS) mixing zone when acidic water is discharged into the water body. Homogeneity in the cross-sectional area and equilibrium between the alkalinity species within the stream is reached immediately after discharge of acidic water. This implies that the mixing time and the length of the mixing zone is zero; thus, the effect of the surrounding environment (bottom minerals and atmospheric gases) is neglected. There might be parts of the stream where the real pH before mixing is complete might be lower than the pH estimated assuming completely stirred due to effect of zonation in large streams (Schemel, Cox, Runkel, & Kimball, 2006). That cannot be compared to the effect of zonation because the processes are slow but neglecting the effect of surrounding environment on pH and alkalinity will make the real resulting pH when the mixing is complete slightly higher than the one estimated assuming complete stirred.

4.3.1.1 Modelling methodology

In the development of the model, the volumetric flows are denoted by Q_1 , Q_2 , and Q_R for the upstream river, acidic discharge, and downstream river, respectively, see Figure 13. Volumes can replace the flows when simulating acidification of lagoons, or other similar water bodies.

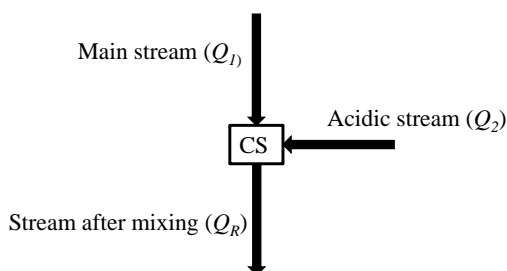


Figure 13 Schematic representation of simulated conditions where an acidic discharge is released to stream. CS = completely stirred (Paper IV)

The main principle used for the development of the model are that the total alkalinity (TA) and total inorganic carbon (TIC) are conservative with respect to mixing. Thus, when Q_1 and Q_2 are mixed the TA and TIC can be added in moles. The resulting total alkalinity (TA_R) and total inorganic carbon (TIC_R) in the resulting stream can be calculated using equations 36 and 37, respectively.

$$TA_R = \frac{TA_1 \cdot Q_1 + TA_2 \cdot Q_2}{Q_1 + Q_2} \quad (36)$$

$$TIC_R = \frac{TIC_1 \cdot Q_1 + TIC_2 \cdot Q_2}{Q_1 + Q_2} \quad (37)$$

Knowing the resulting total alkalinity and total inorganic carbon equation 26, can be used to get the resulting concentration of hydrogen ions in equilibrium. Equation 26 can be written as a function $f([H^+] = 0$, equation 38. Which is solved numerically using an iterative approach.

$$f([H^+]) = TA_R - \frac{K_{a1} \cdot [H^+] + 2K_{a1} \cdot K_{a2}}{[H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2}} \cdot TIC_R - \frac{K_w}{[H^+]} + [H^+] = 0 \quad (38)$$

Newton-Raphson was selected to solve the equation where improved value of $[H^+]$ is determined using equation 39. The derivative of the function is calculated using equation 40. Concentration of other alkalinity species are calculated using equations (4)-(6).

$$[H^+]_{i+1} = [H^+]_i - \frac{f([H^+]_i)}{f'([H^+]_i)} \quad (39)$$

$$f'([H^+]) = \frac{K_{a1} \cdot [H^+]^2 + 4K_{a1} \cdot K_{a2} \cdot [H^+] + K_{a1}^2 \cdot K_{a2}}{([H^+]^2 + K_{a1} \cdot [H^+] + K_{a1} \cdot K_{a2})^2} \cdot TIC_R + \frac{K_w}{[H^+]^2} + 1 = 0 \quad (40)$$

The calculation steps of the full model are given in the flow chart, figure 14. The model is based on input of flows of the streams (Q_1 and Q_2), pH of the streams (pH_1 and pH_2), alkalinity of the streams (TA_1 and TA_2), and the average water temperature (T). The model uses as a default value for temperature 25°C, which can be adjusted if necessary. A function $f([H^+] = 0$, obtained from the theories of carbonate speciation and pH in water is solved using the Newton-Rapson method. The output of the model is pH and TA of the resulting stream (pH_R and TA_R), as well as the carbonate alkalinity species.

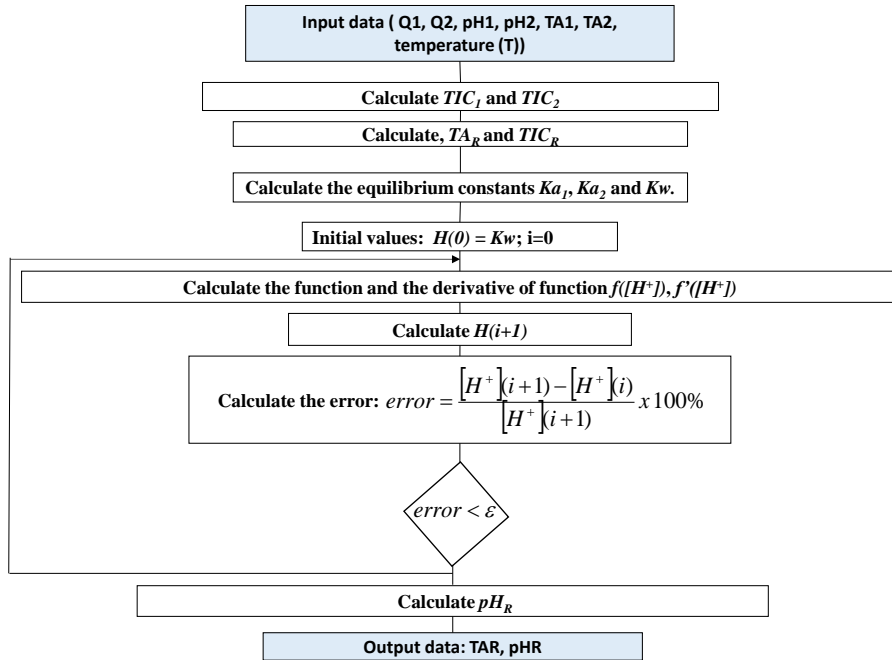


Figure 14 Flow diagram of the model that estimates pH (pH_R) and alkalinity (TA_R) resulting from the mixing of two streams with different pH and alkalinity (Paper IV)

4.3.1.2 Results and discussion

Mixing of two hypothetical streams with the flows Q_1 and Q_2 is used to evaluate if modelled values correctly represent the buffer effect of carbonic acid in water. A broad range of pH (12 to 1.5) was used in order to evaluate the model performance for high, medium, and low values of pH . An alkalinity of 0.086 eq/l was used to allow for the visualization of the buffer effect.

Figure 15 shows that as the flow of acidic water (Q_2) increases, the pH of the resulting stream, pH_R tends to remain constant in three different section, between pH (12-9), (7-5) and (3-1.5) (Paper IV). Between these three sections there are two intervals where the pH drops rapidly with the addition of small amounts of acidic water Q_2 . The two intervals where pH drops with only a small addition of acidic water show the total conversion of CO_3^{2-} to HCO_3^- and HCO_3^- to H_2CO_3 , respectively. The first two sections in figure 15, where the pH tends to remain constant when acidic water is added, is due to the buffer effect of carbonic acid, whereas the third section is only due to the dilution effect, showing that the pH of the resulting stream tends to be equal to the pH of the acidic stream Q_2 . These results show that the model captures well the buffer effect of carbonic acid in water.

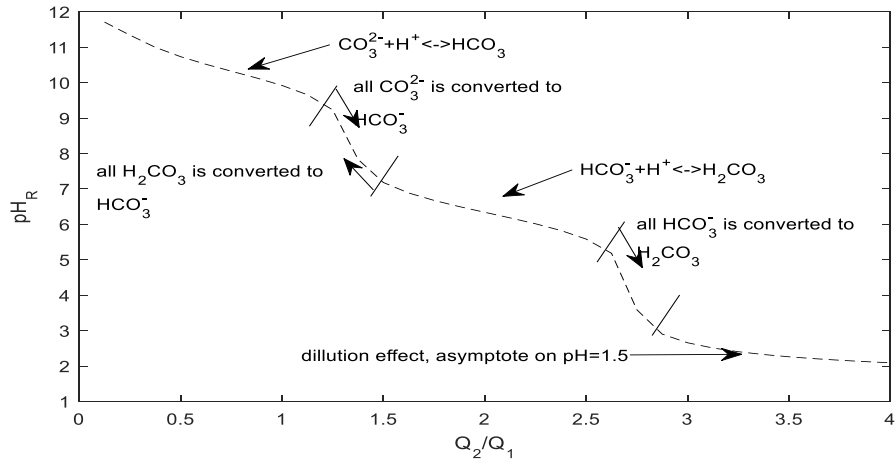


Figure 15 Results showing pH_R vs Q_2/Q_1 , where Q_1 ($pH=12$, alkalinity = 0.086 eq/l) and Q_2 ($pH=1.5$, alkalinity = -0.032 eq/l) are from two streams mixed in different proportions. pH_R is the pH of the stream resulting from the mixing of Q_1 and Q_2 (Paper IV).

The change of concentration of carbonate species (H_2CO_3 , HCO_3^- , CO_3^{2-}), TA , and TIC is as expected; see figure 16 (Paper IV). The TIC at any pH is the sum of inorganic species but it diminishes with the reduction of pH . This is because the TIC in the stream Q_2 is lower than the TIC in the stream Q_1 . The TA reduces with the reduction of pH reaching zero at pH 4.3. After pH 4.3 the alkalinity has been totally consumed. The negative value of TA shows that the water is getting even more acidic.

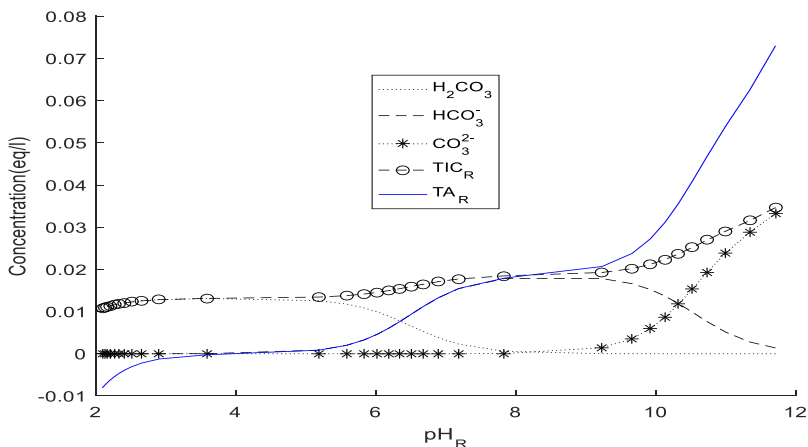


Figure 16 Concentration of carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), TIC_R , and TA_R vs pH_R in eq/l. pH_R is the pH of the stream resulting from mixing of Q_1 and Q_2 , where Q_1 ($pH=12$, alkalinity = 0.086 eq/l) and Q_2 ($pH=1.5$, alkalinity = -0.032 eq/l) are from two streams mixed with different proportions (Paper IV)

- **Comparing modelled results with laboratory experiments**

Six experiments were performed yielding validation data for the model; see table 3. The model was run to simulate *pH* and alkalinity for a river in the mixing zone considering (1) a change of volumetric flow in the acid discharge while *pH* is assumed constant and (2) a change in *pH* of the acidic discharge while the volumetric flow is assumed constant. In both cases the main stream river flow is assumed to be constant (Paper IV). The modelled results were compared with the laboratory measurements using the correlation coefficient (R) and the associated significance level, the p-value, and the Nash-Sutcliffe Efficiency (NSE), equation 41.

Table 3 Overview of laboratory experiments. For laboratory experiments V₁, representing river water before contamination, and V₂, representing acidic discharge, are equivalent to Q₁ and Q₂ in the model (adapted from Paper IV)

Simulation Scenario	Exp.	acidic water reactants (V ₂)	basic water reactants (V ₁)
(1) change of volumetric flow in the acid discharge while pH is assumed constant	1	Deionized water + HCl	Deionized water + NaOH (alkalinity = 0.0093 eq/l)
	2	Deionized water + HCl	Deionized water + NaOH + Na ₂ CO ₃ (alkalinity = 0.054 eq/l)
	3	Tap water + H ₂ SO ₄	Tap water+ NaOH (alkalinity = 0.012 eq/l)
	4	Tap water + H ₂ SO ₄	Tap water+ NaOH+ Na ₂ CO ₃ (alkalinity = 0.033 eq/l)
(2) change in pH of the acidic discharge while the volumetric flow is assumed constant	5	Deionized water+ HCl (pH varying high values to low)	Deionized water + NaOH + Na ₂ CO ₃
	6	Tap water + H ₂ SO ₄ (pH varying high values to low)	Tap water+ NaOH+ Na ₂ CO ₃

$$NSE = 1 - \frac{\sum_{i=1}^n (y_i^{meas} - y_i^{mod})^2}{\sum_{i=1}^n (y_i^{meas} - \overline{y^{meas}})^2} \quad (41)$$

Where, *n* is the total number of observations, y_i^{meas} is the value measured in each experiment, y_i^{mod} is the corresponding modeled value, and $\overline{y^{meas}}$ is the average of the experimental values (Taylor, He, & Hiscock, 2016).

Thus, NSE describes the “goodness-of-fit” between the experimental and modeled values. It can vary from -∞ to 1, where the value of 1 represents a perfect fit. A value between 0 to 1 is generally recognized as acceptable model performance, whereas a value less than zero means that the average of the measured values is a better predictor of a variable compared to the model, indicating unsatisfactory model performance (Taylor, He, & Hiscock, 2016).

Figures 17 and 18 show the predicted and measured values for the first simulation scenario using (1) deionized water and HCl , and (2) tap water and H_2SO_4 , respectively, for two conditions, one with low alkalinity and the other one with high alkalinity (Paper IV). The figures show that the modelled pH and alkalinity agree well with the measured values. However, the measured alkalinity in the experiments with tap water and H_2SO_4 is below the alkalinity estimated by the model. In the high alkalinity experiment the difference is about 0.02 eq/l at higher pH values, figure 18.b. This difference is related to the presence of HSO_4^- introduced by the sulfuric acid used to produce acidic water in the experiments that is not considered in the model, see equation 25.

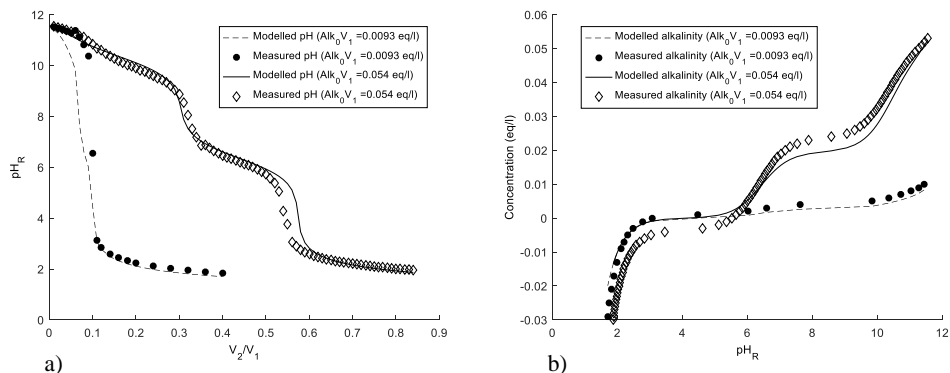


Figure 17 Model prediction and measured values of a) pH and b) alkalinity. The results correspond to experiments (1) and (2) in table 3. pH_R is the pH resulting after mixing V_1 and V_2 . (Paper IV)

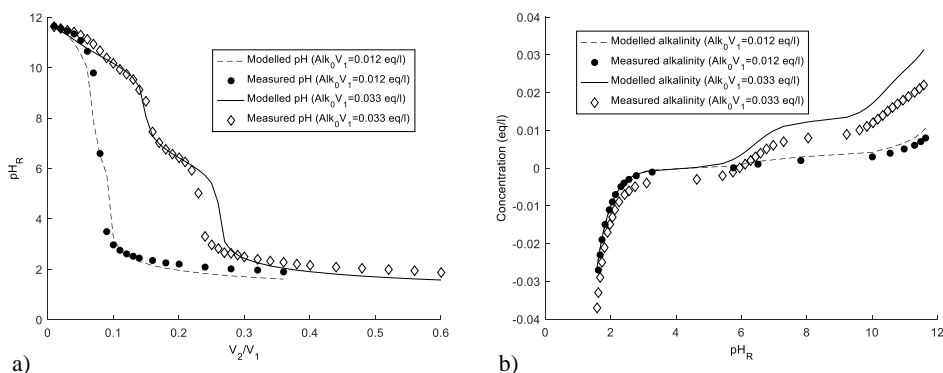


Figure 18 Model prediction and measured values of a) pH and b) alkalinity. The results correspond to experiments (3) and (4) in table 3. pH_R is the pH resulting after mixing V_1 and V_2 . (Paper IV)

Figures 19 and 20 show the modelled and measured values for the second simulation scenario using (1) deionized water and HCl , and (2) tap water and H_2SO_4 , respectively (Paper IV). The figures show that the modelled pH and

alkalinity agree well with the measured values. In the pH change experiment the modelled and measured resulting alkalinity differ at low pH , figure 20.b. This happens because the experiments were performed differently. For the pH change experiments, the initial samples were both prepared with high pH , while for the volume change experiments the initial samples were prepared one with high pH and the other with low pH . For the pH change experiments, the pH was lowered by adding acidic water (prepared with H_2SO_4).

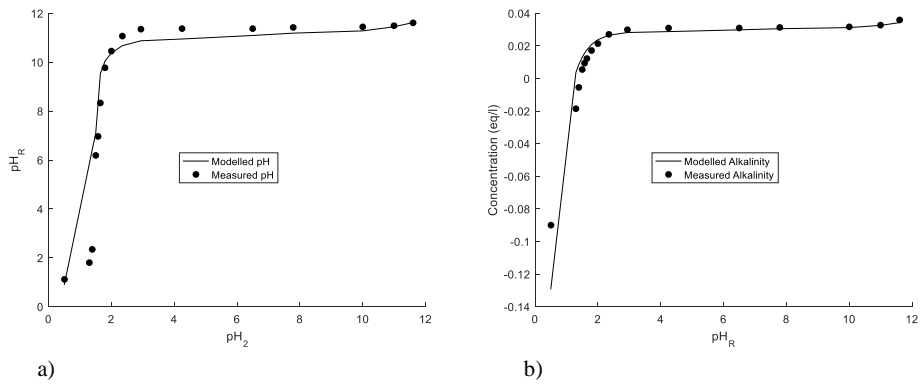


Figure 19 Model prediction and measured values of a) pH and b) alkalinity. The results correspond to experiment (5) in table 3. pH_R is the pH resulting after mixing V_1 and V_2 (Paper IV).

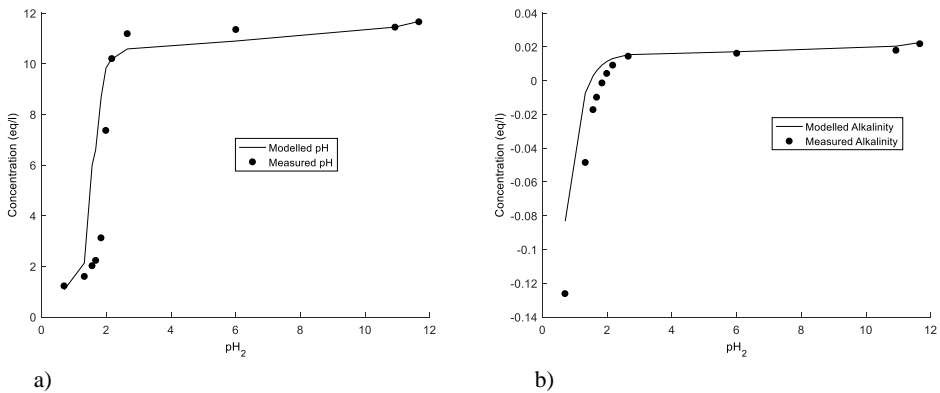


Figure 20 Model prediction and measured values of a) pH and b) alkalinity. The results correspond to experiment (6) in table 3. pH_R is the pH resulting after mixing V_1 and V_2 (Paper IV).

The correlation coefficients in all experiments are significant at a confidence level of 0.95, table 4. Calculated p-values for all correlation coefficients are much less than 0.05. NSE values are between 0 and 1 for all experiments. The correlation coefficient together with NSE values reveal that the model is accurate enough to be

used for practical applications, table 4 (Paper IV). An example of such a practical application is given in chapter 4.3.1.3.

Table 4 Correlation coefficient (R) and Nash-Sutcliffe Efficiency (NSE) values for experiments 1 to 6 expressing the goodness-of-fit of the model compared with measured pH and alkalinity (Paper IV)

Experiment	pH		Alkalinity	
	R	NSE	R	NSE
1	0.95	0.84	0.99	0.92
2	0.99	0.99	0.98	0.88
3	0.99	0.98	0.99	0.98
4	0.98	0.97	0.99	0.98
5	0.86	0.71	0.80	0.90
6	0.94	0.54	0.86	0.59

4.3.1.3 Application of the model for Zambezi River Basin

The task here is to evaluate the threshold pH in the effluent from the mining area that may trigger significant changes in the pH in the Zambezi River. To address this question, the model developed in the present study is used to simulate change in pH in the main stream of Zambezi River as a result of change in pH of incoming waters from the mining area. For the simulation, the pH in the effluent from the mining area is assumed to vary from 7.85 to 2. The average flow, pH, and alkalinity of both the main stream and the tributaries from the mining area are given in table 5. At present, there is no contamination reported in the main stream that indicates acidification (Nhantumbo, Evaluation of Long-term Impact of Coal Mining in Zambezi River Basin in Mozambique, 2013).

Table 5 Average flow, pH and alkalinity of the main stream of Zambezi River Basin upstream the mining area and tributaries coming from the mining area (Nhantumbo, Evaluation of Long-term Impact of Coal Mining in Zambezi River Basin in Mozambique, 2013) (Paper IV)

Parameter	Flow (m ³ /s)	pH	Alkalinity (mg/l as CaCO ₃)
Main stream	2330	7.6±0.3	62±2 (0.00124 eq/l)
Tributaries	1120	7.85±0.4	129±102 (0.00384 eq/l)

The results of the simulation show that when average pH of the water in the incoming tributaries from the mining area is about 3, the pH in the main stream of Zambezi River drops from about 6, to 3, Figure 21 a) (Paper IV). This shows that with the present alkalinity and flows, the main stream of Zambezi River cannot support pH drops in waters coming from the tributaries of the mining area to values below 3. Additional analysis has been done using the speciation of carbonate ions, TIC, and TA from figure 21 b). By comparing figures 21a) and b) it is possible to see that the pH drops when the alkalinity in the main stream is totally consumed.

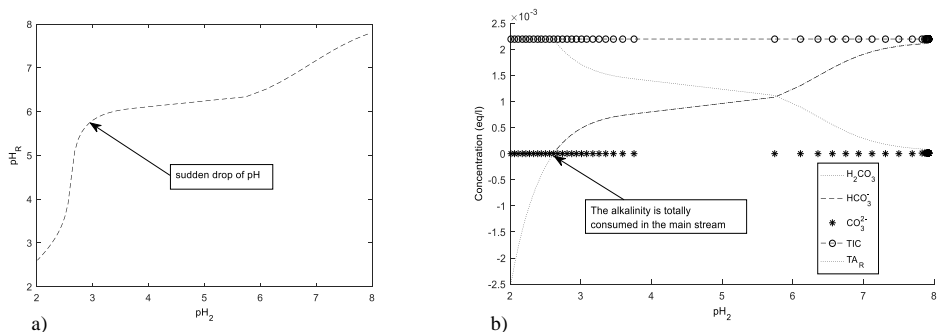


Figure 21 Simulated a) resulting pH [pH_R] in the main stream of Zambezi River (pH₂) and b) concentration of carbonaceous alkalinity species, total inorganic carbon (TIC), and total alkalinity (TA), against pH in the water coming from the mining area (Paper IV).

The pH of the water coming from the mining area should not decrease to values below 3 to avoid significant pH drop in the main stream of the river. However, this does not guarantee that the water is not impacted. The tributary water with *pH* 3, depending on the geology of the area, could probably contain a high quantity of dissolved heavy metals that may impact the water of the main stream, even though the *pH* is still above 6.5.

As the tributaries connect to the river in different points along the mining area, the scenario described above might occur only if there is no CO₂ degassing to the atmosphere or buffer minerals being dissolved at the bottom of the stream. At least CO₂ degassing will take place after each tributary is joining and there is a chance of having buffer mineral at the bottom of the stream. All these effects will contribute to reduce the impact. There is also a chance of having zonation creating localized parts of the river with extremely low pH values (Schemel, Cox, Runkel, & Kimball, 2006), but this effect can only be understood with three-dimensional hydraulic modelling, which is not here.

4.3.2 Methodology for simulating pH and alkalinity in streams

A modelling methodology for simulating pH and alkalinity in streams impacted by acidic discharges is proposed considering both reactions and transport processes as well as the equilibrium between the alkalinity species and the influence of the surrounding environment. The methodology is meant to be used for simulating contamination and for planning reclamation projects in streams already impacted. The modelling methodology proposed is based on the pollutant transport equation (advection-diffusion equation); equilibrium adjustment based on alkalinity species in water, equations 26 and 28; and classical mass transfer modelling procedures for modelling the influence of the surrounding environment, Figure 12. The modelling

methodology suggested can be applied for simulating two different scenarios; *continuous* and *non-continuous* discharge of acidic water into streams. However, the main purpose of this chapter is to develop a modelling methodology for the far field (Paper V). The possibility of extension of the model for the near field, mixing zone is demonstrated by including iron (III).

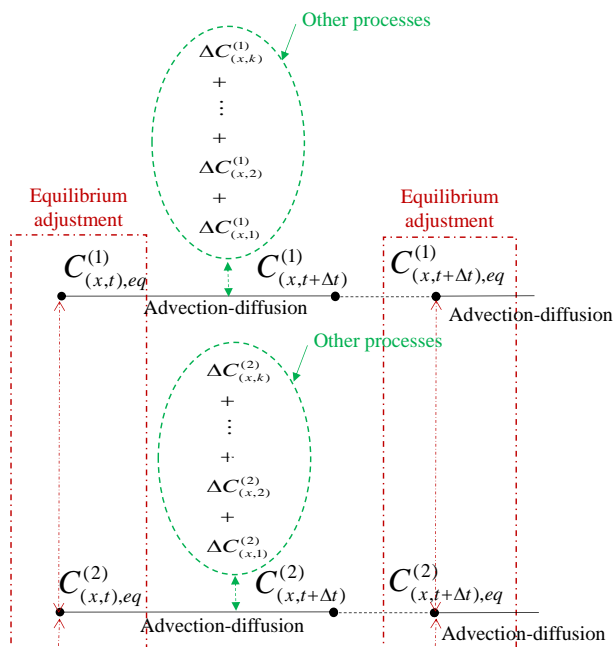


Figure 22 Calculation scheme, change of concentration with time. The concentration of alkalinity specie (1) at position x and time t ($C_{(x,t),eq}^{(1)}$) changes due to advection and diffusion as well as due to other processes ($\Delta C_{(x,1)}^{(1)}$, $\Delta C_{(x,2)}^{(1)}$, ..., and $\Delta C_{(x,k)}^{(1)}$) during the time step Δt , resulting in concentration of alkalinity specie (1) at position x and time $t + \Delta t$ ($C_{(x,t+\Delta t)}^{(1)}$). Similarly for concentration of alkalinity specie (2) changing its concentration from $C_{(x,t),eq}^{(2)}$ to $C_{(x,t+\Delta t)}^{(2)}$. These processes are simulated independently at each time step. After each the advection-diffusion has been solved the equilibrium between all modelled alkalinity species (1, 2, ..., m) is adjusted, getting $C_{(x,t+\Delta t),eq}^{(1)}$ and $C_{(x,t+\Delta t),eq}^{(2)}$. The notation $\Delta C_{(x,1)}^{(1)}$ means the change of concentration of alkalinity specie (1) at position x due to process 1 and $\Delta C_{(x,2)}^{(1)}$ means the change of concentration of alkalinity specie (1) at position x due to process 2 (Paper V).

A schematic representation of the modelling methodology in the “far field” is given in figure 22 and 23. The change of concentration of alkalinity species with time is due to advection and diffusion as well as the added effects of the surrounding environment (other processes), figure 22. The change of concentration of alkalinity species with space is due to advection and diffusion, figure 23. A complete scheme representing both change of concentration of alkalinity species with time and space is given in figure 24.

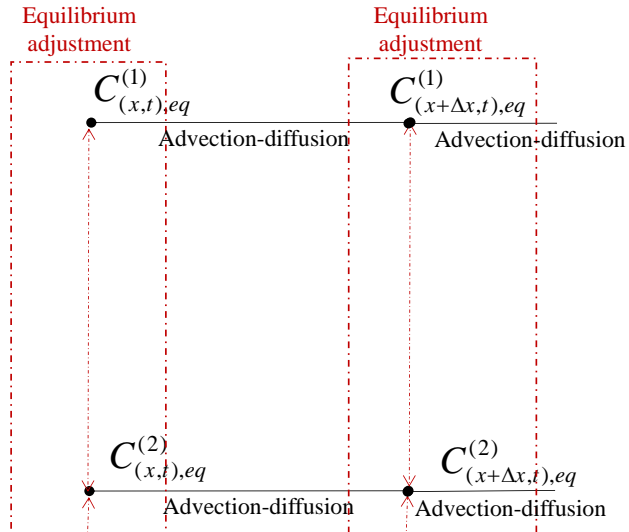


Figure 23 Calculation scheme, change of concentration with space. The concentration of alkalinity species (1) and (2) ($C_{(x,t),eq}^{(1)}$ and $C_{(x,t),eq}^{(2)}$) are simulated as being influenced by advection and diffusion along the space step Δx independently, after which the equilibrium between them is adjusted to get $C_{(x+\Delta x,t),eq}^{(1)}$ and $C_{(x+\Delta x,t),eq}^{(2)}$ (Paper V).

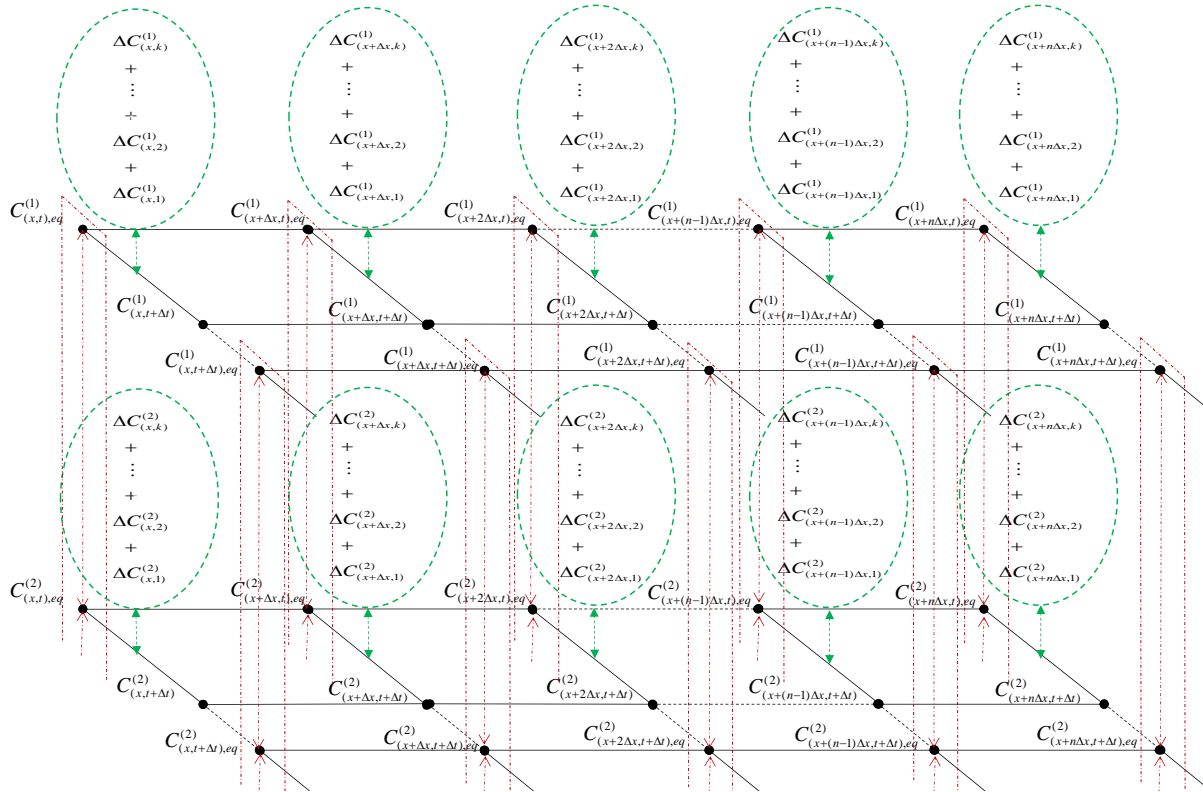


Figure 24 Schematic representation of the modeling methodology. The pollutant transport equation is used to simulate the advection and diffusion of each alkalinity specie. Small steps in time and space are taken because the alkalinity species are simulated as being transported independently. The reaction processes taking place during the transport process that may cause change in concentration of each alkalinity specie are considered at each time step. After each distance and time step the effect of advection and diffusion is added to the effect other process and the equilibrium between different alkalinity specie is then adjusted (Paper V).

4.3.2.1 Mixing

Mixing of an acidic effluent and stream water before transport is simulated using the principles described and demonstrated to be valid for simulating pH and alkalinity in the mixing zone in chapter 4.3.1. The total alkalinity and total inorganic carbon are calculated using equations 36 and 37. Total iron (III) is calculated using the same principle as for total alkalinity and total inorganic carbon being conservative with respect to mixing, equation 42. The parameters in equation 42 refers to Figure 13.

$$TFe_R = \frac{TFe_1 \cdot Q_1 + TFe_2 \cdot Q_2}{Q_1 + Q_2} \quad (42)$$

Knowing the values of total alkalinity, total inorganic carbon and total iron, the only unknown in equation 28 is the concentration of hydrogen protons. Equation 28 can be converted into a function $f([H^+] = 0$, equation 43). The function is solved numerically using an iterative approach. The Newton-Raphson method is not suitable for solving this function because it has sections where the derivative is zero, therefore the bisection method was used. The concentration of hydrogen protons calculated in this way is the resulting equilibrium concentration after mixing of streams Q_1 and Q_2 . Concentrations of other alkalinity species are calculated using equations (4)-(6) and (14)-(17).

$$f([H^+]) = TA_R - \frac{k_{a1} \cdot [H^+] + 2 \cdot k_{a1} \cdot k_{a2}}{[H^+]^2 + k_{a1} \cdot [H^+] + k_{a1} \cdot k_{a2}} \cdot TIC - \frac{3 \frac{K_w^3}{[H^+]^3} + 2K_1 \frac{K_w^2}{[H^+]^2} + K_1 K_2 \frac{K_w}{[H^+]}}{\frac{K_w^3}{[H^+]^3} + K_1 \frac{K_w^2}{[H^+]^2} + K_1 K_2 \frac{K_w}{[H^+]}} \cdot TFe_R - \frac{K_w}{[H^+]} + [H^+] = 0 \quad (43)$$

4.3.2.2 Transport

Transport of carbonate alkalinity species (H^+ , OH^- , H_2CO_3 , HCO_3^- and CO_3^{2-}) are simulated using the advection-diffusion equation, equation 44 solved numerically using an explicit scheme (Benedini & Tsakiris, 2013). The explicit numerical scheme was selected because it allows coupling with models that simulate other processes affecting pH in water and adjustment of chemical equilibrium between the alkalinity species.

$$\left(\frac{\partial C}{\partial t} \right) = - \left(\frac{\partial u_x C}{\partial x} \right) + E \frac{\partial^2 C}{\partial x^2} \quad (44)$$

Where, C is the concentration of the pollutant, x position, t time, E dispersion coefficient and u_x velocity in x direction.

Equation 45 is the numerical solution of equation 44. The parameters in equation 44 correspond to figure 25. Equation 46 defines the stability criterion for equation 45 (Benedini & Tsakiris, 2013). For modelling the user defines the space step (Δx) and the time step (Δt) is calculated to guarantee that the stability criterion is satisfied.

$$C_s^{j+1} = \Delta t \cdot \left(\frac{U_{s-1}^j}{2\Delta x} + \frac{E}{\Delta x^2} \right) \cdot C_{s-1}^j + \Delta t \left(\frac{1}{\Delta t} - \frac{2E}{\Delta x^2} \right) \cdot C_s^j + \Delta t \left(-\frac{U_{s+1}^j}{2\Delta x} + \frac{E}{\Delta x^2} \right) \cdot C_{s+1}^j \quad (45)$$

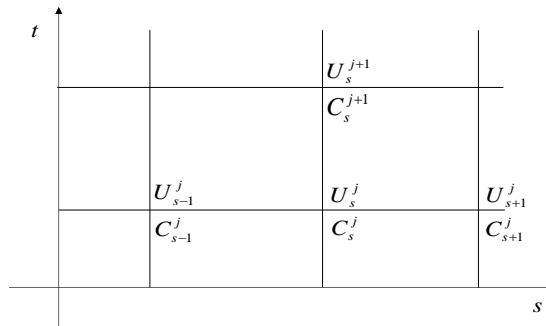


Figure 25 Calculation scheme of numerical solution of advection-diffusion equation. s refers to space and j to time (Paper V).

$$0 \leq \left(\frac{U\Delta t}{2\Delta x} \right)^2 \leq \frac{2E\Delta t}{\Delta x^2} \leq 1 \quad (46)$$

4.3.2.3 Other processes

In the far field, the alkalinity species are transported, and reactions continuously adjust the equilibrium while the surrounding environment (other processes) also affects the concentration of alkalinity species. Other processes include exchange of gases between the atmosphere and stream water, dissolution of stream bed minerals as well as the influence of sources and sinks. How to model sources and sinks is described in hydraulics and water quality modelling books and it is not discussed here (Benedini & Tsakiris, 2013). Modelling of gas exchange between stream water and atmosphere as well as dissolution of stream bed minerals are processes explained through mass transfer principles which are less discussed in surface water modelling. Carbon dioxide, CO_2 , and calcium carbonate, $CaCO_3$, are chosen to demonstrate how to model gas exchange between stream water and atmosphere and dissolution of stream bed minerals, respectively. Carbon dioxide CO_2 degassing and

$CaCO_3$ dissolution were chosen because they are two of the most important processes influencing pH in natural waters; and $CaCO_3$ is commonly used in reclamation projects in streams impacted by acidic discharges (Ziemkiewicz, Skousen, Brant, & Lovett, 1997). Both CO_2 degassing and $CaCO_3$ dissolution are simulated using classical mass transfer theories (Treybal, 1981; Foust, A., Clump, Maus, & Anderson, 1980).

Carbon dioxide CO_2 degassing and $CaCO_3$ dissolution, can be described using the mass balance, equation 47. Taking, $a = S/V$ where S , is the mass transfer area and V the volume of water of stream element; and $N = \left[\frac{\text{moles}}{\text{m}^2\text{s}}\right]$ molar flux of the solute considered. The change of number of moles in given control volume due to moles of solute crossing the surfaces can be calculated using the molar balance, equation 47.

$$A \cdot \Delta x (C_{t+\Delta t} - C_t) = a \cdot A \cdot \Delta x \cdot N \cdot \Delta t \quad (47)$$

Where, A is the stream cross section area, and Δx is equivalent to the length of control volume. For an infinitesimal element of volume, the equation 47 can be re-written as equation 48.

$$\left(\frac{\partial C}{\partial t}\right)_{(\text{mass-transfer})} = a \cdot N \quad (48)$$

Equation 49 defines molar flux. Equation 50 is obtained replacing equation 49 in equation 48.

$$N = h(C_s - C) \quad (49)$$

$$\left(\frac{\partial C}{\partial t}\right)_{(\text{mass-transfer})} = a \cdot h \cdot (C_s - C) \quad (50)$$

Where: h - is the mass transfer coefficient in m/s , C_s - is concentration of solute at the interface (solid-liquid or liquid-gas), that is equivalent to saturation concentration in mol/m^3 , C - is the average concentration of solute in the stream in given location in mol/m^3 . Equation 51 is obtained integrating the equation 50 from t to $t + \Delta t$ and C_t to $C_{t+\Delta t}$. The change of concentration of a certain specie ΔC due to the process described by equation 50 is obtained applying $\Delta C = C_{t+\Delta t} - C_t$ and $C_{t+\Delta t} = \Delta C + C_t$ to equation 51, resulting in equation 52.

$$C_{t+\Delta t} = C_s - (C_s - C_t)e^{-a \cdot h \cdot \Delta t} \quad (51)$$

$$\Delta C_{mass-transfer} = (C_s - C_t) \left[1 - e^{-a \cdot h \cdot \Delta t} \right] \quad (52)$$

i) Calcite dissolution

Calcite dissolution affects directly the concentration of $[CO_3^{2-}]$ in water, thus affecting the total alkalinity and pH. Equation 53 is the chemical reaction of calcite dissolution. The solubility constant is calculated by equation 53a. As the $C_s = [Ca^{2+}] = [CO_3^{2-}]$, the saturation concentration depends only on solubility constant, equation 54. The solubility constant of calcite at 25 degrees is found in chemistry handbooks (Appelo & Postma, 1999).



$$K_s = [Ca^{2+}] \cdot [CO_3^{2-}] \quad (53a)$$

$$C_s = \pm \sqrt{K_s} \quad (54)$$

As $a = S/V$, $S = P \cdot \Delta x$ and $V = A \cdot \Delta x$, the mass transfer area per unit volume is calculated using equation 55. Therefore, the change of concentration of CO_3^{2-} in the stream due to calcite dissolution can be calculated using equation 56.

$$a = \frac{P}{A} = \frac{1}{R} \quad (55)$$

Where: R is hydraulic radio, and P wetted perimeter.

$$\Delta C_{calcite} = \left(\sqrt{K_s} - C_t \right) \left[1 - e^{-\frac{1}{R} h_p \Delta t} \right] \quad (56)$$

ii) Carbon dioxide degassing

Degassing or absorption of CO_2 affects the concentration of carbonic acid, H_2CO_3 , in water, thus affecting the alkalinity and pH. Concentration of carbonic acid in surface water depends on partial pressure of CO_2 in the air (p_{CO_2}), equation 57. When the stream is disturbed by adding acidic water there will be CO_2 exchange with the atmosphere tending to a new equilibrium.

$$C_{s,CO_2} = \frac{P_{CO_2}}{K_H} \quad (57)$$

Where: K_H is the Henry constant, and C_{s,CO_2} is the saturation concentration of CO_2 in water. Concentration of carbon dioxide is related to the concentration of carbonic acid in water through chemical reaction described by equations 58 and 58a. Thus, the changes in concentration of carbonic acid in water within a time interval Δt , can be calculated using equation 59.



$$K = \frac{[H_2CO_3]}{[CO_2]} \quad (58a)$$

Where, K is the equilibrium constant.

$$\Delta C_{\text{carbon dioxide}} = K \cdot \left(\frac{P_{CO_2}}{K_H} - \frac{[H_2CO_3]_l}{K} \right) \left[1 - e^{-a \cdot h_G \cdot \Delta t} \right] \quad (59)$$

If the river has a constant cross sectional area A and width W , equation 60 calculates the mass transfer area per unit volume. Equation 61 gives the change of concentration of H_2CO_3 in the stream water due to CO_2 degassing.

$$a = \frac{S}{V} = \frac{W}{A} \quad (60)$$

$$\Delta C_{\text{carbon dioxide}} = K \cdot \left(\frac{P_{CO_2}}{K_H} - \frac{[H_2CO_3]_l}{K} \right) \left[1 - e^{-\frac{W}{A} \cdot h_G \cdot \Delta t} \right] \quad (61)$$

Where, h_G is the mass transfer coefficient of carbon dioxide.

Other similar processes can be modelled using the same procedure as for calcite dissolution and carbon dioxide degassing. Mass transfer coefficients can be estimated using correlations that have been developed based on momentum, mass, and heat transfer analogies (Treybal, 1981; Foust, A., Clump, Maus, & Anderson, 1980). More accurate values of mass transfer coefficients can be determined experimentally. For this modelling the mass transfer coefficients were estimated using a correlation called Reynolds and Prandtl analogy, equation 62, (Treybal, 1981; Foust, A., Clump, Maus, & Anderson, 1980). Reynolds number (Re), and Schmidt number (Sc) are calculated using equations 63 and 64, respectively.

$$\frac{h}{u} = \frac{0.03 \cdot \text{Re}^{-0.2}}{1 + 2.1 \cdot \text{Re}^{-0.1} (Sc - 1)} \quad (62)$$

$$\text{Re} = \frac{u\rho R}{\mu} \quad (63)$$

$$Sc = \frac{\mu}{D_{AB} \cdot \rho} \quad (64)$$

Where, u is the water velocity, μ is the water viscosity, R is the hydraulic radio, ρ is the water density, and D_{AB} is the diffusivity coefficient.

4.3.2.4 *Equilibrium adjustment*

The carbonaceous alkalinity species are simulated being transported separately. After each calculation step the equilibrium between them is adjusted. The equilibrium is adjusted after taking into consideration both advection-diffusion and the effect of the surrounding environment (other processes) for each carbonaceous specie, figures 22, 23 and 24. Equilibrium adjustment is done using the same principle as the one used for simulating mixing, equation 43. If iron is present in the water, its influence during transport is considered during the equilibrium adjustment.

4.3.2.5 *Analysis of model results*

The pollutant transport equation for a conservative pollutant solved using an explicit solution was previously demonstrated to be accurate enough for practical applications (Benedini & Tsakiris, 2013). Simulating mixing of streams using the principle of conservation of alkalinity and total inorganic carbon with respect to mixing was also shown to yield good results (Paper IV). Carbon dioxide degassing and calcite dissolution were modelled using a classical modelling procedure widely used for modelling mass transfer processes (Foust, A., Clump, Maus, & Anderson, 1980; Treybal, 1981).

The model is tested for simulating pH and alkalinity in the near field, mixing zone (Paper V). It was also tested for the far field with processes including transport, carbon dioxide degassing, and calcite dissolution with equilibrium adjustment between the alkalinity species for *continuous* and *non-continuous* discharge of acidic water, Table 5 (Paper V). Table 6 gives the *pH*, alkalinity and temperature of the main stream and acidic discharge used for all simulations and Table 7 gives the characteristics of the main stream.

Table 5 Hypothetic simulations done to evaluate the modelling methodology. AW=Acidic water (Paper V)

Type		Simulation	Main characteristic
Mixing		1	Without iron
		2	With iron
Transport	Continuous discharge of AW	3	Without equilibrium adjustment
		4	With equilibrium adjustment, calcite dissolution and CO ₂ degassing
	Non-Continuous discharge of AW	5	Without equilibrium adjustment
		6	With equilibrium adjustment, calcite dissolution and CO ₂ degassing

The pH, alkalinity, and temperature in table 6 are real data from Zambezi River in Mozambique. The flowrate of both the hypothetical main stream and the acidic discharge as well as the values of stream characteristics in table 7 were selected to get reasonable value of the dispersion coefficient. Acidic water characteristics were selected to allow easy visualization of the reaction due to iron (III) buffer effect, occurring for pH below 4.3. Values of the mass transfer coefficient can be estimated from the literature or measured experimentally (Foust, A., Clump, Maus, & Anderson, 1980; Treybal, 1981). For the present modelling, the mass transfer coefficients were estimated using equation 62. The values of diffusivities of CO₂ and CO₃²⁻, water viscosity and density were taken at 25°C. The stretch of stream used for the simulation had a 10-km length and the total simulation time was 2 hours. For the non-continuous simulation, the acidic water discharge time used was 10 minutes. The space step for the numerical calculation was 2 meters. These parameters were also selected to permit a clear illustration of the impact of the acidic water discharge on the stream without having extremely long simulation times.

Table 6 Data used for hypothetic simulation. pH, alkalinity, temperature, and flowrate of acidic discharge, upstream the mixing zone and in the main stream before contamination (Paper V).

	Upstream the mixing zone	Stream before discharge of acidic water	Acidic discharge
pH	7.9	7.9	3.5
Alkalinity (eq/l)	0.009	0.009	0.000
Temperature (°C)	25	25	25
Flow(m ³ /s)	1.94	-	0.2

When the main stream water and acidic discharge are mixed, table 6, there is a significant difference of pH depending on whether iron is present or not in the acidic water, table 8 (Paper V). Three simulations were done, the first without Fe³⁺, the second with 0.09 eq/L of Fe³⁺, and the third with 0.3 eq/L of Fe³⁺ in the acidic discharge. When the concentration of Fe³⁺ increases in the acidic discharge both resulting pH and alkalinity decrease, as expected. The behaviour is explained by Fe³⁺ capturing OH⁻ radicals successively as Fe(OH)²⁺, Fe(OH)₂⁺ and precipitating as Fe(OH)₃, thus reducing both the pH and alkalinity, equation 27.

Table 7 Stream characteristics used for hypothetical simulation. Stream width, cross section, wet perimeter and dispersion coefficient (Paper V).

Width (m)	6
Cross section area (m ²)	7.2
Wetted perimeter (m)	8.4
Dispersion coefficient (m ² /s)	5

Table 8 pH and alkalinity resulting after discharging the acidic water in the near field. Simulations correspond to table 5 (Paper V)

Simulation	Main characteristic	pH	Alkalinity (eq/l)
1.	(without iron)	5.94	0.0081
2.	(with iron = 0.09 eq/l)	5.09	0.0015
	(with iron = 0.3 eq/l)	4.25	0.0002

There is a significant difference when pH is simulated as a conservative pollutant compared to when it is simulated with equilibrium adjustment, see figures 25 and 26 for the continuous and non-continuous discharge, respectively (Paper V). For the case of continuous discharge of acidic water, the contamination front travels downstream with pH between 5 and 7.9. These values are equal to the pH immediately after mixing is completed and the pH in stream before contamination, respectively (see figures 25a and 25b). This shows that the effect of the carbon dioxide degassing and calcite dissolution is not significant during the first 2 hours of simulation. However, the shape of the front of the polluted water for the case of equilibrium adjustment (figure 25b) differs from the one without equilibrium adjustment, see figure 25a. This is because when hydrogen ions together with other ions considered (OH^- , H_2CO_3 , HCO_3^- and CO_3^{2-}) being transported are affected by the dispersion creating a front with pH varying from 5 to 7.9. When carbonaceous species are simulated separately, the concentrations in the front are not in equilibrium and when the equilibrium between the them is adjusted there is a tilting of the front upwards, see (figure 25c).

The effect of equilibrium adjustment is even more evident in non-continuous discharge of acidic water (figure 26c) (Paper V). When simulating transport without equilibrium adjustment, the minimum value of pH in the polluted water when it travels downstream increases due to dispersion (figure 26a), tending towards the original value of pH in the stream (pH=7.9). The same behaviour can be seen in the simulation of all alkalinity species (H^+ , OH^- , H_2CO_3 , HCO_3^- and CO_3^{2-}) without equilibrium adjustment; they tend to the original value of its concentration in the stream before contamination, as expected. Therefore, when adjusting equilibrium between the alkalinity species the pH in the stream recovers more rapidly. After two hours of simulation the pH recovers from 5 to 5.5 without equilibrium adjustment (figure 26a) and from 5 to 6.2 with equilibrium adjustment (figure 26b).

The effects of carbon dioxide degassing and calcite dissolution are demonstrated not to be significant for short simulation times for the simulated conditions (Paper

V). This is concluded using the results for the continuous discharge of acidic water, as discussed previously. However, for long simulation times in small streams or using procedures that increase the mass transfer process either by increasing turbulence or the mass transfer area, the effect of CO_2 degassing and calcite dissolution will have a significant contribution.

Despite the fact that the effects of carbon dioxide degassing and calcite dissolution are negligible in the present hypothetical simulation, including the influence of the surrounding environment using these processes in the model is relevant due to their importance in natural waters (Polsenaere & Abril, 2012; Ziemkiewicz, Skousen, Brant, & Lovett, 1997; Choi, Hulseapple, Conklin, M, & Harvey, 1998; Zhai, Dai, & Guo, 2007; Jiang & Wang, 2008). Although widely discussed, determination of mass transfer coefficients for these processes is quite ambiguous and the values obtained using mass transfer handbooks models (Foust, A., Clump, Maus, & Anderson, 1980; Treybal, 1981) differ from the ones obtained in studies about degassing of CO_2 in natural waters (Jiang & Wang, 2008; Zhai, Dai, & Guo, 2007). Studies about more accurate and specific procedures to estimate mass transfer coefficients is necessary for future development of the modelling methodology.

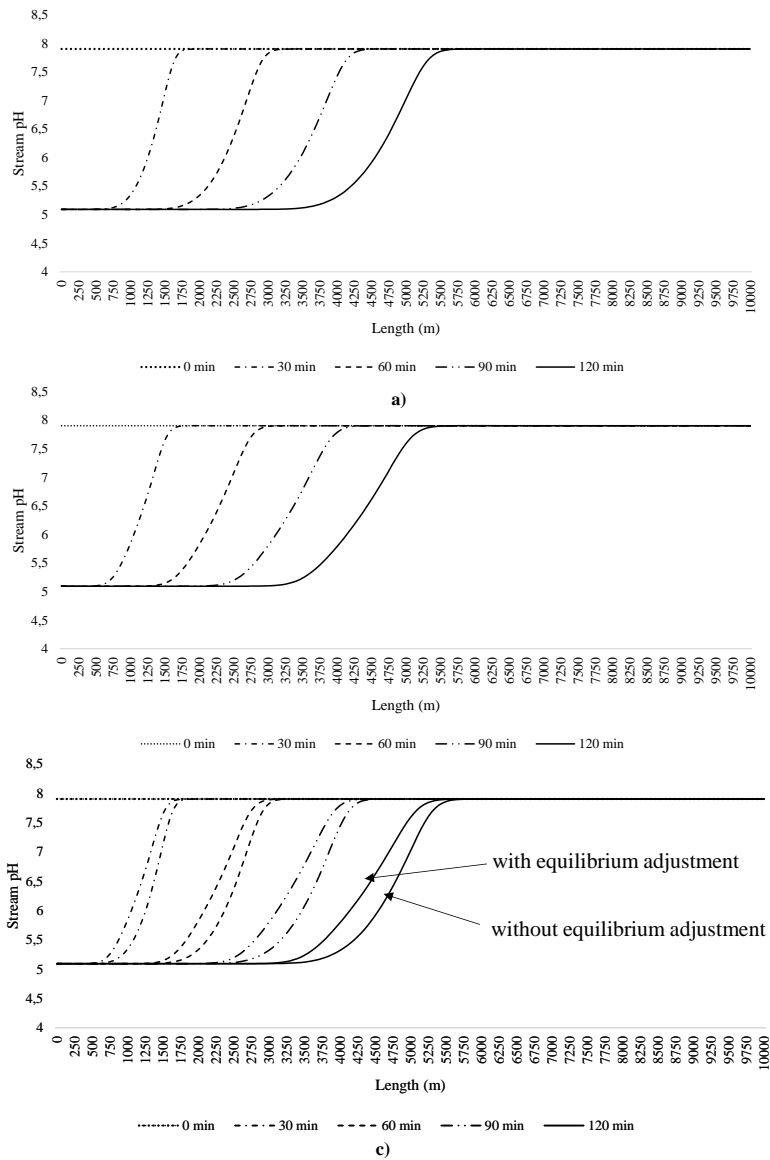


Figure 25 Simulated results for continuous discharge of acidic water. a) pH is simulated without equilibrium adjustment as a conservative pollutant, where only advection and diffusion is considered. b) pH is simulated using advection-diffusion equation with equilibrium adjustment, CO₂ degassing, and calcite dissolution. c) comparison of pH with and without equilibrium adjustment (Paper V).

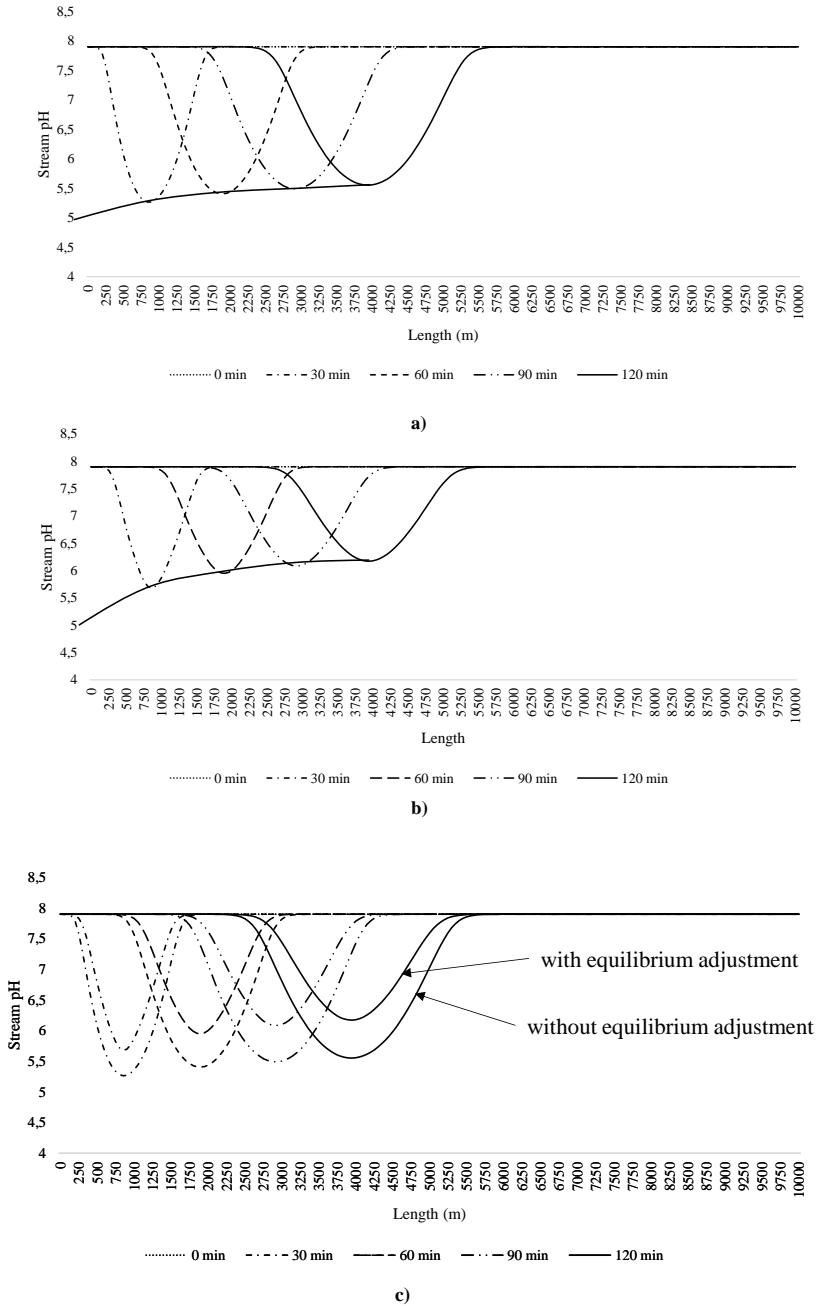


Figure 26 Simulated results for non-continuous discharge of acidic water. a) pH is simulated without equilibrium adjustment as a conservative pollutant, where only advection and diffusion is considered. b) pH is simulated using advection-diffusion equation with equilibrium adjustment, CO₂ degassing, and calcite dissolution. c) comparison of pH with and without equilibrium adjustment (Paper V).

4.4 Applicability and limitations of the models

All process based models proposed in this thesis are to be used in freshwater. Freshwater means that the TDS or electrical conductivity should be below 1000 mg/L or 1500 $\mu\text{S}/\text{cm}$, respectively (Pacific, 2016; Walton, 1989). The reason for this restriction is that, for sake of simplicity it was assumed that the activity coefficients of chemical species in water are close to one; thus, the molar concentration of an ion is assumed to be equal to its activity. The models are not recommended for saline water such as seawater or saline lagoons. Usage of models for saline water requires updating the molar concentrations to activities.

The Model 1 and Model 2 were developed to minimize the input data to be used, while still yielding satisfactory estimates. This makes the models suitable for use in developing countries, but also in developed countries when there is no need to have very accurate information about the water quality obtained through sophisticated and costly monitoring programs.

Model 1

The model is a simple tool that estimates the concentrations of major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) as well as some minor ions and heavy metals (Fe^{2+} , Mn^{2+} , Cd^{2+} , Cu^{2+} , Al^{3+} , Pd^{2+} and Zn^{2+}) in rivers when the pH , alkalinity, temperature, and electric conductivity are known (Paper II).

As discussed before, when using the *generalized method*, the model employs continental averages for calibration, which may induce large uncertainties in the results (Paper II). However, these uncertainties can be partly overcome by using the *customized method*, which, instead of using continental averages, relies on baseline data for the specific river. Even with the uncertainty introduced by the continental averages, the concentrations of major ions estimated using the *generalized method* are reasonably good, as previously shown, although it is important to consider the recommended limits for DiffEC (difference between the measured and estimated in relation to measured electrical conductivity in percentage). It should be noted that all processes in the model are globally valid and therefore the use of Swedish data for validation is not restriction.

Unfortunately, it was not possible to validate the predictive capability of the model for several continents or countries, especially for developing countries where the model is expected to be used, due to lack of data. This is something to be investigated in the future; however, the model was tested using Swedish data and gave good results.

There are many possibilities to further develop the model, such as including more ions, finding different methods to estimate the minor ions and heavy metals that do not use equilibrium concentrations, and including complex compounds in the model estimates. All these improvements, however, require data and more detailed studies.

Model 2

The model is developed to simulate pH and alkalinity in streams. The model has two main components, one for near field or mixing zone and other for far field. The model for simulating pH and alkalinity in the near field, mixing zone was developed considering carbonaceous alkalinity species and tested using laboratory data and an extension for including the effect of iron was proposed but not tested (Paper IV, Paper V). Although not tested using laboratory or field data a modelling methodology for far field was proposed based on principles already validated in previous studies and the quality of results were found qualitatively good based on hypothetical simulation.

The main limitations of Model 2 are: (1) the model assumes instantaneous mixing of acidic discharges and stream water, mixing in natural rivers is affected by river width, depth, water velocity, roughness of the stream bed, and the ration between the flow of the main stream and the acidic discharge; (2) the model cannot capture zonation in wide and deep streams; and (3) the model can only be employed when the purpose is to investigate the *pH* of rivers impacted by acidic discharge and no detailed information about the concentrations of metals are required.

These limitations can be overcome by (1) using mixing theory and real data to obtain mixing zone length; (2) including three-dimensional transport in the mixing zone; and (3) including simulation of concentration of metals in the models.

a) Modelling pH and alkalinity in the near field

The model can be applied to simulate different scenarios of contamination of river waters by acidic discharges in the near field, mixing zone (Paper IV). The model allows simulation of contamination with two different approaches. The first approach is to consider a change of *pH* in the acidic discharge, assuming constant flow, and the second approach is to consider a change in the flow of acidic discharge with constant *pH*. In practice, the model can be used as a decision support tool by authorities for granting new mining licenses, and by different industries that produce acidic wastewaters to manage their discharges to the environment.

At the present stage, this model is limited because it includes only carbonaceous alkalinity species; the effect of other alkalinity species, e.g. iron, manganese, and aluminum are not considered although they would affect the results of the model when dealing with water having *pH* below 4.3. However, the model approach can be improved by (1) including more alkalinity species as well as the effect of iron, manganese, and aluminum in the derivation of equation 32. Despite the limitations of the model it can be used to get a first evaluation of the impact of acidic discharges into rivers. The approach can be further developed to simulate extremely low *pH* cases, such as Iron Mountain in California by expanding equation 38 (Nordstrom, Alpers, Ptacek, & Blowes, 2000).

b) Modelling pH and alkalinity in the far field

A modelling methodology is suggested which can be used to simulate different types of contamination of water which includes acidification and reclamation of streams already impacted by acidic discharges (Paper V). Both continuous and non-continuous discharge of acidic water can be simulated. The modelling methodology can be used by both water quality monitoring authorities and industries. Water quality monitoring authorities can use the modelling for simulating acidification or reclamation of streams. Simulating acidification or reclamation of streams allow allocating resources where there is high risk of impacts. Appropriate allocation of resources is particularly important in developing countries where the resources are limited. The industries can use the model for managing their acidic discharges to the environment.

The model is not tested with real data because of its complexity. Parts and processes of the model must be investigated and optimized separately, before testing the full model to simulate real conditions. The parts and processes include: mass transfer coefficients for CO_2 degassing and calcite dissolution; defining appropriate method for estimating the mass transfer and dispersion coefficients. Also in order to improve the model all ions which may affect significantly the alkalinity when there is acid mine drainage should be included.

5. Conclusions and recommendations

A water quality monitoring system is proposed for the Zambezi River Basin in Mozambique. It has the following characteristics: (1) produces consistent and comparable water quality information; (2) provides feedback to outcomes and goals of the government; and (3) is implemented in a way that allows continuous improvement of water quality information produced, in the context of mining development, and under the constraint of lack of human and financial resources. The system includes two alternative monitoring procedures. One procedure that consists of improving the current situation, which is characterized by multiple actors doing monitoring in isolation, by standardizing the analytical methods and improving data sharing through a common web-based reporting system. The other proposed monitoring procedure is a centralized approach, which consists on having a consulting company doing the monitoring for the whole river basin in Mozambique. The second option has the advantages of improving consistency and comparability of the data, thereby allowing for more accurate trend analyses. However, it would probably be a challenge to convince all stakeholders to have the same consulting company doing the water quality monitoring. It is concluded that the best way forward is to implement the first procedure and slowly move to the second.

One of the major issues of water quality in rivers impacted by mining is acid mine drainage. Acid mine drainage impacts both surface and ground water. When acid mine drainage impacts a water body, it lowers the *pH* and causes an instant threat to the biota and the ecological balance.

Models can be used together with the water quality monitoring system suggested for Zambezi River basin to reduce the overall monitoring cost. Modelling of groundwater contamination due to mining is more common than surface water, while human activities and biodiversity are mainly based on surface water; thus, modelling in this thesis focuses on surface water. Models are to be used both for (1) estimating water quality parameters that are difficult and costly to measure and for (2) simulating acidification or reclamation of streams already impacted by acidic discharges allowing to allocate resources to areas with high risk of pollution. Being able to allocate resources in areas at high risk of pollution is important for developing countries because the resources are limited.

Analysed water quality models are limited to simulate pH and alkalinity in streams impacted by acid mine drainage. Models such as OITS and PHREEQ C can simulate mixing and transport of non-conservative pollutant but they fail when the task is to simulate pH which is influenced by equilibrium reactions between the alkalinity species and interaction with the surrounding environment simultaneously. As the pH influences solubility of minerals in the stream, thus affecting greatly the concentration of inorganic solutes, it is also useful to have a model that estimate other water quality parameters based on pH.

Two models were developed: (1) to estimate the concentration of inorganic ions based on pH, alkalinity, and temperature, thus reducing the cost of sampling and analysis; and (2) to simulate pH and alkalinity in streams impacted by acidic discharges, thus allowing for allocating properly the human and financial resources. Major ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , HCO_3^- , SO_4^{2-} , Cl^- , and NO_3^-) together with the maximum possible concentrations of minor ions and heavy metals (Fe^{2+} , Mn^{2+} , Cd^{2+} , Cu^{2+} , Al^{3+} , Pd^{2+} and Zn^{2+}) are estimated based on pH, alkalinity and temperature using a physical processes based model. The model performance was compared with artificial neural networks which yielded slightly better results than the physical processes based model. However, the physical process based model has the advantage of not requiring historical data. It also has a way of evaluating the quality of results through comparison of the measured and estimated electric conductivity based on modelled results of concentration of major ions making it favourable to be used in developing countries where there is a lack of historical data.

A simple and easy-to-use physical process based model that simulates pH and alkalinity considering equilibrium between the alkalinity species in water was developed to overcome the limitations of available models for simulating acidification of streams. Simulation of pH and alkalinity in the near field, mixing zone considering only carbonaceous alkalinity was tested using laboratory data and it was concluded that it yields satisfactory results. Further, an extension of the model to include iron (III) effect on alkalinity in the near field was demonstrated and, a modelling methodology for simulating *pH* and alkalinity in the far field was proposed. Although, not tested quantitatively using laboratory or field data the modelling approach is based on already tested principles and the results obtained from a hypothetical simulation behave qualitatively as expected. Calibration, by adjusting modelling parameters such as dispersion and mass transfer coefficients will be necessary before practical application.

6.Future work

There is a need of promoting the use of the water quality monitoring system and the models presented in this thesis. The system and the models are expected to be used in Mozambique and other places with similar conditions; i.e. in developing countries with potential environmental problems due to mining. The results of this study will be shared with the Mozambican government water quality monitoring authorities. The system and the models might be optimized to fulfil the actual needs of government authorities. However, with some improvements the models developed in this study can be used also in developed countries to make the water quality monitoring programs and reclamation of streams impacted by acidic discharges more sustainable.

Activities planned for future development of the models include for **Model 1** – (*using pH, alkalinity, and temperature to estimate the concentration of major ions*): (1) design of a water quality monitoring device that measures pH, alkalinity, temperature and electric conductivity and uses the model to estimate the concentration of major ions as well as evaluating the water quality change based on the value of DiffEC (difference between measured and estimated with relation to measured electric conductivity); **Model 2** - (*Modelling pH and alkalinity in stream*): (1) include more ions that influence alkalinity for simulating mixing and test it using laboratory and real data; (2) conduct study about the mass transfer coefficients for dissolution of some minerals and gases such as calcite, gypsum and carbon dioxide; (3) conduct study about appropriate space step to perform simulation; (4) investigate the length of mixing zone as function of river conditions, such as water velocity, stream depth and roughness as well as the influence of dissolution of solid materials at the bottom of the stream and gas exchange with the atmosphere; (5) test the full optimized model using laboratory and field data.

The final task will be combining model 1 and 2. The water quality monitoring device that contains **model 1** is to be used to generate input data for **model 2**. During simulation of contamination or reclamation using **model 2**, **model 1** can also be used to get speciation of water in terms of inorganic ions. The **models 1** and **2** will be combined to produce a computer software that simulates contamination by acidic water or reclamation of already impacted streams, providing both pH and alkalinity values and concentration of inorganic ions.

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