

Process Enhancement of a Cr (VI) Remediation Method to Minimize the Hazardous By-products in the Treated Water

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I declare that this research project is my own, independent work. This research report is being submitted in partial fulfilment of the requirements for the degree, Master of Science (Research) in Hydrogeology at the University of North West, Potchefstroom. It has not been submitted for degree awarding or examination purposes at any other university.

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ABSTRACT

A Cr(VI) contamination at the study area is related to the leaking baghouse slimes dam which was decommissioned 18 years ago, in order to manage and control excessive Cr(VI) contamination impacting the aquifer, and thereafter impacting the off-site receptors. The baghouse slimes dam was decommissioned in the year 2000 and covered with polyethylene thermoplastic to prevent leaching prompted by rain water and to prevent Cr oxidation. Cr(VI) contaminated groundwater is pumped from the underlying aquifer system to the two existing surface treatment settling ponds and thereafter the water is treated by means of dosing system (FeSO_4) and electrochemical or reducing system. These treatment systems are effective in managing or controlling the Cr(VI) contamination. However, neither system can work effectively independently. Hence, the installed liner is another mechanism that was implemented to enhance the remediation systems at the study area.

The main purpose of this project is to determine the effect of the polyethylene thermoplastic liner on the seepage water quality observed in the monitoring boreholes. The plume movement from the source area to the impact monitoring boreholes was modelled in order to ascertain the plume mass, plume movement during abstraction and the plume capture zone. The water chemistry data was used to achieve the objective of the study.

The definite decreasing Cr(VI) concentrations in nine (9) of seventeen (17) existing monitoring boreholes were observed from the year 2000 to 2017. This confirms that the installed liner was capable of ceasing the recharge in the slimes dam and minimizing the chromium oxidation. Six (6) of the seventeen (17) monitoring boreholes showed fluctuating concentrations, which could be attributed to interaction of groundwater chemistry and geological formation. The remaining two (2) monitoring boreholes showed an increasing trend, that stipulates that the plume is localised within that area and the Cr(VI) concentrations trend in these boreholes indicate a potential gradual decrease. Based on the Mann-Kendall trend analyses result, the installed liner is proved to be effective on the seepage water quality.

Given that the plume has reached the impact boreholes, it was deemed necessary to ascertain plume movement, plume mass and the plume capture zone via transport and numerical model using Groundwater Modelling System (GMS10.0).

A conceptual site model was used to develop the numerical and transport model for the study area. GMS runs modular finite difference codes, using modflow in conjunction with its several packages to formulate three-dimensional flow conditions in the vicinity of the baghouse slimes dam. The model was subjected to both calibration and sensitivity analysis. The calibration results indicated a few outliers, which can be attributed to pumping activities

taking place at the study area and they were within an acceptable error. Sensitivity analysis indicated certainty for most stressed parameters. Only two off-set values were evident for recharge and hydraulic conductivity of layer number two.

Based on the modelling results, the movement of the plume is controlled by sorption process. The plume was characterised by means of considering and disregarding sorption. This exercise proved that the plume is moving rapidly when sorption is not considered. The plume mass was also calculated with and without sorption and a difference in mass was observed. When sorption is considered the mass over time is larger than when it is not considered. This proved that when sorption is not considered in the numerical or transport model, inaccurate predictions of plume mass and movement can be calculated and this can lead to negative impacts on plans and finances of the mine.

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CHAPTER 1

1. INTRODUCTION

South Africa is a large-scale ferrochrome producer. The ferrochrome industry is driven by the economic growth of the country and the fluctuating prices of electricity. Although South Africa is facing challenges of economic growth, shortages of electricity and rising electricity prices, it still remains the biggest role player in ferrochrome production (Beukes, et al., 2010). When considering the global amount of mineable chrome ore, studies indicate that South Africa hosts approximately 75% to 80% of economic chromite ore reserves (Beukes, et al., 2010). Therefore, it is expected that large volumes of sludge containing Cr(VI) will be generated.

During the processes of ferrochrome production, oxygen is introduced in the process leading to the oxidation of Cr(III) to Cr(VI). Chromium in the natural environment is commonly present in two states, which are Cr(VI) and Cr(III) (Beukes et al., 2010). The trivalent Cr predominates and very limited hexavalent Cr is normally present. Cr(VI) is regarded as carcinogenic and can have irreversible human health effects. Cr(III) is regarded as non-carcinogenic and does not cause human health effects. It is imperative to reduce Cr(VI) in water to the targeted levels, which are dependent on the characteristics of the site, in order to reduce human health risk to acceptable levels. Although the site setting plays a major role in the target levels required, studies indicate that uncontaminated water should have concentrations of Cr(VI) less than 0.5 mg/l and when the concentrations are above 0.5 mg/l remedial options should be considered (DWAF, 1996) to reduce risk to groundwater users and the environment.

Several methods used to treat Cr(VI) contaminated water exist and some methods are deemed infeasible in comparison to other methods depending on site-specific conditions. Methods which can be considered to treat Cr(VI) contaminated water or prevent further leaching of Cr(VI) include in-situ biological reduction, in-situ chemical or sorption precipitation, electrochemical reduction and physical methods such as installing the impermeable liner (Fang, et al., 2012). Hazardous by-products in large amounts are produced when some of the methods to treat Cr(VI) contaminated water by means of dosing with chemical products or physical redox manipulation are used. The treatment of Cr(VI) contaminated water by means of a reducing agent (FeSO_4 or FeCl_2) increases concentrations of other by-products such as SO_4^{2-} , NO_3^- and salinity in the treated water. These by-products are often hazardous to human health, the environment and in the production processes when not treated. Cr(VI) contaminated water and the chemical dosing thereof, should be monitored and assessed in order to avoid the possibility of causing

contamination in groundwater and the receiving environment (U.S. Environmental Protection Agency, 2000).

2. PROBLEM STATEMENT

At the study area, the groundwater contamination by Cr(VI) was initially detected in 1997, about a year after the leaking slimes dam was commissioned. Since then measures were implemented to prevent further chromium contamination. The leaking slimes dam was decommissioned in 2000 and covered with polyethylene thermoplastic to prevent leaching by rain water and Cr oxidation. All furnaces used for metallurgical processing of the chromite ore were converted to closed furnaces. Based on site-specific hydrogeological risk assessments and monitoring events, a remedial action plan was developed. Site characterisation and risk management studies lead to the conclusion that remediation was necessary. The restoration of groundwater quality to drinking water standards is generally considered impractical and technically not feasible. Corrective action following groundwater resource contamination is based on a risk-based approach. Thus, remediation is required when the contamination poses a risk to the receiving environment and human receptors. The pump and treat system was designed and implemented in February 2015. The system focuses on pumping the water from the aquifer to the surface, after which a dosing system using FeSO_4 as a reducing agent is used to treat the contaminated water.

The dosing system managed to treat Cr(VI) contaminated water. However, in the process of treating Cr(VI) contaminated water, excessive amounts of hazardous by-products (SO_4^{2-} and salinity) were prominent. In order to address both Cr(VI) contaminated water and hazardous by-products at the study area, the pump and treat (P&T) system remediation plan was reviewed. Upon review, it was deemed feasible to fit another system into the existing dosing system infrastructure, in order minimize both Cr(VI) and hazardous by-products in the contaminated water. Although the remediation systems can be implemented and managed to treat the contaminated water, the effectiveness of these systems is dependent on the integrity of the polyethylene thermoplastic liner, and as a result it is essential to determine whether or not the liner is effective to prevent recharge into the slimes dam. The research presented in this dissertation seeks to examine the efficiency of the liner and the existing remediation methods.

3. GENERAL AND SPECIFIC OBJECTIVES

The main objective of the study is to assess the effectiveness of installed liners (polyethylene thermoplastic) after release of the Cr(VI) contamination in the groundwater. Therefore, the following objectives were also formulated:

- Determine the effect of the liner on the seepage quality observed in the monitoring boreholes.
- Assess the water quality after implementation of the remediation systems.
- Determine the extent of the Cr(VI) contamination plume in the groundwater on-site taking into account the plume mass and sorption.
- Determine if the capture zone of the P&T boreholes can capture that plume so as not to reach the impacted monitoring boreholes or receptor boreholes.

CHAPTER 2

2. LITERATURE REVIEW

2.1 Generation of Cr(VI) in Ferrochrome (FeCr) Industry

Chromium can be found in different oxidation states from zero to six (Kamaludeen, et al., 2003). Chromium can occur naturally or as a soluble or insoluble compound. The oxidation states of chromium are named as Cr(0), Cr(III) and Cr(VI) (Beukes, et al., 2010)

Cr(0) is not naturally occurring, this metal is generated during industrial processes. Cr(III) is naturally occurring, this state of chromium is stable, immobile and has no harmful impact on human health and the environment. Hexavalent Cr exists as an oxyanion chromate (CrO_4^{2-}) and originates from anthropogenic activities (Kamaludeen, et al., 2003). Hexavalent chromium is unstable, mobile and harmful to human health and the environment. This oxyanion is produced from activities such as ferrochrome production processes, chromium plating, textile manufacturing, leather tanning, pigment manufacturing, wood preserving and chromium waste disposal (Beukes et al, 2010).

Understanding the Cr(VI) related aspects within the ferrochrome industry requires a broad review of the production and processes undertaken. A generic process employed by the ferrochromium industry is depicted below (Figure 1).

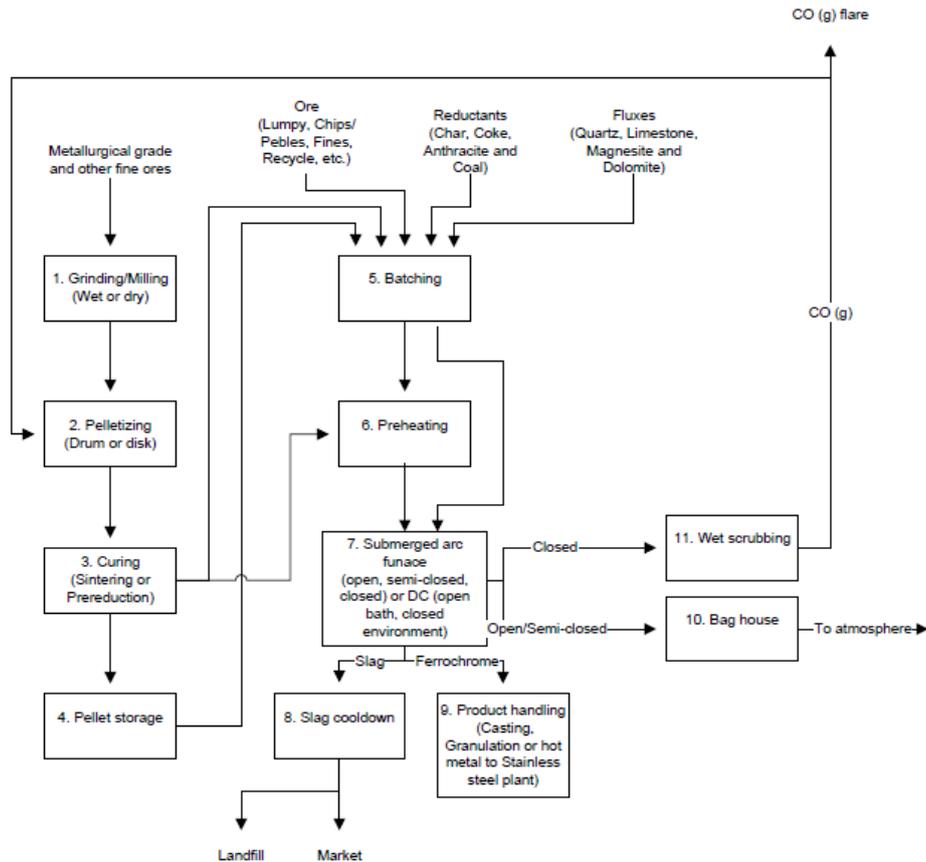


Figure 1: A flow diagram from Riekkola-Vanhanen indicating the most common process steps utilised for FeCr production in SA (Beukes et al, 2010)

Chromite ore is converted to chromite mineral after being mined and crushed (Mining Watch Canada, 2012). This process requires high temperature submerged arc furnaces or direct current arc furnaces and oxygen can be limited or not limited from these processes. During the process a small amount of Cr(VI) can be generated.

2.1.1 Slimes dam cover

Section 24(7) of the National Environmental Management Act, 1998 (Act No. 107 of 1998), clearly states that the mining companies are liable for the management and control of hazardous waste during and after the mine closure. The impacts must be communicated, investigations to assess the extent of the impact should be implemented, action to redress the impacted environment, to achieve practical natural state or to attain acceptable sustainable development should be taken.

Section 24(7) together with environmental management plans or authorised environmental programmes, will assist in safeguarding human health and environment. For this reason, practical environmental programmes have been developed. This includes but is not limited to the installation of liners to prevent acid rock drainage through infiltration of acid seepage.

Limiting oxygen and water ingress into the slimes dam helps to prevent or manage the infiltration of acid water into the aquifer (Fourie & Tibbett, 2009). Studies by MiMi (2004) show that water covers are the best available method to minimize oxygen and water recharge into the slimes dam. This method is said to be cost effective, low maintenance and suffocates the generation of dust.

There are a number of slimes dam liners which are available and considered to be effective in the industry. One of the many liners which are cost effective, is known to be a polyethylene thermoplastic liner. The liner acts as a temporary measure to prevent water ingress and dust generation which can assist in avoiding the Cr oxidation (USEA, 1994).

2.2 Trend Analyses of Groundwater Chemistry

The purpose of the Mann-Kendall (MK) test (Kendall, 1975) is to statistically assess if there is a monotonic upward or downward trend of the variable of interest over time. A monotonic upward (downward) trend means that the variable consistently increases (decreases) over time, but the trend may or may not be linear. The MK test can be used in place of a parametric linear regression analysis, which can be used to test if the slope of the estimated linear regression line is different from zero. The regression analysis requires that the residuals from the fitted regression line be normally distributed; an assumption not required by the MK test, that is, the MK test is non-parametric (distribution-free) (Pohlert, 2018).

Studies (Kendall, 1975) further show that this software is associated with the assumption that, when there is no evident trend, the collected data is not serially corrected over time.

The GSI Mann-Kendall Toolkit is an easy-to-use spreadsheet system for analysing time series groundwater monitoring data to quantitatively determine if the measured concentrations of a chemical are increasing, decreasing, or stable over time, based upon use of the Mann-Kendall statistical method. The software can be applied to data from monitoring points for which groundwater sampling and testing have been conducted at multiple episodes over time (i.e. time-series sampling) to evaluate the concentration trend of each chemical at each monitoring location.

2.3 Transport of Cr(VI) in the Environment

It is important to understand the distribution and transportation of metals in the subsurface when dealing with toxic substances which are harmful to humans and to the environment. This involves the understanding of the mechanisms which drive the distribution and transport of metals. Studies by (Palmer, et al., 1994), state that the speciation of chromium indicates the mobility and chemical transformation in water and soil.

(Shriver et al., 1994) in their study, illustrate how Cr(III) can be favoured and be stable in the environment in relation to Cr(VI). Cr(III) is regarded stable in water with negative Eh and the oxidation state is more favourable, and when Eh is positive the reduction conditions are more prominent. The oxidation states in relation to the potential energy are shown below (Figure 2). Another condition which determines whether the chromium will be in the state of being mobile and harmful is the pH of water. Cr(III) and Cr(VI) species are stable in basic and acidic conditions, however, this is also dependent on the Eh. Looking at Figure 3, it can be seen that a relationship exists between the Eh and the pH and different species of chromium can be identified. When Eh is positive and pH is basic the Cr(VI) is prevalent and when the reverse relationship is considered, the Cr(III) is prevalent.

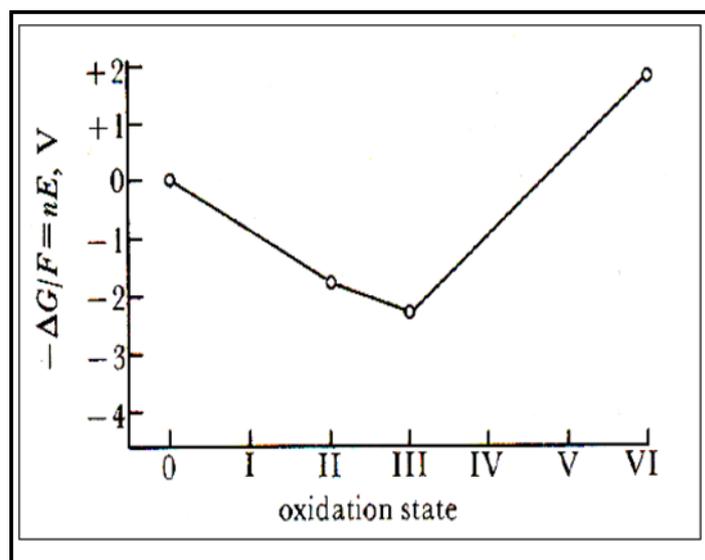


Figure 2: The oxidation state and potential energy of chromium

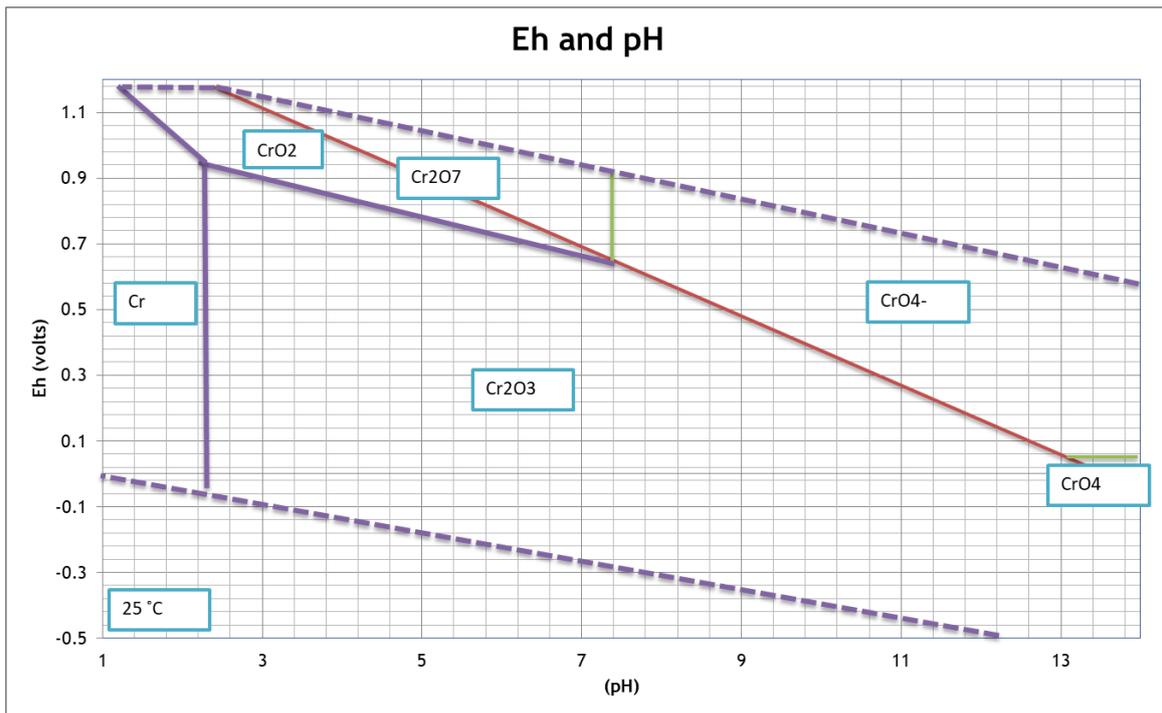


Figure 3: The relationship between Eh and pH

The contaminants tend to follow the groundwater flow direction, however, some contaminants tend not to follow the groundwater flow direction and that depends on their physical, chemical and biological properties. The contaminants and groundwater follow the topography from recharge zone to discharge zone.

Groundwater and contaminants can move rapidly through fractures in rocks. Fractured rock presents a unique problem in locating and controlling contaminants because the fractures do not follow the contours of the land surface or the hydraulic gradient. Contaminants can also move into the groundwater system through macropore root systems, animal burrows, abandoned wells, and other systems of holes and cracks that supply pathways for contaminants (Allwright, 2014).

Movement of solutes which progressively detach from the source area in the subsurface is strongly dependent on the positive gradient, the physical properties of an aquifer as well as the chemical properties of the contaminant of concern. The solutes steadily migrate away from the source area and are dependent on the advection and dispersion processes via groundwater (Verral, et al., 2008). The movement of solutes in the material is conceptualised by (Strassberg, et al., 2011) (see Figure 4).

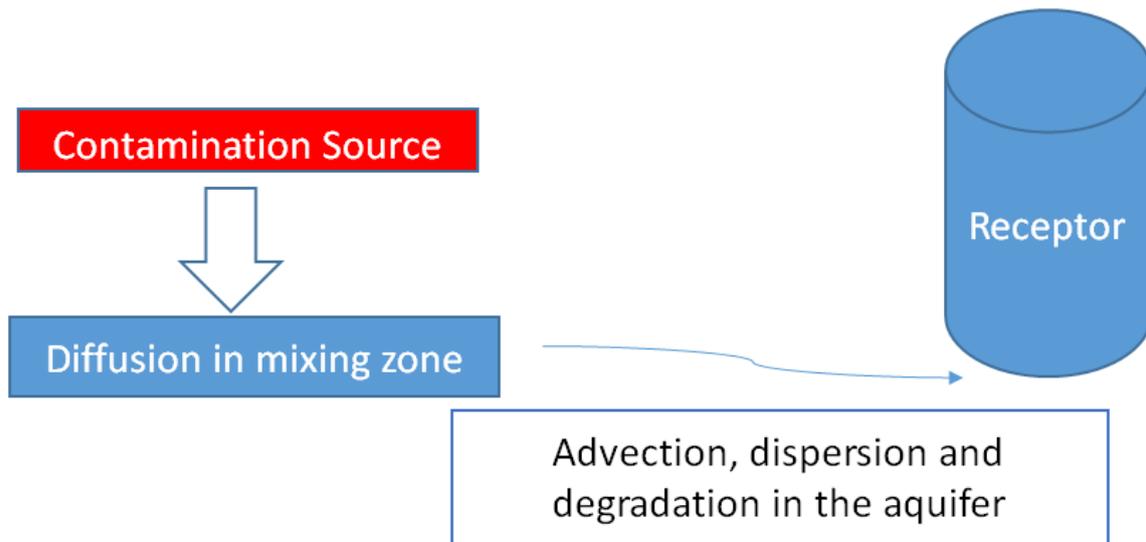


Figure 4: Three dimensional model illustrating contaminant transport by advection (Strassberg, et al., 2011)

Dispersion

Dispersion refers to a mass transferred from one point to another and is subjected to properties of the media and chemical features of the solute. Dispersion is classified as mechanical (Figure 5) and hydrodynamic dispersion (Figure 6); the two are defined by macroscopic transport parameters. Mechanical dispersion is controlled by media intrinsic permeability, substance environment dependence such as distribution coefficients in numerical models and substance dependant such as decay constant (Kalmaz & Barbierri, 1980). Hydrodynamic dispersion is a function of porous material, i.e. the ability of the fluid to pass through the material. Coefficient mechanical dispersion can also not be ruled out, and lastly, the coefficient of molecular diffusion of that medium is required (Craig, 2004). Understanding of these processes can be crucial in viewing or determining the movement of solutes from the source to receptor points. This also contributes in development of the transport models.

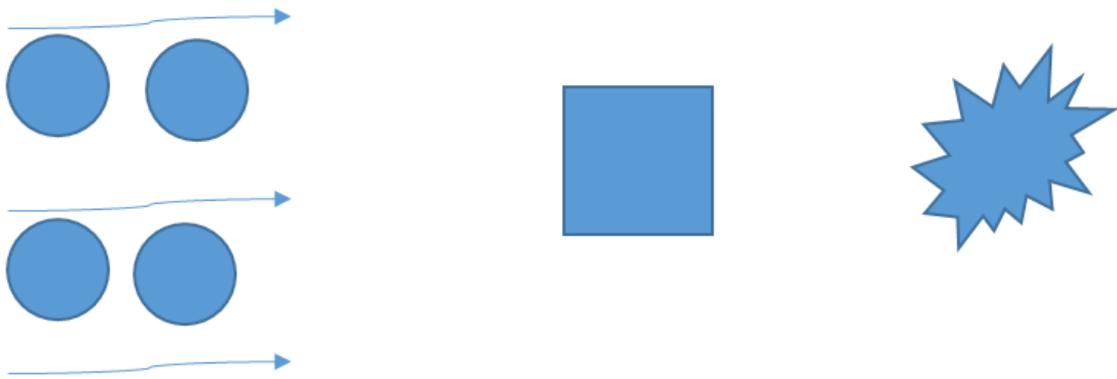


Figure 5: Mechanical dispersion transport on the microscopic scale
(Adapted from Amy Allwright, 2014)

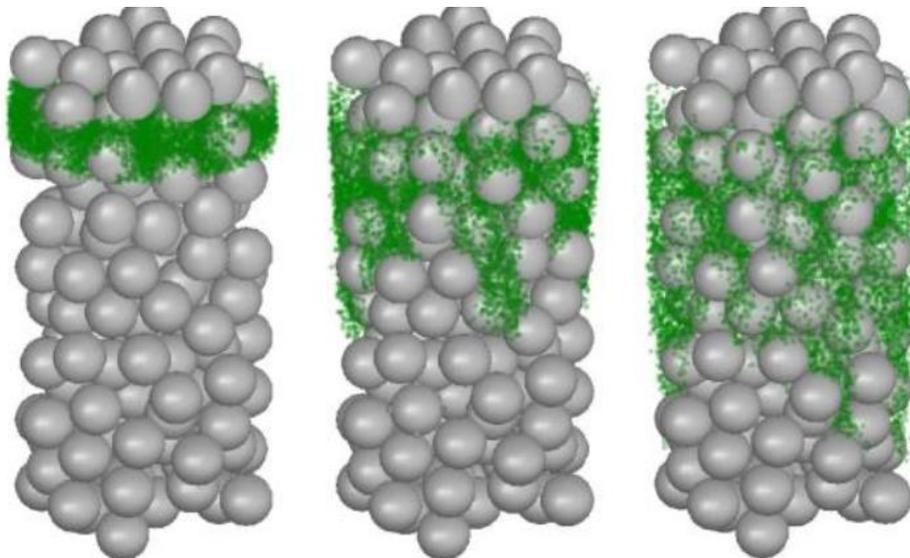


Figure 6: Hydrodynamic dispersion transport on the microscopic scale
(Amy Allwright, 2014)

When solutes move in the soil media, there are several processes that play a major role for the solute to be transported over a short or long distance. This involves sorption, which is divided into absorption and adsorption. Absorption is the incorporation of a substance in one state into another of a different state. Adsorption is the physical adherence of ions and molecules onto the surface of another molecule. This process is the main one which can assist in determining the actual solute velocity in groundwater (USEPA, 1999).

Sorption can affect the contaminants' velocity in groundwater and the correction factor known as retardation requires to be taken into account. This process is based on quantifying the amount of concentration remaining in the soil during the process of contaminant movement in the soil (Kumar & Peter, 2016).

The overall correction factor takes into account the bulk density of the media, porosity and distribution coefficient, which cannot be done using a flow model. This can be done by means of leachate testing or through literature (USEPA, 1999).

The distribution coefficient used to calculate the retardation factor for turf at the study area was based on the adsorption isotherm (Mikołajków, 2003). Freundlich isotherm shows that, when the solute concentration is introduced on the solid surface area, the solutes cover the whole surface area, until a log curve is noticed, which is subsequently followed by a straight line. This means the solutes have covered the whole surface area, however in the later stages the solute is continually introduced to the surface area and steady state is not reached (Mikołajków, 2003). This isotherm is best suited to calculate small data sets compared to Langmuir isotherm which considers large data sets and indicates that the steady state is reached when the whole surface area is covered by solutes. Both isotherms can be used to represent the early stages of the solutes being introduced onto the solid. However, Langmuir isotherm is best suited for early and late concentration rates.

The distribution coefficient used to calculate the retardation factor is known as 1st sorption constant in the transport model and was sourced from the experiments conducted by (Wójcik & Hubicki, 2003). The experiment showed a value of 20 for the distribution coefficient (K_d) of the Xeolith material in alkaline conditions by means of using Freundlich isotherm.

2.4 Numerical Flow Models

A numerical model is a mathematical representation of a real system in a simplified form and takes its physical properties into account to make calculations and inferences about system behaviour. Physical properties are relevant in a flow model while chemical properties are relevant in a geochemical model (Reilly, et al., 2004). It is realised that models cannot address all problems, hence it is important to evaluate the model for its use and consider the assumptions related to the model.

Evaluation of the model is fundamental. Realistic and conclusive decisions can be made with respect to both water quality and water quantity pertaining to the future response of the groundwater system. The evaluation process provides an indication of system behaviour for management of the system. Part of the evaluation process is the understanding of the application of the model. There are several potential applications of the model some of which are listed below (Milovan & Randall, 1992):

- Design and/or evaluation of pump-and-treat systems
- Design and/or evaluation of hydraulic containment systems
- Evaluation of physical containment systems (e.g. slurry walls)

- Analysis of "no action" alternatives
- Evaluation of past migration patterns of contaminants
- Assessment of attenuation/transformation processes
- Evaluation of the impacts of non-aqueous phase liquids (NAPL) on remediation activities (dissolution studies)
- Determining the effectiveness of the slimes dam liners

Given that abstraction of groundwater is taking place at the study area, radial directions are expected. This means that there are limitations to the model that can be used: simple models such as one dimensional and two dimensional models can be deemed not suitable for modelling the study area, given that they focus on simple calculations to assess the groundwater behaviour (one-dimensional model) and assessing only the vertical flow processes (two-dimensional). A three dimensional model focuses on complex calculations and considers both vertical and horizontal flow processes and it is deemed suitable to simulate the groundwater behaviour at the study area (Allwright, 2014).

When working with a model, it is important to note that for one to acquire defensible results, assumptions are considered to play a major role. Assumptions which are considered in most models are the boundaries, hydraulic heads and hydrological capabilities such as wells, particle tracking, recharge and groundwater evaporation (Reilly, et al., 2004). The numerical model at the study area will be used to forecast the future and understanding of groundwater systems and how the pumping at the study area controls the flow paths.

A number of mechanisms are considered when a transport model is developed. Complex models are developed as a mathematical representation of the hydrogeological system to assess advective, diffusive, advective-dispersive, density-dependent, multiphase and other transport problems. Transport modelling is similar to groundwater flow modelling, in that all the same steps are required, i.e. defining model objectives and complexity, data collection, developing the conceptual model, developing the numerical model, refining the numerical model, and applying the numerical model. Transport modelling is dependent on a groundwater flow model as simulation of contaminant transport requires the simulated flow field calculated by a groundwater flow model. A transport model is built upon the basis of a groundwater flow model (Amy Allwright, 2014).

CHAPTER 3

3. SITE SETTING

3.1 Site Location

The study area is situated in North West Province, South Africa. The study area is surrounded by industrial, agricultural and informal land uses. The hydrocensus study indicates that groundwater users are present within a 2 km radius of the site. Industrial land use is limited to the east and north of the contamination source. The site locality study area layout can be seen in Figure 7.

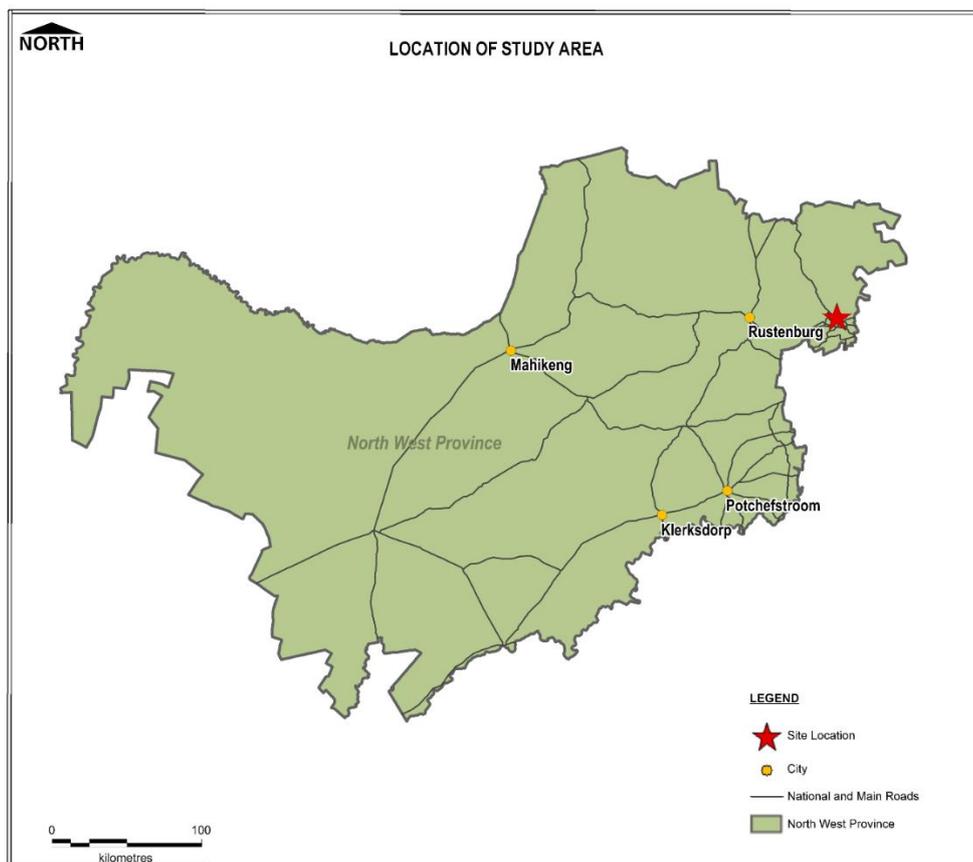


Figure 7: Site location

Chromium (VI) contaminated groundwater at the study area was reported in 1997. The contamination followed after the Old baghouse slimes dam liner ruptured and Cr(VI) leachate infiltrated into the groundwater. The initial detection of Cr(VI) in 1997 was reported following a hydrocensus study conducted at the site in 1997. The leaking baghouse slimes dam was decommissioned in the year 2000 and covered with polyethylene thermoplastic to prevent leaching by rain water and Cr oxidation. All furnaces used for metallurgical processing of the chromite ore were converted to closed furnaces.

Considering the Cr(VI) contamination levels found during hydrocensus at the study area, a risk management approach indicated that a remedial action plan was necessary for the study area. The risk assessment evaluates practices with traditional site investigation and remediation selection activities. However, cost-effective measures for the protection of human health and environmental resources are important. These risk-based corrective actions can address any of the steps in the exposure process, such as removing or treating the residual source, interrupting contaminant transport mechanisms or controlling activities at the point of exposure.

Based on the site classification for contaminated land within a framework of the South African National Environmental Waste Act (Act 59 of 2008) the Baghouse Slimes was classified as a high risk site.

Prior to Implementation of Two (2) Remediation Methods

After the study area was deemed to be hosting hazardous facilities, in view of waste control and environmental impact management, a remediation strategy was developed. The formulated strategy began to address the handling of waste and sought to characterise and remediate the contamination at the study area to the acceptable levels. This began by reviewing the historical data and installing abstraction groundwater boreholes to the existing groundwater monitoring system.

During the review of the existing monitoring groundwater system, it was determined that an additional four groundwater monitoring boreholes to the existing thirteen (13) monitoring boreholes should be installed to act as abstraction groundwater boreholes, while the existing thirteen boreholes will act as source, plume and impact monitoring boreholes. Beside the seventeen existing monitoring boreholes, two monitoring boreholes (PIM5 and IM1) were found at the study area and were only monitored and sampled in 2015.

The thickness of the vadose zone and geology was determined from the geological logs of the four drilled monitoring boreholes. The overview of the soil profile and geology descriptions, vadose zone and geology thicknesses are presented below (Figure 8).

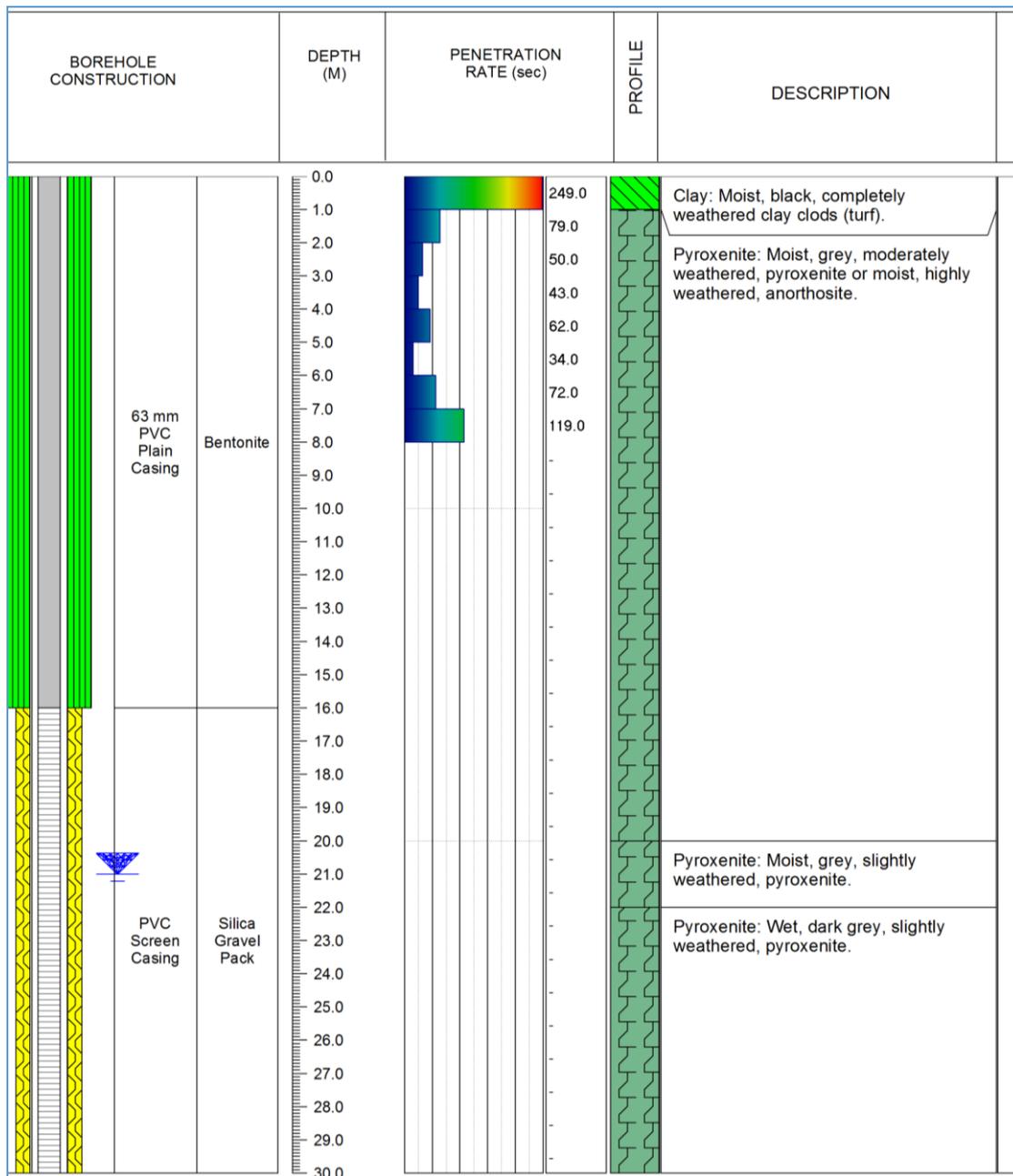


Figure 8: Overview of the vadose zone and geology of the area

A total of four abstraction boreholes were installed in order to form part of the existing groundwater monitoring and treatment system. The boreholes were subjected to pumping tests to attain suitable long term abstraction rates, to allow maximum drawdown. This in turn was required to intercept and retrieve the maximum allowable volume of Cr(VI) contaminated groundwater. The boreholes subjected to the aquifer test are shown in Table 1 below. A summary of the FC results is shown in Table 2.

Based on the drawdown data below, boreholes BH-BH1, BH-PM2 and BH-PM3 were selected to be suitable to be long term abstraction boreholes. Borehole PMA was not

recommended for long term abstraction, as it will run dry within minutes even at very low pumping rates and is therefore not suitable for long term abstraction.

Aquifer Test Summary

Three (3) low flow pumps were installed in BH-BH1, BH-PM2 and BH-PM3. The pumps were determined to have a flow rate of less than 0.5 ℓ/s . As a safety measure, the pumps were set to automatically switch off when the water level reaches the pump inlet to prevent pump burnout. The volume of water permitted to be abstracted ranged between 43 m^3/day and 67 m^3/day . The total amount abstracted is 130 m^3/day .

Table 1: Pump tested boreholes

Borehole Number	Borehole Depth (m)	Water Strikes (mbgl)	Pumping Time (min)	Constant Rate Discharge (ℓ/s)	Recovery Time (min)	Static Water Level (mbgl)	Drawdown (m)
BH-PM2	30	21	210	0.25	30	13.51	0.14
BH-BH1	30	21	180	0.25	40	12.04	0.27
BH-SM3	58.5	21	35	0.25	90	12.56	12.09
BH-PM3	40.5	21	120	0.25	60	14.24	0.1

Table 2: Long term abstraction rates

Borehole Number	Transmissivity (m^2/d)	Sustainable Yield (ℓ/s)	Sustainable Yield (m^3/day)	Sustainable Yield ($m^3/week$)	Sustainable Yield ($m^3/month$)
BH-PM2	130.0	0.2	17.3	121.0	3628.8
BH-BH1	62.9	0.5	43.2	302.4	9072.0
BH-PM3	79.1	0.8	67.4	471.7	14152.3
Total		1.5	127.9	895.1	26853.1

Based on the abstraction volumes calculated, a Pump and Treat System, which constituted three abstraction groundwater boreholes and two settling ponds with a dosing tank was developed. The system was implemented in February 2015. The pump and treat system consists of the following infrastructure and follows the steps below:

- Three abstraction boreholes equipped with low-flow rate pumps (BH-BH1, BH-PM2 and BH-PM3).

- Two settling ponds (pre-treatment and post-treatment).
- One dosing pump.
- Two tanks storing and transmitting aqueous FeSO_4 to the dosing pump.

Prior to implementation of the system a geochemical model to assist in calculating the volume of product to be applied to allow the reduction of Cr(VI) to Cr(III) by means of dosing with FeSO_4 or FeCl_2 was developed. The following parameters were used:

- Volume of Cr (VI) contaminated groundwater of 130 m³/day;
- Concentration of Cr (VI) contaminated groundwater containing 5 mg/ℓ;
- Average hydrochemistry of extracted groundwater; and
- TDS of Cr (VI) contaminated groundwater of 2600 mg/ℓ

Based on the geochemical modelling results, a volume of 0.13 m³/day (FeCl_2) solution was calculated be added to a volume 100 m³/day of Cr(VI) contaminated groundwater on a daily basis to allow for reduction of Cr(VI) to Cr(III). Additional to this, low grade chromite ore and scrap metal were added to settling ponds in the pilot system to further promote the precipitation of Cr(VI) to a Cr(III) oxide form.

Associated risks with ferrous chemicals

Although highly effective in reducing Cr(VI) to Cr(III), the use of ferrous chemicals has numerous disadvantages. These include:

- Their use increases the total dissolved solids (TDS) content of the process and waste water. Fe(II) is removed by oxidation to Fe(III), which consequently forms an Fe(III) hydroxide. This hydroxide precipitates from solution at the pH levels relevant to the FeCr process and waste water. However, the chloride or sulphate remains in solution, causing the increase in TDS.
- The abovementioned increase in TDS could result in increased scale build-up in pipes, spray nozzles of wet scrubber systems, and other equipment.

Although the 'major' environmental and health risk, i.e. Cr(VI), is effectively dealt with during the reduction of Cr(VI) to Cr(III) by Fe(II), the increased TDS and chloride or sulphate load could result in increased salination of surface and groundwater, due to potential process and waste water leakages. Although salination of surface and groundwater is not regarded as crucial as Cr(VI) contamination, it is certainly not acceptable.

P&T system for the current study area indicated that monitoring of the system has shown performance in line with the remediation expectations. Residual concentrations of Cr(VI)

were found to be below detectable levels. However, the hazardous by-products were deemed to be of concern. Hence, an enhancement of the remediation system was considered and concluded to be required.

An electrochemical method was selected at the study area in order to assist the already existing chemical Fe(II) reduction method. This method was selected given that the chemical reduction method had disadvantages in the process of treating the Cr(VI) contaminated water. Although the electrochemical method is currently employed by South African FeCr producers, there is not sufficient research that indicates the effectiveness and environmental soundness of the method. Hence the traditional chemical Fe(II) reduction is currently a preferred method (Beukes, et al., 2012).

Electrochemical method is an alternative method which was considered to be competitive and effective in comparison to chemical reduction method. Studies by Wittbrodt & Palmer, 1992 show that residual Cr(VI) is difficult to remove as the concentration decreases during the pump and treat remediation process. Moreover, studies by Gonzalez, et al., 2003 further show that agents used for reduction of Cr(VI) generate toxic sludge that may be a challenge to remediate.

The electrochemical research (Barrera-Diaz, et al., 2011) indicates that the Cr(VI) is reduced to Cr(III) without introducing chemicals in the process of treating Cr(VI) contaminated water. Subsequently chromium hydroxide is formed and is attracted to the electrode surface area.

Based on the study by (Fang, et al., 2012), it can be deduced that the electrochemical reduction method is best suited to lower Cr(VI) concentrations without generating hazardous by-products as is the case with the chemical reduction method. Electrochemical effectiveness was investigated in detail (Fang, et al., 2012) and it was found that the removal of Cr(VI) is driven by various properties such as the type of cathode material, solution pH, PANI film thickness and electrolyte temperature on the Cr(VI). When the solution pH is low and the PANI film thickness is suitable, the potential to remove the Cr(VI) in the solution is increased. Although the method can be regarded as beneficial in removing the Cr(VI) and no hazardous by-products are generated, it should be noted that the method can pose operational glitches.

In August 2016, an electrochemical unit was installed at the study area. This remediation method was aimed at reducing both the Cr(VI) contaminated water, high dissolved ions, acidic pH levels, water with a high TDS and contamination level of major ions. The system is fitted with electrodes which electrolyse the contaminated water pumped from abstraction boreholes to Settling Pond A. An electrolytic cell was introduced between the pump outlet and Settling Pond A (pre-dosing) to improve efficiency of the treatment system. The

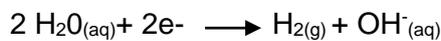
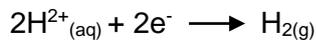
implementation of electrolysis prior to treatment and in situ electrolysis at boreholes, and the electrochemical system are in its pilot phase and will be up-scaled if considered successful.

In the case of the electrochemical system, the geometry, material and reactor configuration play a major role in electro-reduction of Cr(VI). For the purpose of this study, only the electrode material was considered. Barrera-Diaz, et al., 2011, in their research, have illustrated that aluminium and stainless steel do not provide less time of reduction of Cr(VI) compared to iron and copper, where approximately 16% less time is required to reduce Cr(VI) to less than 1 mg/l. The use of iron electrode was proven to be successful in comparison to the copper electrodes. The copper electrodes experience the limitation of mass transfer, while the iron electrode has been proven to adequately handle the mass transfer. Hence the iron electrode was selected to be suitable to build the electrochemical system implemented at the study area. The iron electrodes have the ability to liberate iron ions into the Cr(VI) contaminated water and in turn the ions act as the removal agents of Cr(VI) in the solution. The process of chemical reduction which is followed is represented in the following equations (Barrera-Diaz, et al., 2011).

Anode



Cathode



Bulk solution



3.2 Climate and Drainage

The study area is located in the Highveld climatic zone where summer rain occurs mainly in the form of thunderstorms with the majority of rainfall events occurring between January and April. Winter is cool and dry. Evaporation volumes in the area on a monthly basis greatly exceed rainfall volumes. Temperatures in the region tend to be warm to mild. The average maximum temperature is 25°C and the average minimum temperature is 9°C. The average monthly rainfall and evaporation at Hartebeespoort Dam is shown below (Figure 9).

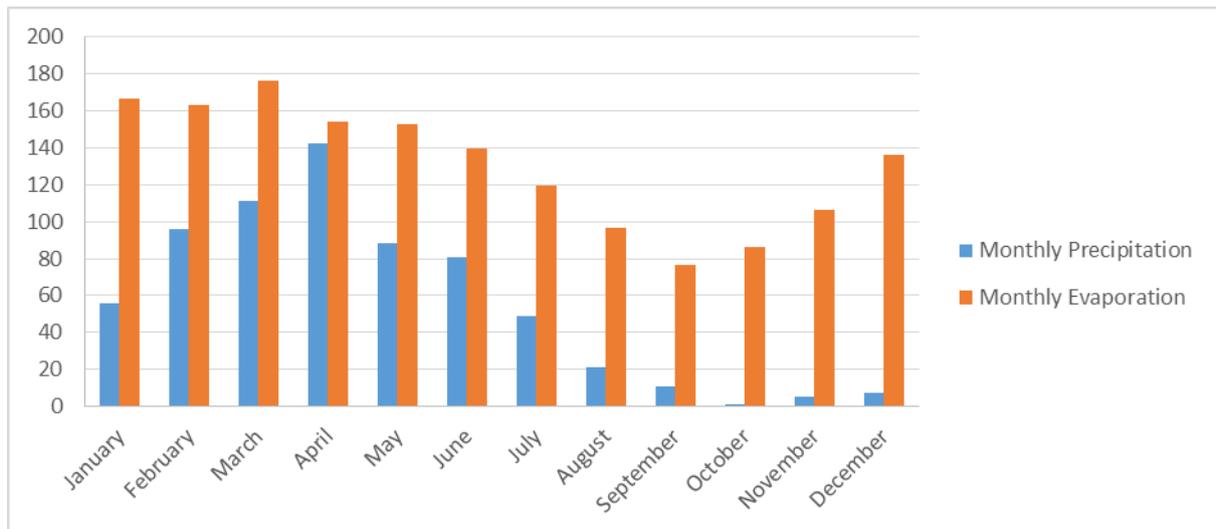


Figure 9: Mean monthly rainfall and evaporation data as recorded at the Hartebeespoort Dam Meteorological Station (A2E001) over a 17-year period (Department of Water and Sanitation, 2017)

3.3 Geology

The well-known largest intrusion on earth is known as Bushveld Complex, with lateral extent over 65 000 km² and up to 8 km thickness (Von Gruenewaldt, 1977). The intrusion is confined within the boundaries of the Transvaal sedimentary basin. The intrusion together with the sedimentary rock formation is due to intracratonic rifting (Eriksson et al. 1991). About 80% of world's resources of PGE and the majority of resources in Cr and V is embedded in the Bushveld Complex (Naldrett, 2004).

Studies by Kruger (2005) indicate that the Bushveld Complex includes four distinct igneous suites. These suites are known as Uitkont Complex, Rooiberg Felsites, Rustenburg Layered Suite and the younger Lebowa Granite Suite (Naldrett et al., 2009; 2012). The Bushveld Complex is divided into three limbs, western, eastern and northern limbs (Wilson and Chunnett, 2006; McDonald et al., 2009; Maier et al., 2013).

The western and eastern limb of Bushveld Complex comprises abundant chromite, as opposed to its northern limb. The study area is situated within the western limb of the Bushveld Igneous Complex. The western limb extends for approximately 200 km along an arc from near Thabazimbi to near Pretoria. The mineral deposit on-site is that of the middle group (MG) chromite seams. The Chrome Middle Group (MG0, MG1 and MG2) seams are currently being exploited by the approved mining operations on-site. The seams have an east-west strike. There are faults and dykes within the study area (Wilson & Anhaeusser, 1998).

The Bushveld Complex consists of basal mafic and ultramafic rocks, named as the Rustenburg Layered Suite and divided into the Marginal zone, Lower zone, the Critical zone (which consists of chromite deposits and the Platinum Group Metals), Main zone, and Upper zone. The economic minerals such as Chromium and Vanadium are contained in the Merensky Reef, which is located within the Rustenburg Layered suite of the Bushveld Complex (Wilson & Anhaeusser, 1998).

The local geology is typical of the Bushveld complex based on the 2526 Rustenburg 1:250 000 geology series map (Figure 10). The area is predominantly underlain by the gabbro-norite of the Rustenburg Layered Suite of the Bushveld Igneous Complex with sporadic areas underlain by diabase. The gabbro-norite is stratigraphically located in the Main zone of the Rustenburg Layered Suite of the Bushveld Igneous Complex. The Main zone is a succession of norite and gabbro-norite with minor anorthosite and pyroxenite. The area is characterised by thick black clay turf.

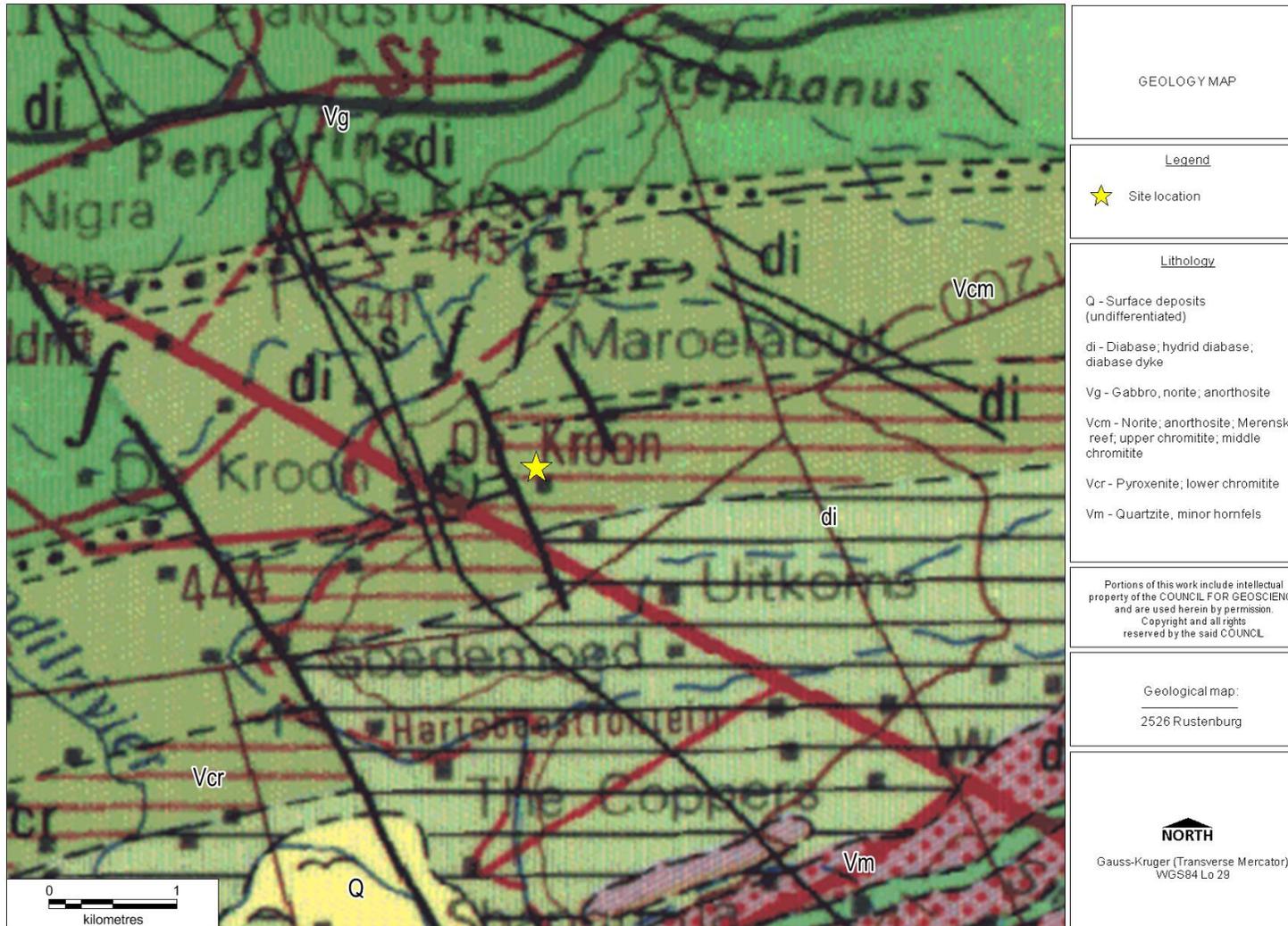


Figure 10: Local geology of the study area (1:250 000 geological series; 2526 Rustenburg)

3.4 Hydrogeology

The study area is underlain by a weathered and fractured aquifer. This is expected given that the Bushveld Igneous Complex comprises a shallow weathered aquifer with deeper semi-confined fractured bedrock. The igneous rock is classified as crystalline and is associated with fractures and lineaments. Groundwater at the study area occurs in the fractures network (Wanner, et al., 2011). The underlying aquifers in the area are semi-confined aquifers in the weathered zone of pyroxenite, norite and anorthosite. Based on geological logs, the study area is underlain by pyroxenite, norite and anorthosite. The dykes run across the study area and three major faults run parallel to each other (see Figure 11). These dykes and faults act as the conduit for groundwater flow (Bense, et al., 2013) and have an effect on water levels. The abstraction of groundwater for the purposes of groundwater remediation and mining activities also influence the groundwater flow direction. The groundwater flow direction was calculated to be in a north-westerly direction as shown in Figure 11 below.



Figure 11: Groundwater flow direction of the study area

CHAPTER 4

4. METHODOLOGY

4.1 Monitoring and Sampling of Groundwater Boreholes and Settling Ponds

Groundwater monitoring and sampling was effective from 1995 prior to the detection of the Cr(VI) contamination in 1997. The surface water sampling of the settling ponds started in 2015 after the remediation systems were installed at the study area. The sampling procedure is outlined below.

Sampling procedure

Groundwater samples were collected by purging (pumping and bailing where possible). The groundwater level was measured using a dip meter before introducing any equipment into the borehole. The groundwater samples were collected by means of a bailer/pumping to draw water from the borehole. The water samples were collected in a 1.5 litre pre-cleaned plastic bottle and a 100 millilitre acid prepared plastic bottle. All samples were kept on ice during fieldwork sampling and later in a refrigerator until delivered to the laboratory. All relevant field information collected was logged. Chain-of-custody documents were prepared as part of the QA/QC and submitted to the laboratory to allow tracking of the samples through the process. The groundwater samples were submitted for major cation/anion analyses, including some constituents associated with activities taking place on the study area.

Sampling of the settling ponds was conducted on a monthly basis to assess the P&T and electro-reduction remediation systems. The abstraction boreholes were selected to pump Cr(VI) contaminated water into the built settling ponds for treatment purposes. These boreholes were drilled within the plume. The source, plume and impact monitoring boreholes were selected to monitor groundwater, in order to assess the groundwater status at certain areas in such a way that an overview of the pollution status of the area could be obtained.

Source monitoring boreholes were selected or placed close to, or in, the source of contamination to indicate its impact on the groundwater chemistry in its immediate vicinity. The plume monitoring boreholes were selected or placed in the primary groundwater plume's migration path to evaluate the migration rates and chemical changes along its pathway. The impact monitoring boreholes were selected to monitor the possible impacts of contaminants on sensitive ecosystems or other receptors. These monitoring points are also installed as early warning systems for contamination break-through at areas of concern. The monitoring points are presented below (Figure 12).

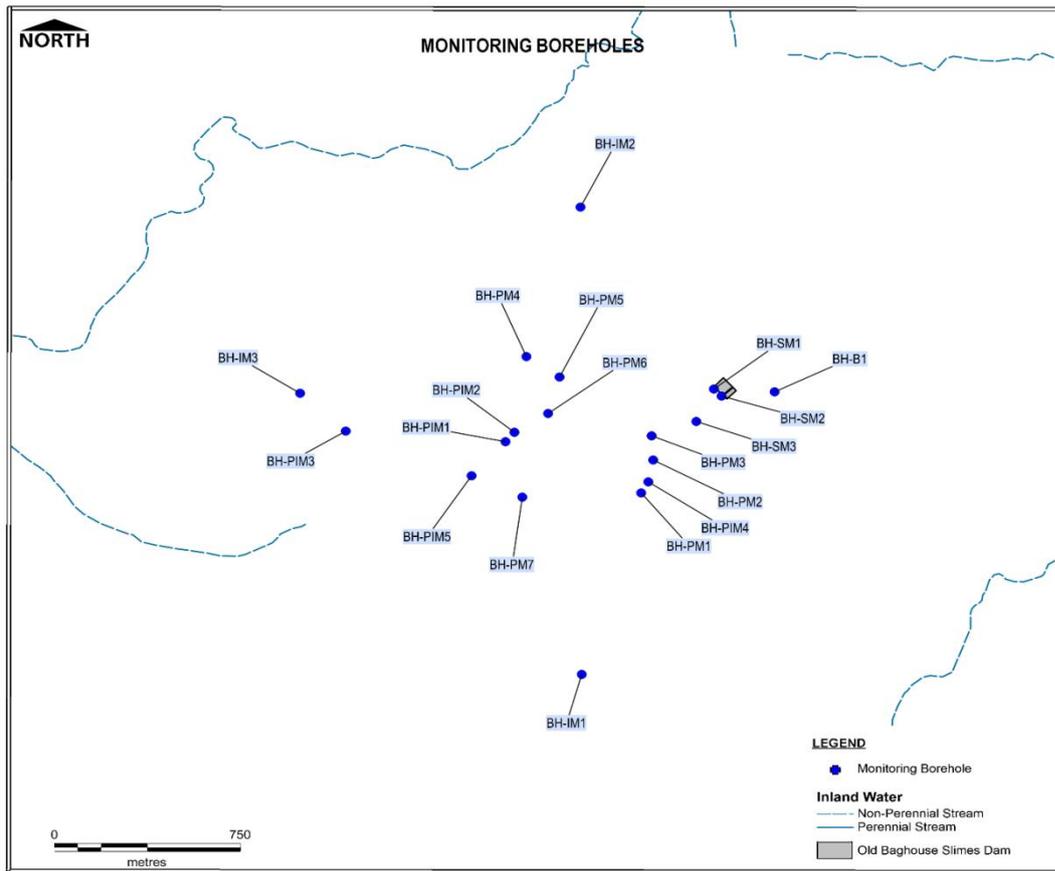


Figure 12: Site showing monitoring points in relation to the Old baghouse slimes dam

4.2 Trend Analyses

Water samples were collected from the existing monitoring boreholes, from the surface water body (dam) and from the settling ponds (A and B). All collected water samples were submitted to a SANAS accredited laboratory. The method used to analyse the cations was the inductively coupled plasma optical emission spectrometry, while the anions were analysed by spectrophotometry. Cr(VI) was analysed using ion chromatography.

The trend analyses were conducted in order to determine whether the installed liner is capable of reducing the generation of Cr(VI) and minimizing further Cr(VI) leachate. The trend analyses for the study area were conducted prior to and after installation of the liner. The analysed parameters and the methods used for analyses are presented in Table 3 below. To determine the upward and downward trend, the Mann-Kendall (MK) test was used.

Table 3: The analysed parameters and the methods

Analyses in mg/l	Method Identification	Original Method
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pH – Value at 25°C	WLAB001	4500-H+ pH Value: Standard Methods for Examination of Water and Wastewater; 20th Edition, Instrument manual
Electrical Conductivity in mS/m at 25°C	WLAB002	2510 Conductivity: Standard Methods for Examination of Water and Wastewater; 20th Edition, Instrument manual
Chloride as Cl	WLAB046	Instrument manual
Sulphate as SO ₄	WLAB046	Instrument manual
Hexavalent Chromium as Cr ⁶⁺	WLAB032	3500-Cr Chromium; Colorimetric Method: Standard Methods for Examination of Water and Wastewater; 20th Edition, Instrument manual
Iron as Fe	WLAB015	3500-Fe Iron; Phenanthroline Method: Standard Methods for Examination of Water and Wastewater; 20th Edition, Instrument manual

4.3 Conceptual Site Model

The conceptual site model was considered in terms of the source, pathway and receptor methodology. The source of Cr(VI) contamination at the study site is associated with the decommissioned baghouse slimes dam. Since the baghouse slimes dam was decommissioned in the year 2000 it has been covered with polyethylene thermoplastic to prevent leaching by rain water and Cr oxidation. Based on the literature review performed and data obtained from the study area, a conceptual site model was developed to provide a conceptual understanding of the hydrogeological and geological characteristics of the aquifer system.

Residual Cr(VI) contamination in the sub-surface acts as a secondary source of contamination. The Cr(VI) plume has migrated from the study area to the impacted supply groundwater boreholes BH-PIM1 and BH-PIM2 through the weathered zone and fractures underlying the site. The weathered zone and fractures underlying the study area are seen to be the preferential pathway and the impacted supply groundwater borehole is a receptor of concern.

Groundwater abstraction is occurring in the agricultural land use surrounding the study area and from the three remediation boreholes. The study area water levels are mainly influenced by the pumping of remediation boreholes. A recharge of 5% and evaporation of 0.0043 m/d

were calculated for the regolith. The hydraulic properties and geological layers underlying the study area are presented in Figure 13. The source of contamination was identified to be a decommissioned slimes dam which was afterwards covered with an impermeable liner. The contamination leaching into the groundwater is regarded as the secondary source. The contamination migrates via the preferential pathways such as the faults and fractures into groundwater. Based on the measured Cr(VI) contamination in the impact monitoring boreholes, it can be deduced that a linkage exists between the source, pathway and receptor. The concentration levels of Cr(VI) presented in the conceptual model in Figure 13, indicate Cr(VI) concentrations before the polyethylene thermoplastic liner was used to cover the slimes dam. The concentrations in the conceptual model in Figure 14, indicate Cr(VI) after the polyethylene thermoplastic liner was used to cover the slimes dam. The presence of the underlying clay liner could not be confirmed.

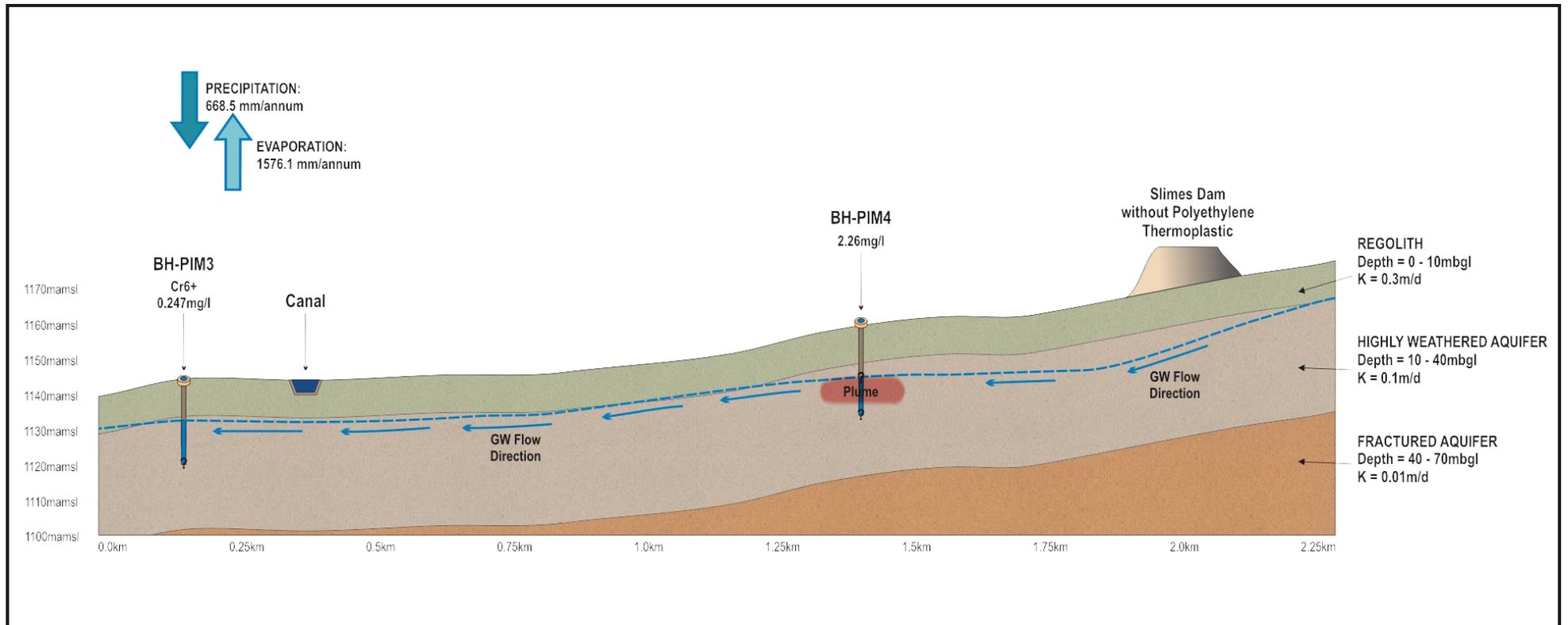


Figure 13: Conceptual Site Model (without polyethylene thermoplastic liner)

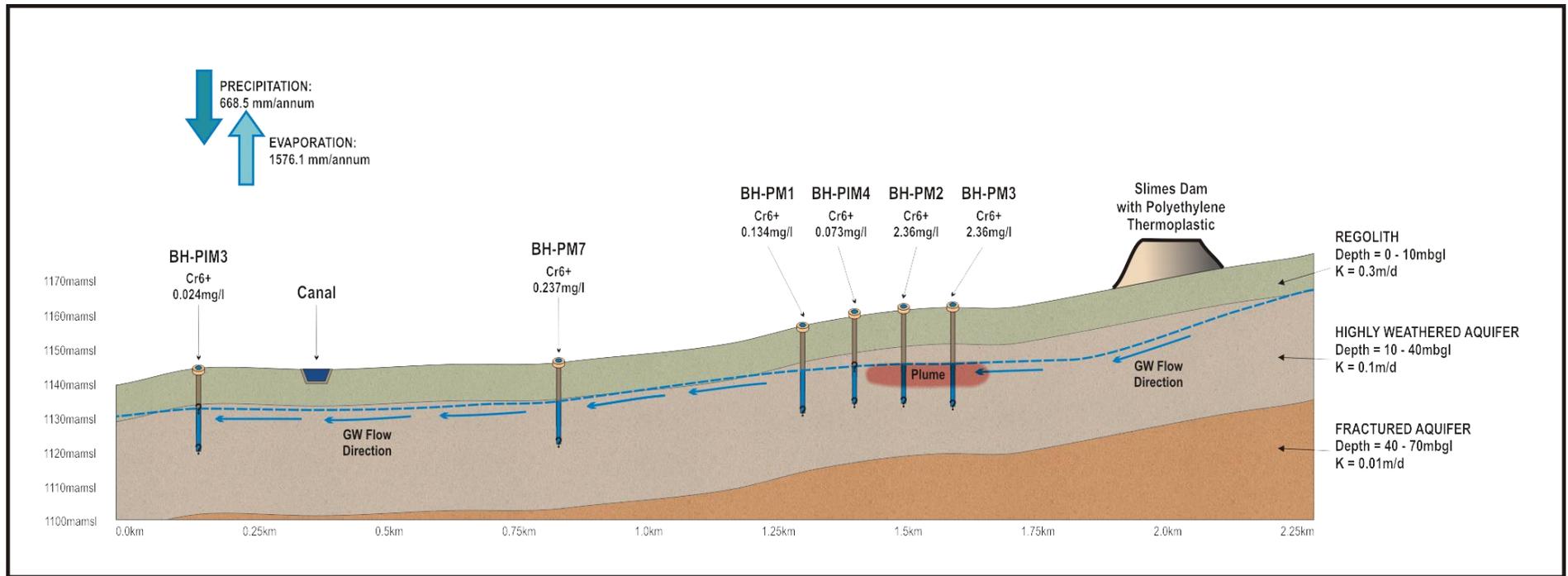


Figure 14: Conceptual Site Model (with polyethylene thermoplastic liner)

4.4 Numerical Modelling

A conceptual model was used to develop the numerical model which was used to assess groundwater flow, mass of the plume and the capture zone of the plume. The finite difference model was used to simulate the conditions at the study area. This was done by means of using the Groundwater Modelling System (GMS10.0).

4.4.1 Model objectives

A local groundwater flow model was developed based on the available aquifer parameters and model assumptions to calculate the potential hydraulic trends of the groundwater system in relation to the contaminant of concern. The numerical model was developed in order to determine the groundwater flow direction, the mass of the plume and the capture zone of the abstraction system.

4.4.2 Assumptions

- The geological structures were not taken into account during modelling.
- The Dry deposition CI used in the mass chloride programme was unknown and as a result the Dry deposition CI from the Recharge programme was used.
- The abstraction remediation boreholes are continuously pumping without interruption.
- To calibrate the model, eight (8) boreholes were used as observation boreholes to calibrate the numerical groundwater flow model.

4.4.3 Data sources

The development of the hydrogeological conceptual and numerical groundwater model was based partly on the following information and data made available to the project team or gathered as part of the groundwater investigations.

- 1:250 000 Geology Map of the area (2526 Rustenburg, Council for Geoscience).
- 1:500 000 Hydrogeological Map sheet (2526 Johannesburg, DWA).
- Digital elevation model (DEM) converted into a 90 m x 90 m grid.

The upper (first) metre below the surface consists of turf. This turf layer is anticipated to have a reasonably high hydraulic conductivity and a seasonal water level is expected in this layer, especially after high rainfall events. Flow in this perched aquifer is expected to follow the surface contours.

The next few tens of metres can be subdivided into two aquifer systems, which are composed of igneous rocks such as pyroxenite or anorthosite or gabbro-norite. The

geological layers are vertical presented (Figure 15). The main aquifers supplying groundwater in the area are fractured aquifers, which have a lower hydraulic conductivity. The permanent groundwater level resides in this unit and ranges between 7.16 m and 20.53 metres below ground level. The groundwater flow direction in this unit is influenced by the regional topography and is generally from high lying areas to the surface drainage courses.

Below a few tens of metres the fracturing of the aquifer is less frequent due to increased pressure. This results in an aquifer of lower hydraulic conductivity and very slow groundwater flow velocities (pyroxenite or anorthosite or gabbro-norite).

Hydraulic conductivity in the constructed models was decreased by an order of magnitude in each successive layer. This was performed based on the work by (Wang et al., 2009) and (Cheema, 2015) which shows that hydraulic conductivity often decreases exponentially with depth. The model inputs are presented in Table 4 below.

Although the most relevant aquifer parameters are optimised by the calibration of the model, many parameters were calculated and/or judged by conventional means. The following fixed assumptions and input parameters were used for the numerical model of this area (Table 4).

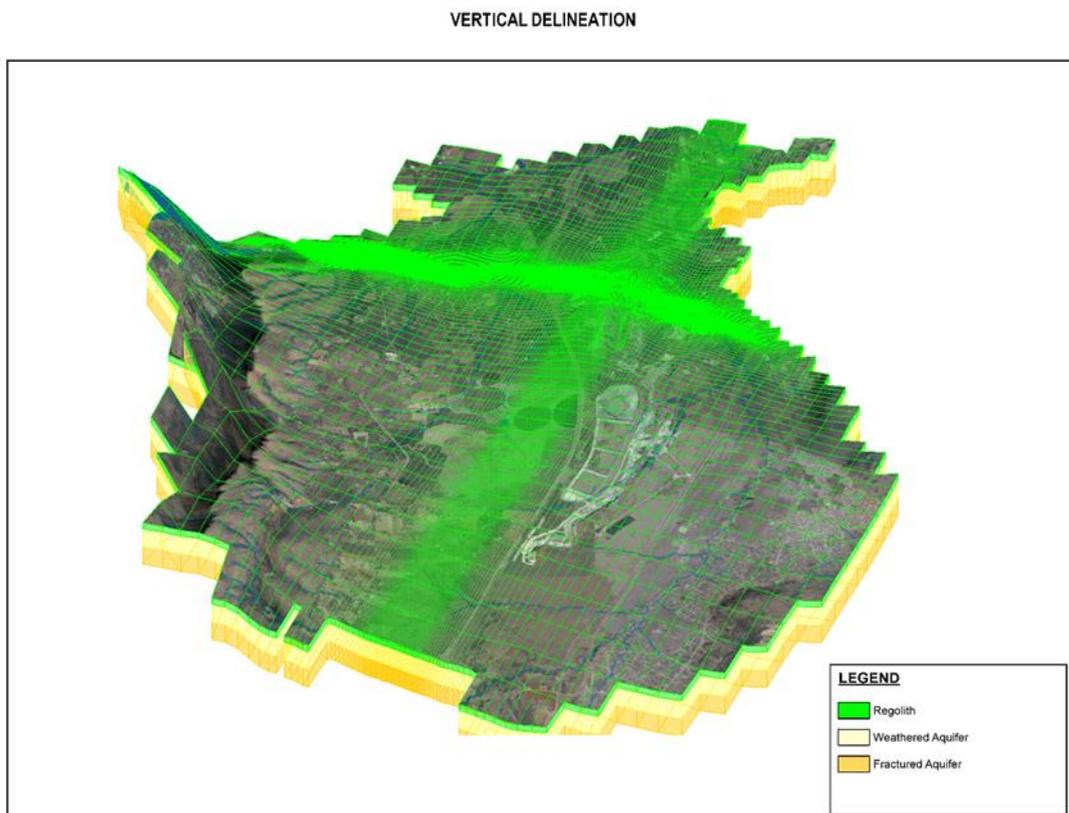


Figure 15: Vertical delineation of the study area

Table 4: Input parameters to the numerical model

	Model Parameter	Value	Unit	Reason
1	Recharge to the aquifer	0.0001	m/d	Calculated (5%)
2	Evaporation	0.0043	m/d	Calculated (Department of Water and Sanitation, 2017)
3	Boundaries	River and escarpment	-	Existing boundary conditions present at the site that would potentially include modelled impacts
4	Refinement	20	m	Based on the scale of the baghouse slimes dam
5	Grid dimensions	90 x 90	Cell count	Product of the grid refinement
6	Hydraulic conductivity	Layer 1 = 0.3 Layer 2 = 0.1 Layer 3 = 0.01	m/d	Du Toit, G.J. (2010)
7	Hydraulic anisotropy (vertical)	10	-	Anderson et al. (2015)
8	Effective porosity	(30% for regolith) 5 declining to 3 with depth in each layer	%	Wang et al. (2009) (Jiang)
9	Layers	3	Count	10 m Regolith, 30 m weathered aquifer and fractured aquifer (1:250 000 geological series; 2526 Rustenburg)
10	Longitudinal dispersion	50	m	Schulze-Makuch (2005)

	Model Parameter	Value	Unit	Reason
11	Mean residual head error	1.97	m	Head error statistics
12	Head error range	10	m	Calculated as 10% of the difference between the maximum and minimum calculated head elevations

4.4.4 Model boundaries

Model boundaries were identified on the premise that natural topographical features such as mountains and rivers served as either no-flow boundaries or constant head boundaries. In addition, model grid refinement at the decommissioned baghouse slimes dam allowed for an accurate and detailed solution of the model matrix in an area (Figure 16).

The same finite-difference flow model was used as a basis for the contaminant transport model; i.e. the 3-dimensional, regional three-layer steady-state groundwater model. However, due to the intensive computer calculations required for each grid cell and associated computer resource limitations, the model grid was adapted to be coarser away from the baghouse slimes dam site, with decreased cell sizes (more refined model grid) towards the baghouse slimes dam (90 m x 90 m).

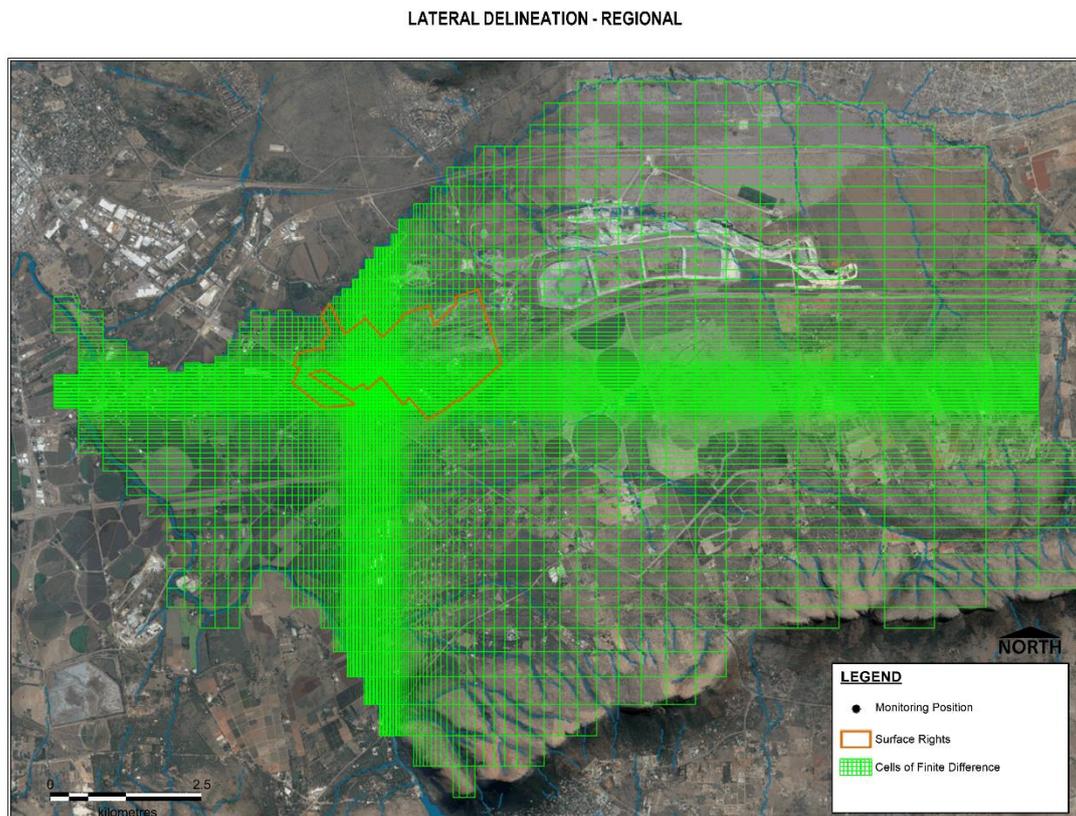


Figure 16: Lateral delineation of the study area

4.4.5 Recharge

Calculation of recharge was done by means of using chloride mass balance method for the local area. This was done by means of using the parameters described below (Van Tonder & Xu, 2000) in the recharge programme. The average rainfall = 668.5 mm/a (DWS, 2017). The Cl in rain = 0.2207 mg/l for inland (The Cl in rain water was unknown; as a result the Cl from the Recharge programme was used). The dry deposition Cl = 0.1 mg/l x (Cl of rain) for inland if no forest exists (The Dry deposition Cl was unknown; as a result the Dry deposition Cl from the Recharge programme was used.). The least contaminated boreholes (PIM3 and IM3) located outside the plume were used to calculate the Cl in groundwater = 35 mg/l (From non-impacted monitoring boreholes)

q = average ground water recharge

Clr = Cl in rain

Cp = Average annual precipitation

Dc = Dry deposition Cl

Cgw = average Cl in groundwater

$$q = \frac{Clr \times Cp + Cp \times Dc}{Cgw}$$

$$q = \frac{1.3 \times 668.5 + 668.5 \times 0.02}{35}$$

$$q = \frac{100 \times 35}{668.5} = 5\%$$

4.4.6 Evaporation

Evaporation data obtained from the Department of Water Affairs was applied in the first layer of the model, as it is expected that the evaporation can only occur on the shallow layer (regolith). The evaporation was converted from mm/a (1576.1 mm/a) to m/d (0.0043 m/d) prior to being imputed in the model.

4.4.7 Calibration

To render a model successful or not, a model should be calibrated prior to being used to calculate the possible trends of the groundwater system. Calibration also aims to prove that the input parameters and boundary conditions are coupled to represent the aquifer system as these parameters produce the same calculated water levels as were measured in the field. The model input data can be modified to fit the observed heads and flows (Reilly, et al.,

2004). However, if the data does not yield the desired results, then the conceptual model can be re-evaluated. When the observed values are far off from the calculated values, it indicates that there is an error in the parameters used in the conceptual model. The best fit and the extent to which aspects of the simulation are incorporated in the model are both crucial in determining how well the model is calibrated (Reilly, et al., 2004). The parameters which can be calibrated are shown in Table 5 below.

Table 5: Calibration Parameters

Group	Parameter
Hydraulic properties	Hydraulic conductivity
	Evapotranspiration, Recharge
Boundary conditions	Precipitation

To calibrate the model, eight boreholes were used as observation boreholes to calibrate the numerical groundwater flow model. These boreholes were selected on the basis that a water levels trend was obtained from the early to latest stages of monitoring when compared to the remaining eleven monitoring boreholes. Four groundwater boreholes of the eight are pumping boreholes and as a result perfect calibration was not expected. If these values fall within the allowed calibrated error range (10% of the maximum minus the minimum calculated groundwater head elevation) the model is considered to be successfully calibrated (Reilly, et al., 2004). The elevations were retrieved from a DEM and were used to create the elevations for each cell within the model grid. Once each cell was allocated an elevation, the measured water levels in metres above mean sea level from the observation boreholes were used to calibrate the model.

4.4.8 Sensitivity analysis

The model requires to be stressed differently from the calibrated conditions. Moreover, calibration is difficult as values for hydrologic parameters, stresses and boundary conditions are typically known at only a few nodes and are associated with uncertainty. In addition, there is even uncertainty about the geometry of the hydrologic system being analysed. In order to reduce the uncertainty, it is essential to subject the (already) calibrated model to a so-called sensitivity analysis. Studies by Reilly, et al., 2004 show that the sensitivity analysis can be conducted manually or automatically. The former investigates a single parameter and adjusts it by an arbitrary amount. The results can be presented in the form of graphs or tables. If the sensitivity analysis is conducted automatically, parameters are automatically adjusted to cause the model to best match observed heads and flow.

4.5 Transport Modelling

As proven by (Zheng & Wang, 1999) MT3D transport package can be used to simulate advection and dispersion of solute, and the retardation factor of turf should be considered. This programme is designed to work with finite difference flow models. In this programme, the limitations of the model, assumptions and strengths are considered. Given that this programme considers the mentioned factors, it can be said to be the best approach to solve the mathematical problems which are representative of the conceptualised study area.

The following inputs and calculations were used to determine the retardation factor for the Cr(VI) concentrations at the study area (Table 6). A source concentration of 10% of Cr(VI) was used to develop the transport model and this is equivalent to an average of Cr(VI) concentrations of 1.0 mg/l, given that the software is unable to calculate small figures. The movement of contamination was assumed to be controlled by pumping that is occurring at the study area at a pumping rate of 130 m³/day from the three abstraction boreholes. The model inputs presented (Table 6) were also used to develop a transport model.

Table 6: Values of Freundlich constants for the adsorption of Cr(VI) at phase contact time 72 h (Wójcik & Hubicki, 2003).

Parameter	Value	Reason
Bulk density	1.1	(Agricultural Information Bank, 2018)
Total porosity	58	(Agricultural Information Bank, 2018)
Distribution Coefficient (L ³ /M)	20	(Wójcik & Hubicki, 2003)
1 st sorption constant	20	(Wójcik & Hubicki, 2003)
2 nd sorption constant	72hrs	(Wójcik & Hubicki, 2003)
Concentration of Cr(VI)	10%	Groundwater concentrations

4.6 Mass of the plume

Modflow for flow solution M3TDS concentration and contamination dataset were used to calculate the mass of Cr(VI) plume and this was calculated with retardation and without retardation. The following formula derived from modflow was used to calculate the mass of the plume over time via transport model. The borehole logs were also considered during the calculation of the mass of the plume.

Mass Calculation

(Top – bottom of the model) x length of the plume x width of the plume x porosity x concentration of the plume x unit conversion factor

CHAPTER 5

5. RESULTS

5.1 Hydrochemistry of Study Area

The results from the collected groundwater, dam and settling ponds samples were used to assess the spatial distribution of contaminants and water quality of the study area. The results were further used to map the Cr(V) within and around the study area.

Analysed groundwater, dam and settling ponds samples represent the hydrochemistry of the studied area. The ions in groundwater were analysed and compared to SANS-241 standards. The major ions for the study area were determined to be Calcium, Magnesium, Sodium, Potassium, Bicarbonate, Chloride, Sulphate, Nitrate, Iron, Manganese, Fluoride, Chromium and Zinc. The source of Cr(VI) groundwater pollution was identified as the Old baghouse slimes dam and other sources for dissolved ions at the study area (Table 7).

Table 7: Sources of dissolved ions at the study area (Berkowitz, et al., 2007)

Dissolved ions in water	Likely local sources
Major Ions	
Calcium	Gypsum (hydrated calcium sulphate)
Magnesium	Olivine, pyroxene
Sodium	Clays, Feldspars, wastes
Potassium	Feldspar, Fertilisers, K-evaporites
Bicarbonate	Soil and atmospheric CO ₂
Chloride	Windborne, rain water, pollution
Sulphate	Gypsum and anhydrite. Windborne, oxidation of pyrite
Nitrate	Windborne, oxidation of ammonia or organic nitrogen, pollution

Dissolved ions in water	Likely local sources
Minor Ions	
Iron	Oxides and sulphides, corrosion of iron pipes
Manganese	Oxides and hydroxides
Fluoride	F-bearing minerals (e.g. Fluorite, biotite)
Trace Elements	
Cr	Baghouse dust, tailings and igneous rock weathering under mildly reducing conditions
Zn	Wastes

Based on the early Cr(VI) contamination in 1997, a concentration of Cr(VI) of 2.27 mg/l was evident in monitoring borehole BH-PIM1. This concentration was the early alarm of source of Cr(VI) contamination at the study area. Based on the mapped plume in 2015 and 2017 at the study area, the concentrations exceeding 0.05 mg/l of Cr(VI) are located in the immediate vicinity of the decommissioned baghouse slimes dam. Based on the impact monitoring boreholes, the plume has been delineated and is limited from the impact monitoring boreholes BH-IM2, BHIM3, BH-PIM3, and BH-PIM4. However, the impact monitoring boreholes BH-PIM1 and BH-PIM2 have been impacted; this indicates that if the abstraction of the contamination is ceased before the required time, more impact monitoring boreholes will be affected and continuous migration of the plume can be experienced to reach non-impacted boreholes (Figure 17 and Figure 18).

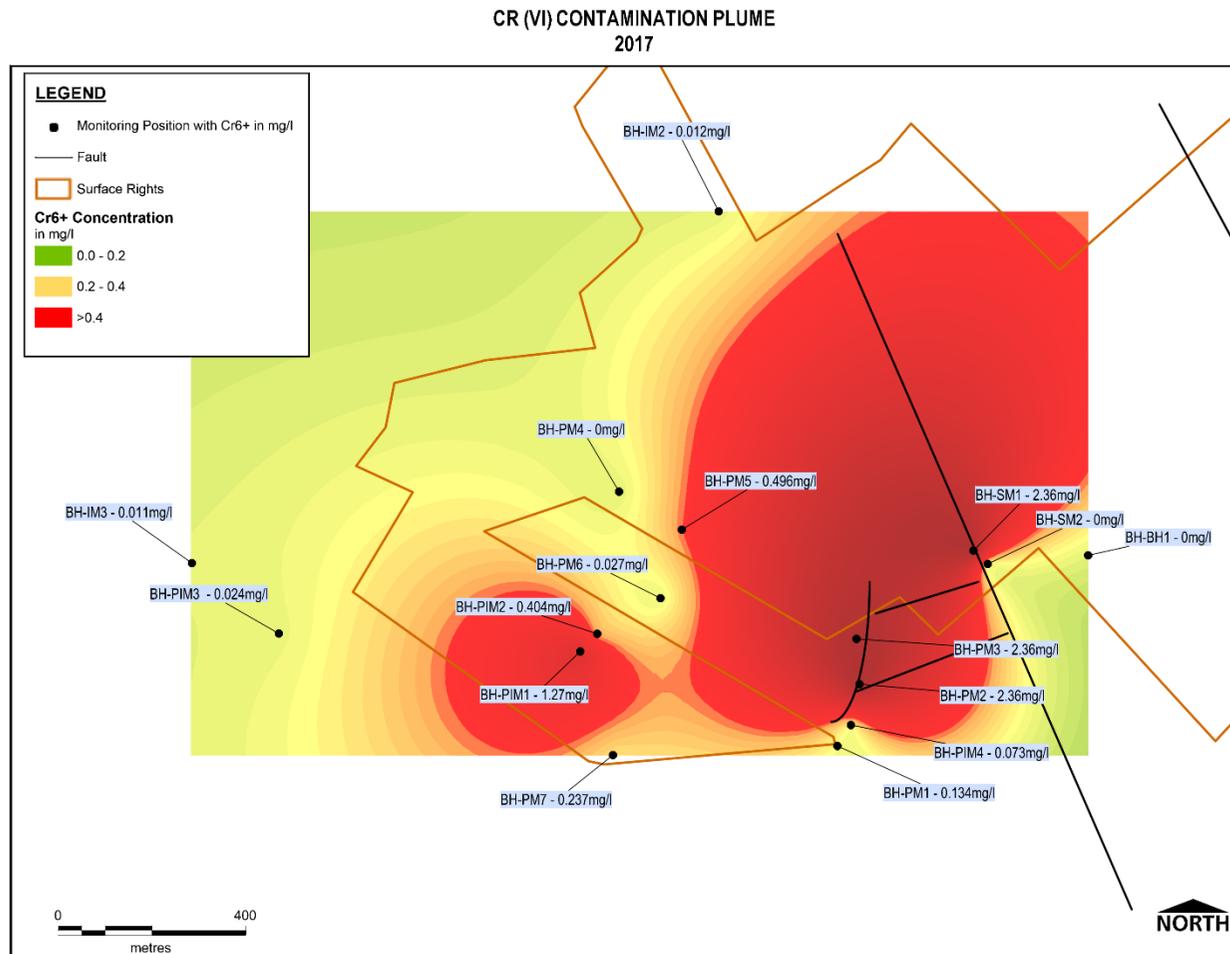


Figure 18: Concentrations of Cr(VI) across the study area (2017)

The results from the chemical analyses were plotted on a stiff pattern map and a piper diagram to visualise the ionic signatures and hydrochemical facies of the samples. There are several types of graphical representation used to represent the chemical component of water (Garba & Mohammed, 2015); the piper and stiff diagram were used to represent the groundwater of the study area.

The piper diagrams aim at grouping sampling points based on similarities or differences. The sampling points that have similar water chemistry will be plotted together (Garba & Mohammed, 2015). On the piper diagram the cation and anion compositions of all the surface and groundwater samples were represented in Figure 19. The relative concentrations of the major ions in meq/l are plotted on cation and anion triangles, and then the locations are projected to a point on a quadrilateral representing hydrochemical facies.

A stiff pattern is a polygon created from four horizontal axes using the equivalent charge concentrations (meq/l) of cations and anions. Stiff patterns allow for visualisation of ionic signatures spatially. The stiff patterns for the groundwater samples are displayed in Figure 20.

The analysed major ions indicate that the source water quality is dominated by Calcium and Magnesium cations and Chloride and Sulphate. These major ions (Chloride and Sulphate) indicate that the contamination is related to the mine activities and at the study area the source of contamination is the decommissioned baghouse slimes dam. The Calcium and Magnesium is mostly related to the weathering of the pyroxenite mineral from the mafic rocks underlying the study area. The sulphate at the study area is not only related to the mine activities; gypsum is also regarded as the source of origin from the fertilising processes in the surrounding agricultural land setting. The degree of weathering of the minerals was not considered for this study. The analysed water sample from the potable water dam, indicate the Calcium and Magnesium and bicarbonate anion species. This indicates unpolluted water, and hence the water from the dam is used for consumption purposes. An ion exchange interaction due to groundwater water and rock interaction is indicated by water type of Sodium, Potassium, Chloride and Sulphate from the water sample collected from BH-IM1. This can also be attributed to protracted groundwater residence times leading to the accumulation of solutes.

Samples collected from the boreholes, which are located within the plume, indicate mine water type. Away from the plume and within the boundary impact monitoring, samples indicate a similar water signature and indicate that the water in those areas is not contaminated.

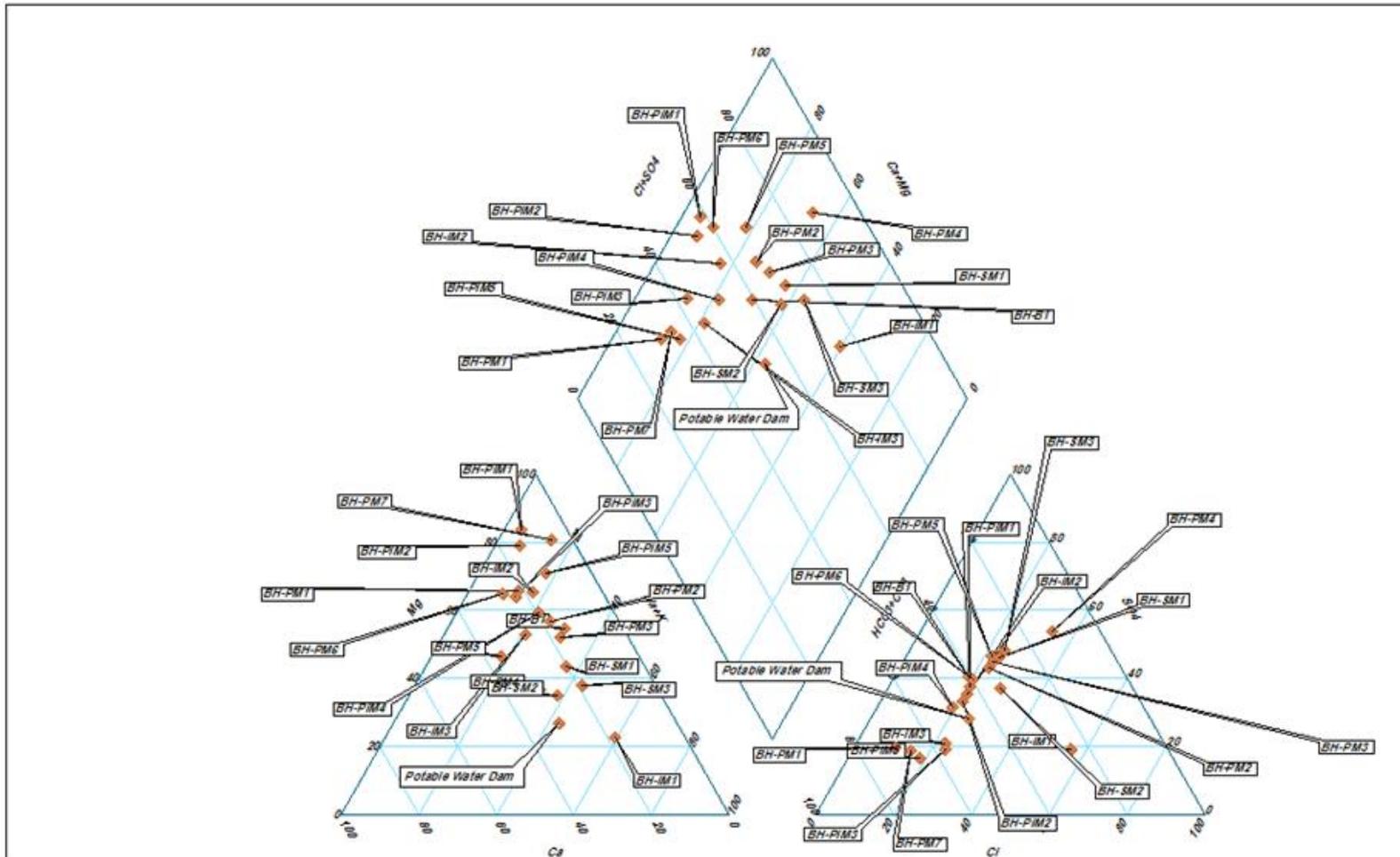


Figure 19: Illustration of cation and anion compositions of all the surface and groundwater samples

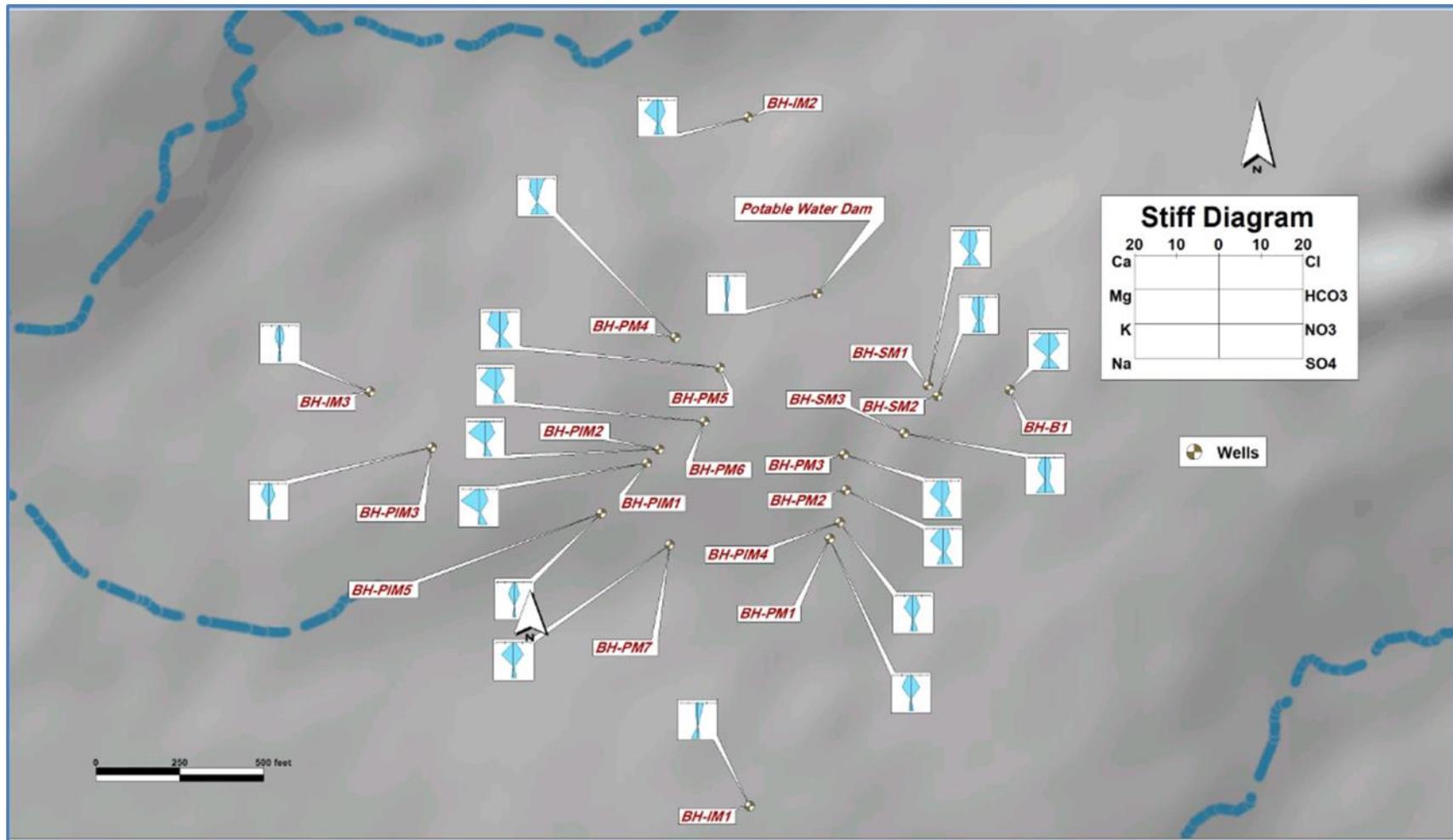


Figure 20: Lateral distribution of major ions at the study area

5.2 Trend Analyses

5.2.1 Source monitoring boreholes

Trend analyses of seven source monitoring boreholes are presented below. Based on the trend analyses of the selected boreholes, two boreholes (BH1 and SM2) indicate that the Cr(IV) concentrations are definitely decreasing at the source area. Four monitoring boreholes (SM1, SM3, PM2 and PM3), indicate that the Cr(IV) concentrations are fluctuating over time and a trend could not be established (Figure 21 – Figure 26).

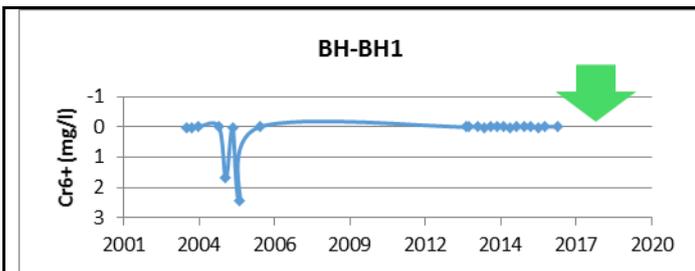


Figure 21: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

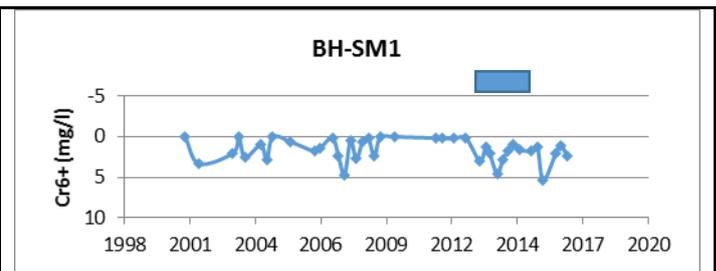


Figure 22: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

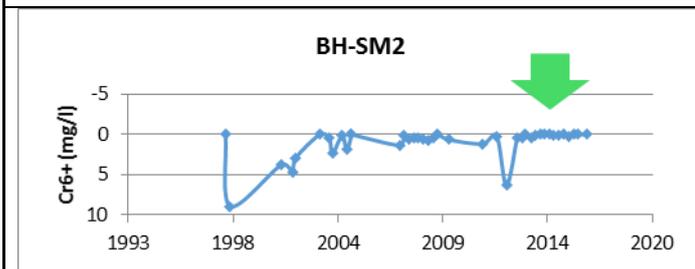


Figure 23: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

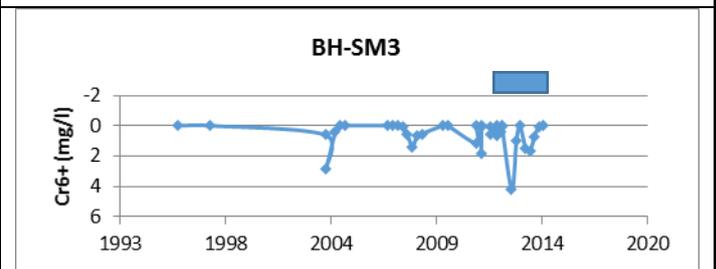


Figure 24: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

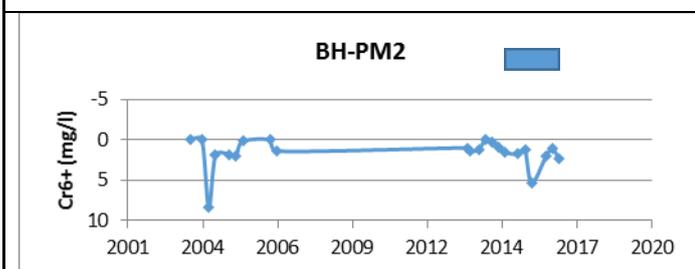


Figure 25: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

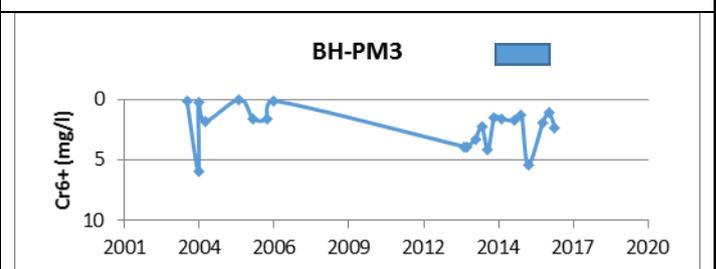


Figure 26: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

5.2.2 Plume monitoring boreholes

Trend analyses of eight plume monitoring boreholes are presented below. Based on the trend analyses of the selected boreholes, five boreholes (PIM4, PM1, PM4, PM6 and PIM2) indicate that the Cr(IV) concentrations are definitely decreasing at the plume area. One monitoring borehole (PM7), indicates that the Cr(IV) concentrations are fluctuating over time and a trend could not be established. The remaining two monitoring boreholes (PM5 and PIM1), indicate the increasing trend of the Cr(IV) concentrations (Figure 27 – Figure 34).

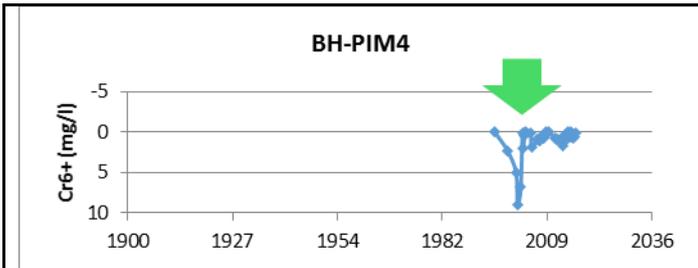


Figure 27: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

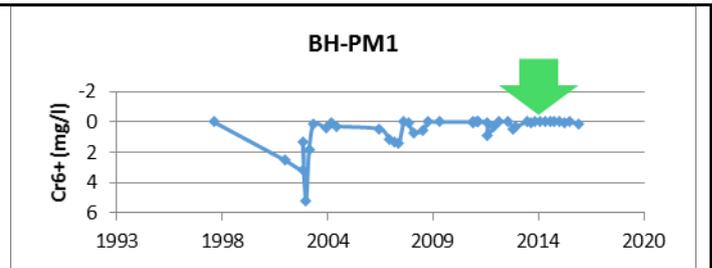


Figure 28: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

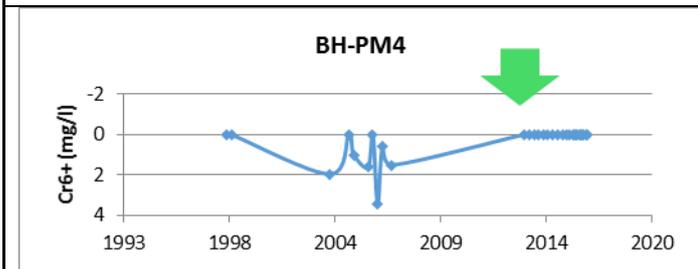


Figure 29: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

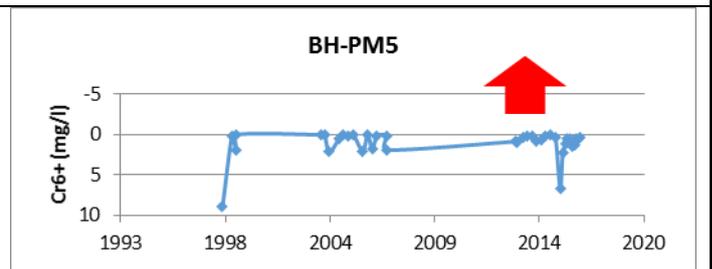


Figure 30: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

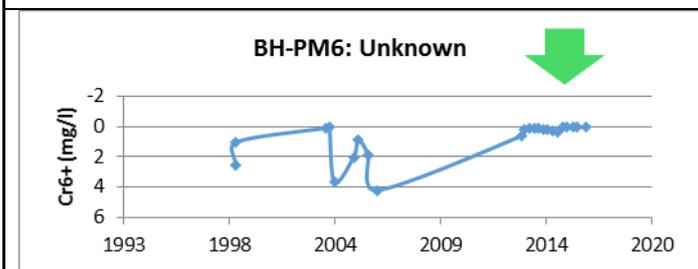


Figure 31: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

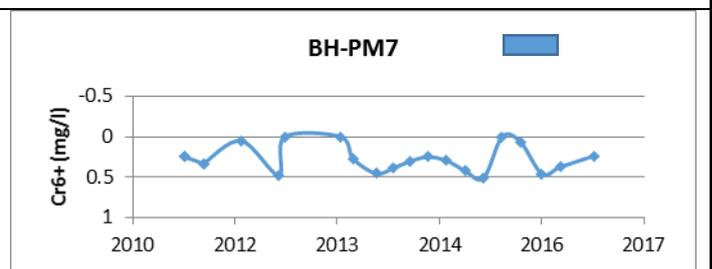


Figure 32: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

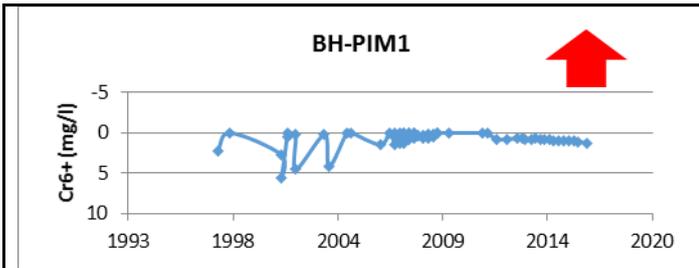


Figure 33: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

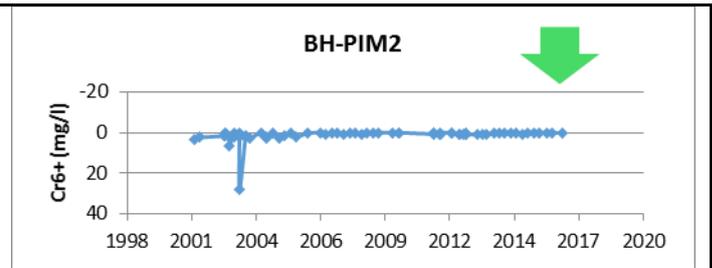


Figure 34: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

5.2.3 Impact monitoring boreholes

Trend analyses of three impact monitoring boreholes are presented below. Based on the trend analyses of the selected boreholes, two boreholes (IM2 and IM3) indicate that the Cr(IV) concentrations are definitely decreasing at the impact area. One monitoring borehole (PIM3) indicates that the Cr(IV) concentrations are fluctuating over time and a trend could not be established (Figure 35 – Figure 37).

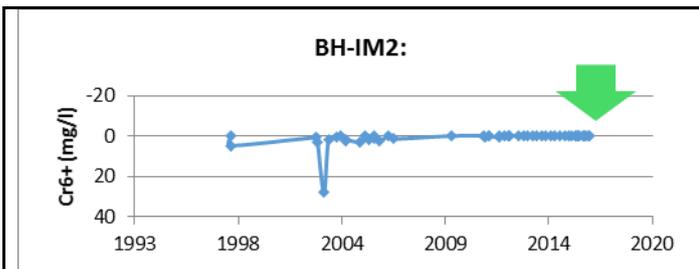


Figure 35: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

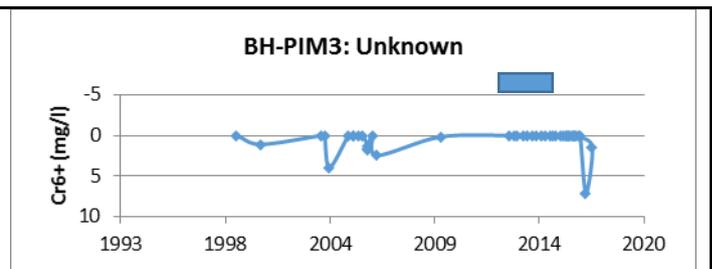


Figure 36: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

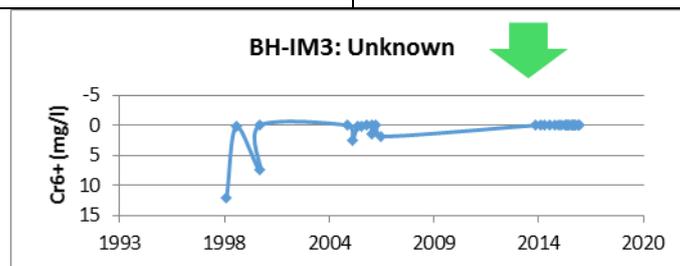


Figure 37: Trend analysis of Cr(VI) at the study area prior to and after installation of the liner

The laboratory results of the sampled settling ponds are presented in the schematics below. For the purpose of this project, dosing with FeSO_4 was started from February 2015. From August 2016 the electrochemical treatment was applied. In cases where the electrochemical method failed or the system was undergoing maintenance, dosing with FeSO_4 or FeCl_2 was

activated. The days when electrochemical treatment was not operational between January 2017 and May 2017 are presented below (Table 8).

The laboratory results from water samples collected from the settling ponds, indicate that Cr(VI) concentrations are treated with FeSO₄ to below 0.05 mg/l (drinking water limit) after dosing has occurred (Figure 38).

Dosing with FeSO₄ or FeCl₂ is likely to lead to elevated major ions. Iron concentration increased after treatment (in settling pond B) following chemical dosing before and after August 2016. Sulphate concentration was elevated during the treatment process between February 2015 and August 2016 (Figure 39). Chloride concentrations were elevated after treatment process (in settling pond B) following chemical dosing with FeCl₂ during August 2016 and May 2017 where electrochemical treatment was ineffective (Figure 40). Other observations made of dosing with FeSO₄ or FeCl₂ were that pH values of settling ponds A and B lead to more acidic conditions (Figure 41). Electrical Conductivity is elevated in the treated water due to the addition of Fe(II) in solution and this means elevated dissolved solids are present in the treated water (Figure 42).

Table 8: Effectiveness of Electrochemical method

Dates	Comments
2017/01/11	Unit working effectively.
2017/03/03	Electrolysis unit not effective. Chemical dosing in progress.
2017/03/17	Electrolysis treatment working effectively. Pumps running adequately. The ponds are full.
2017/03/29	Water treatment running adequately.
2017/04/12	Did not discharge the water. The chemical dosage was increased.
2017/05/04	Water not discharged due to results being high. Electrolysis is being repaired. The chemical dose was increased.

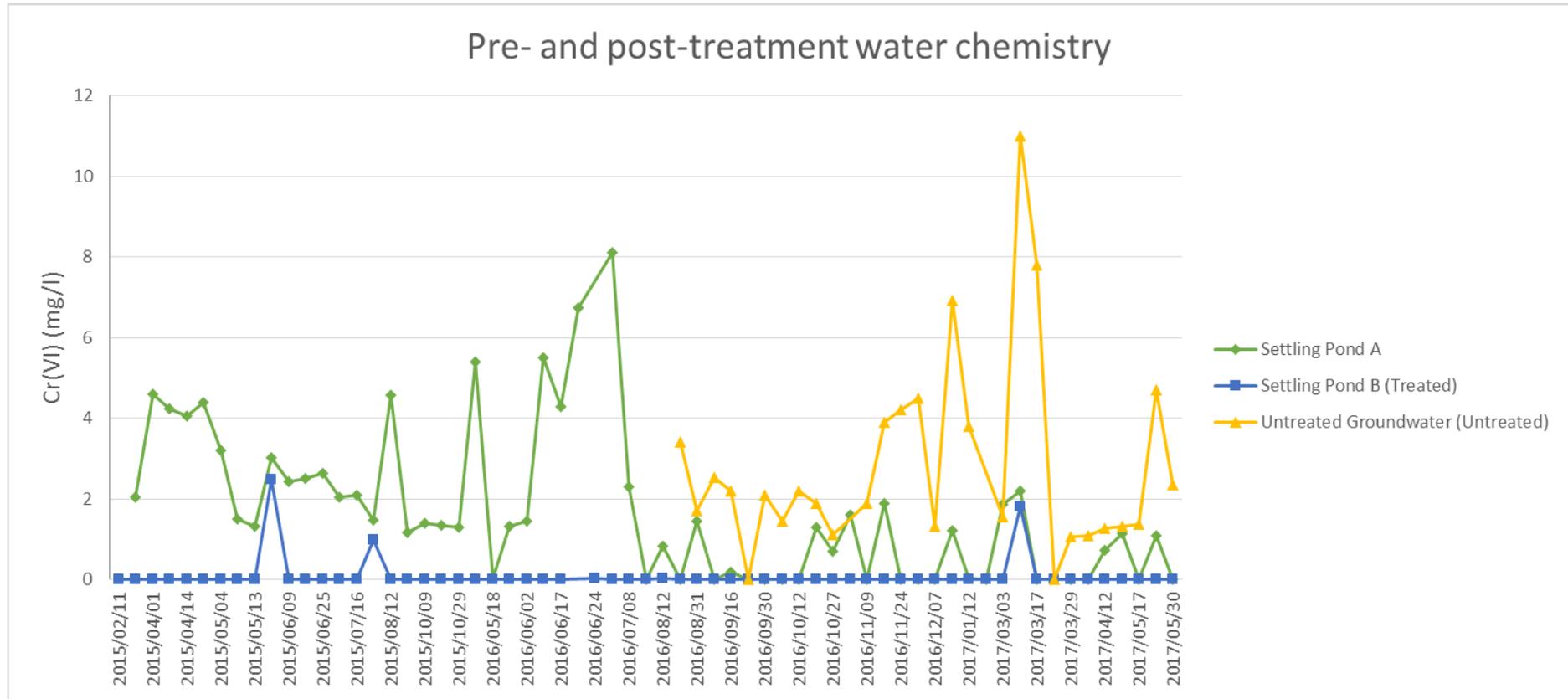


Figure 38: Trend analysis of Cr(VI) at the study area

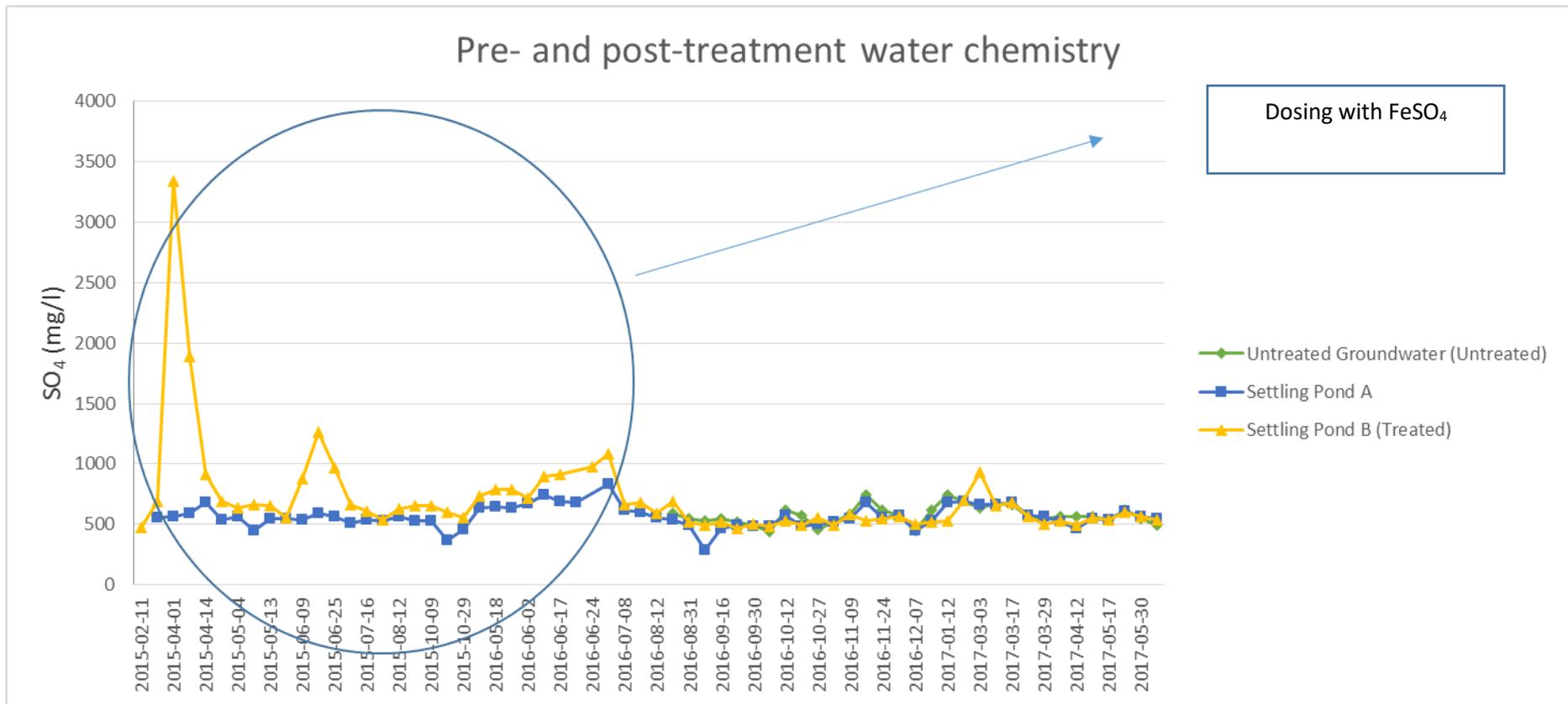


Figure 39: Trend analysis of SO₄ at the study area

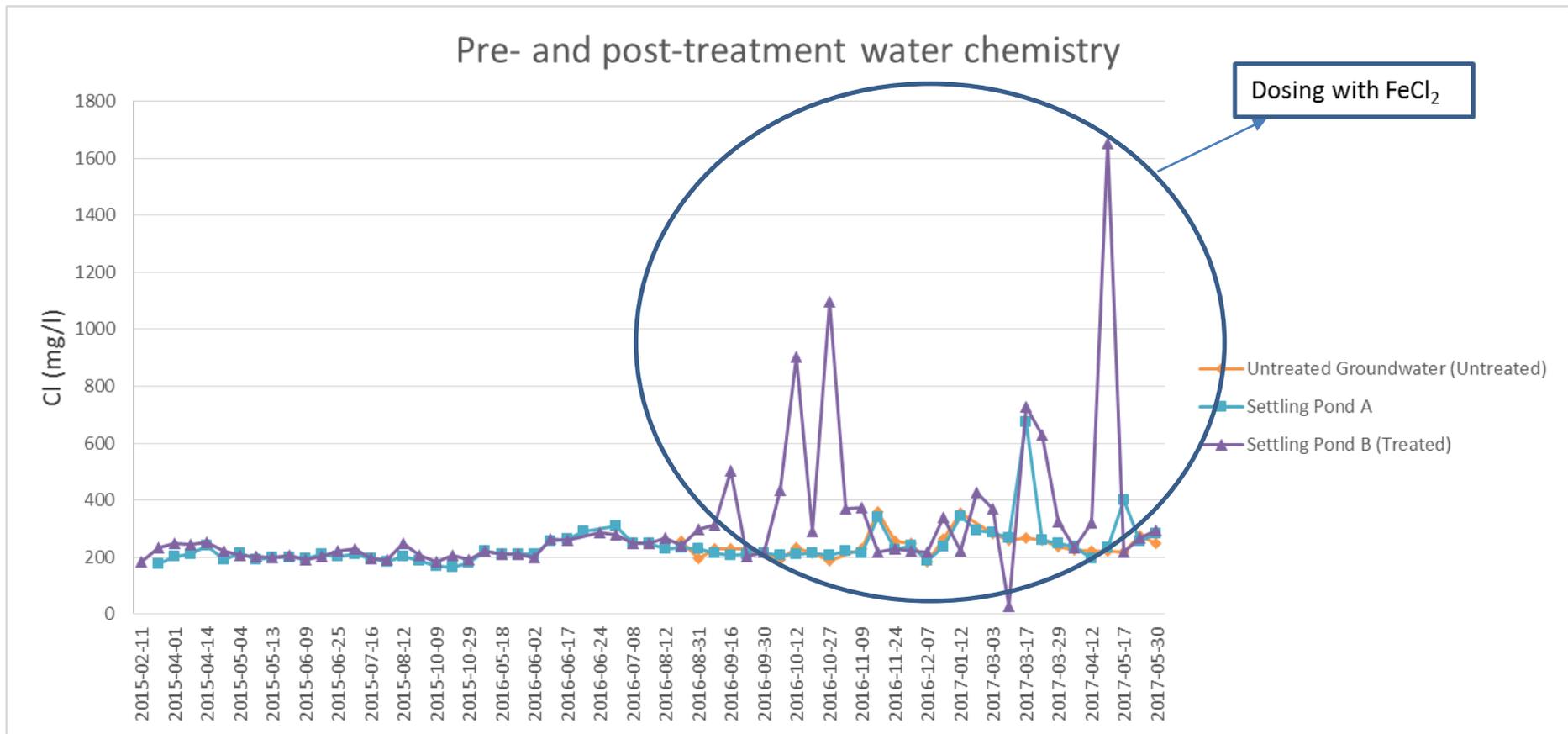


Figure 40: Trend analysis of Cl at the study area

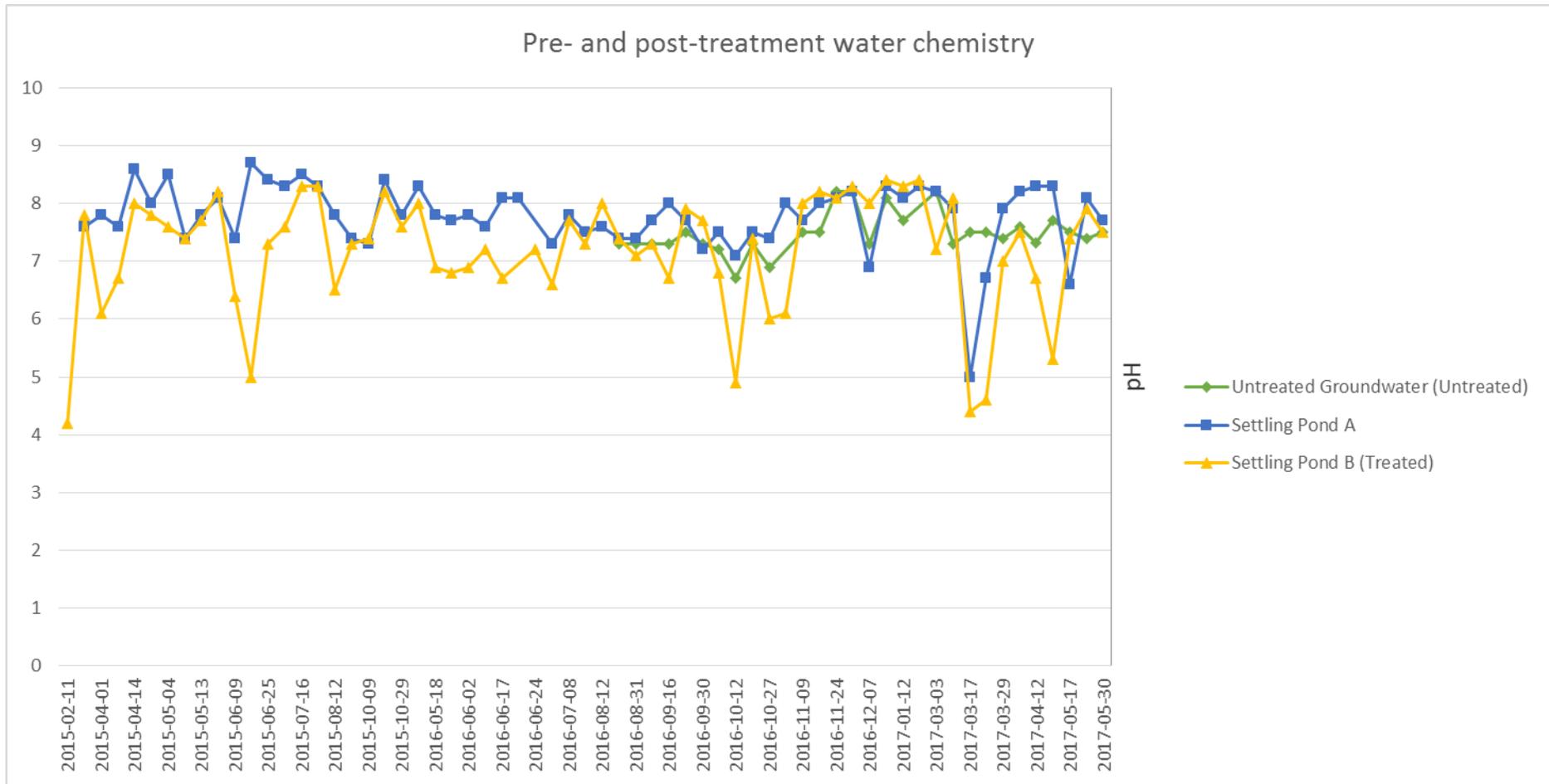


Figure 41: Trend analysis of pH at the study area

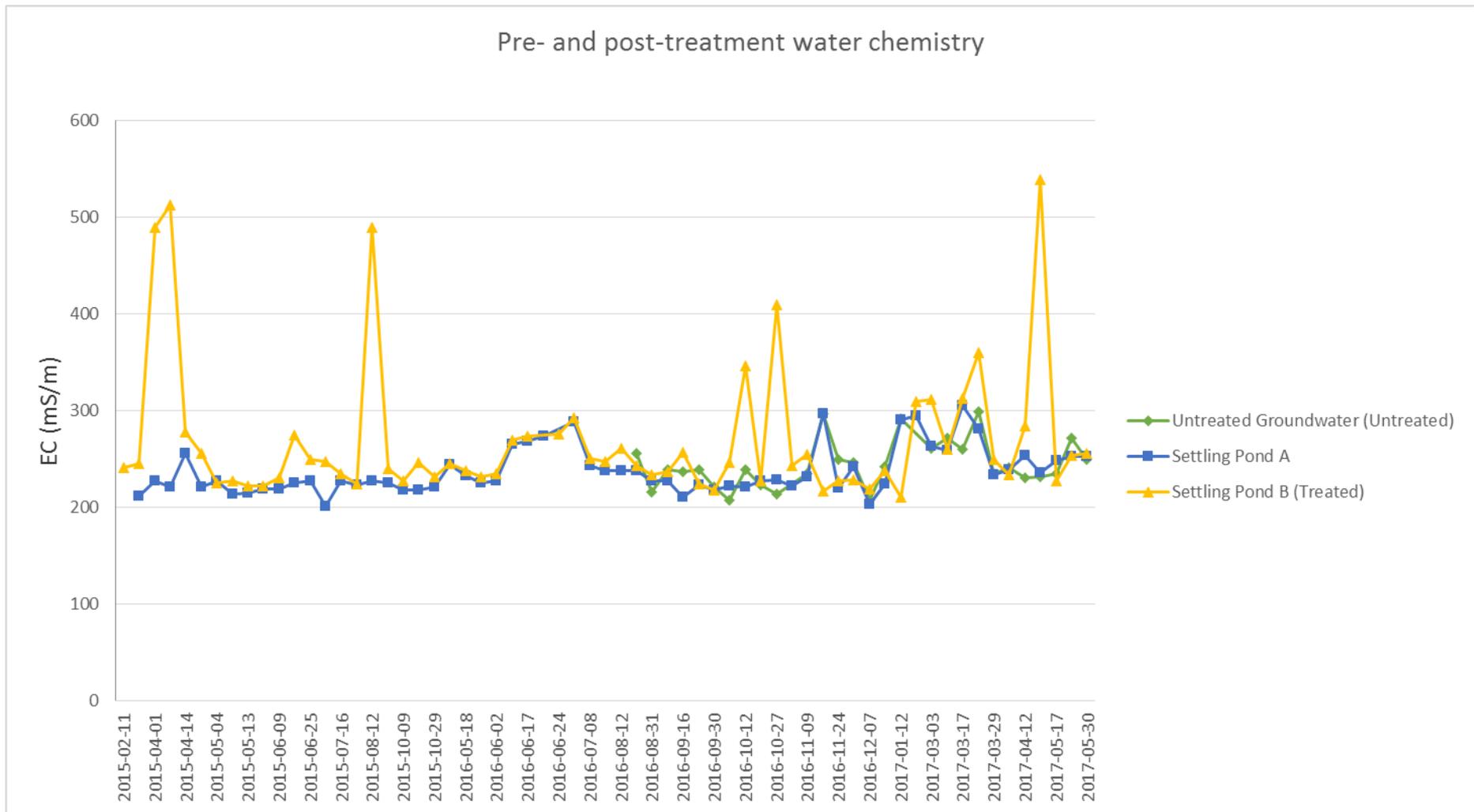


Figure 42: Trend analysis of EC at the study area

5.3 Transport Stability and Model

5.3.1 Calibration

The model calibration is presented in Figure 43. The calculated water levels and computed water levels were compared to each other. None of the values differ from each other by a large margin. Hence, these values indicate that the model is positively calibrated. However, four outliers were observed as indicated on the map (in green). These outliers can be related to pumping activities at the study area.

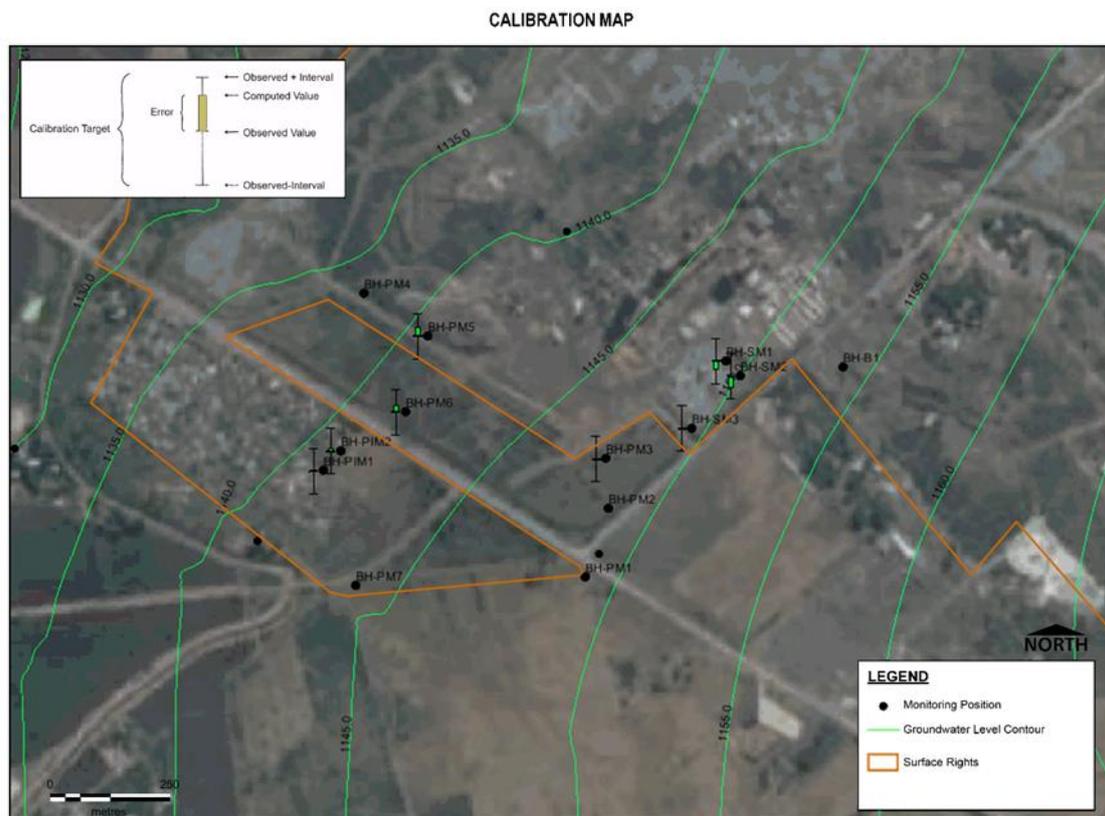


Figure 43: Calibration map

5.3.2 Sensitivity analysis

The input parameters used in the numerical and transport model were subjected to a stress of lower and higher magnitude as shown in Table 9. The purpose of stressing these parameters was to demonstrate that the used values can be more or less sensitive and this can indicate uncertainties about the used parameter.

Table 9: Adjusted parameters to up and down order of magnitude

Parameters	Order of Magnitude down	Specific values	Order of Magnitude upward
Recharge	0.00001	0.0001	0.001
Evapotranspiration	0.00046	0.0046	0.046
Hydraulic conductivity (Layer 1)	0.1	1.0	10
Hydraulic conductivity (Layer 2)	0.003	0.03	0.3
Hydraulic conductivity (Layer 3)	0.0003	0.003	0.03

The mean residual head values for the model are presented below (Table 10). These values are plotted below (Figure 44 and Figure 45) and most have a similar order of magnitude with certainty. Two off-set values were evident for recharge and Layer 2 hydraulic conductivity.

Table 10: Mean residual heads

Parameters	Order of Magnitude down	Specific values	Order of Magnitude upward
Recharge	9.1	0.12	-6.33
Evapotranspiration	8.16	0.12	9.40
Hydraulic conductivity (Layer 1)	8.71	0.12	10.10
Hydraulic conductivity (Layer 2)	3.44	0.12	11.36
Hydraulic conductivity (Layer 3)	9.33	0.12	9.96

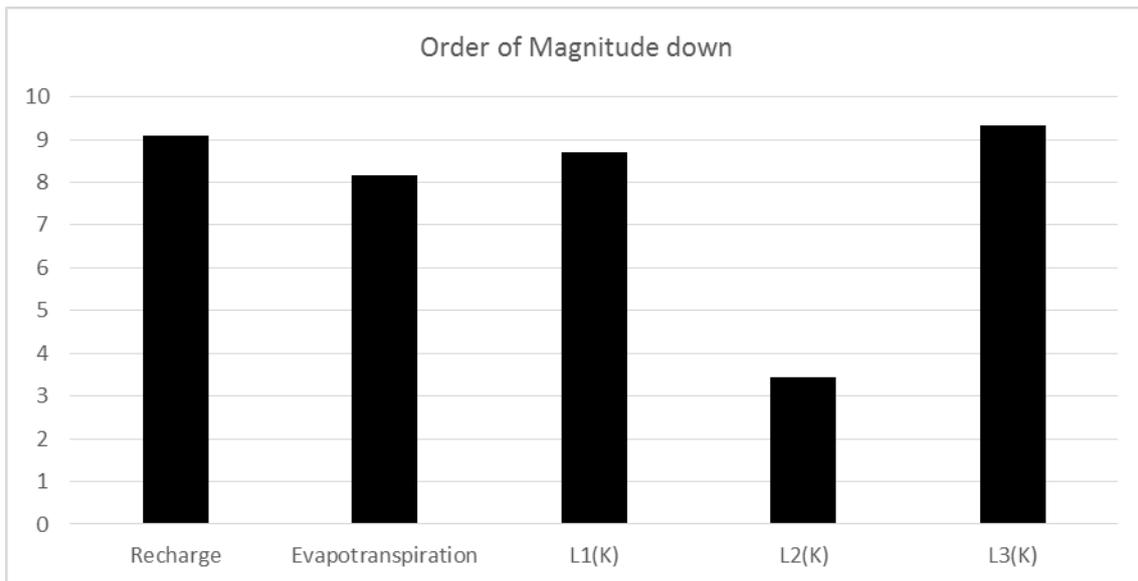


Figure 44: Mean residual head for input parameters (order of magnitude down)

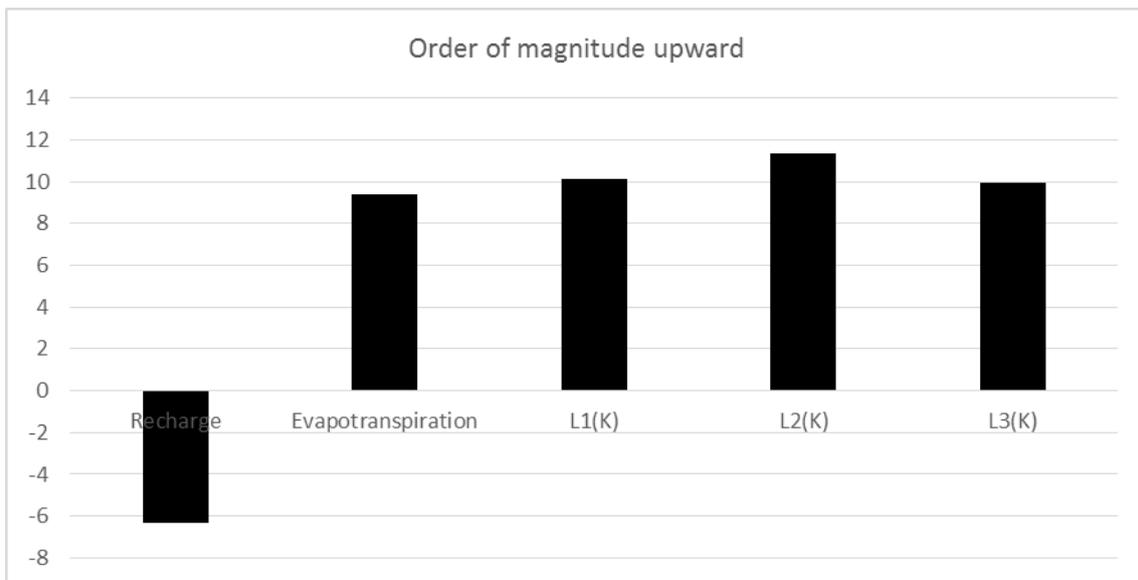


Figure 45: Mean residual head for input parameters (order of magnitude upward)

The stability of Cr(VI) is presented below (Figure 46). The majority of the samples plot on the CrO_4^{2-} stability field. The sample pH and Eh values are favourable to Cr(VI) which is soluble and mobile in groundwater. The stability diagram indicates that the Cr(VI) in the study area can be transported from the primary source area to the impact monitoring boreholes, based on the Eh and pH illustrated below.

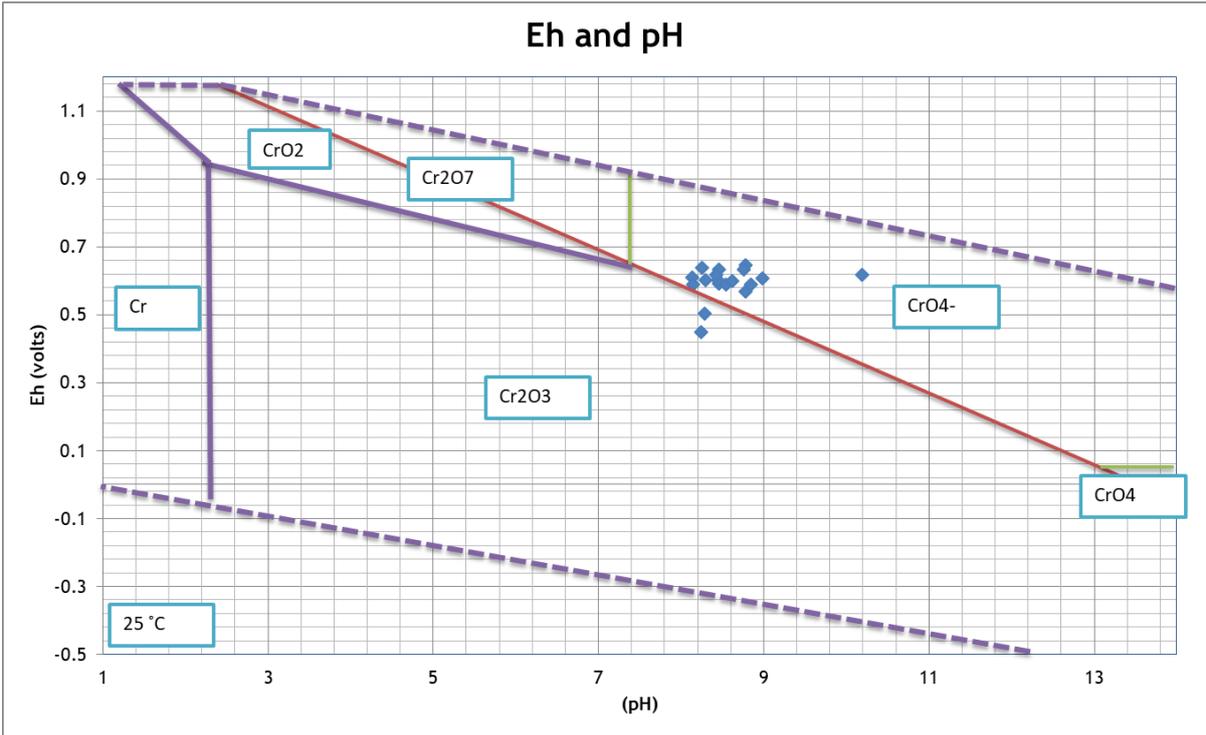


Figure 46: Results of the stability of the CrO4 transition in terms of chromate concentrations over time

The transport model was simulated with and without sorption, in order to determine the effect of retardation factor on the solute over time as indicated below (Figure 47 and Figure 48). The 1st and 2nd sorption constants sourced from the literature were used.

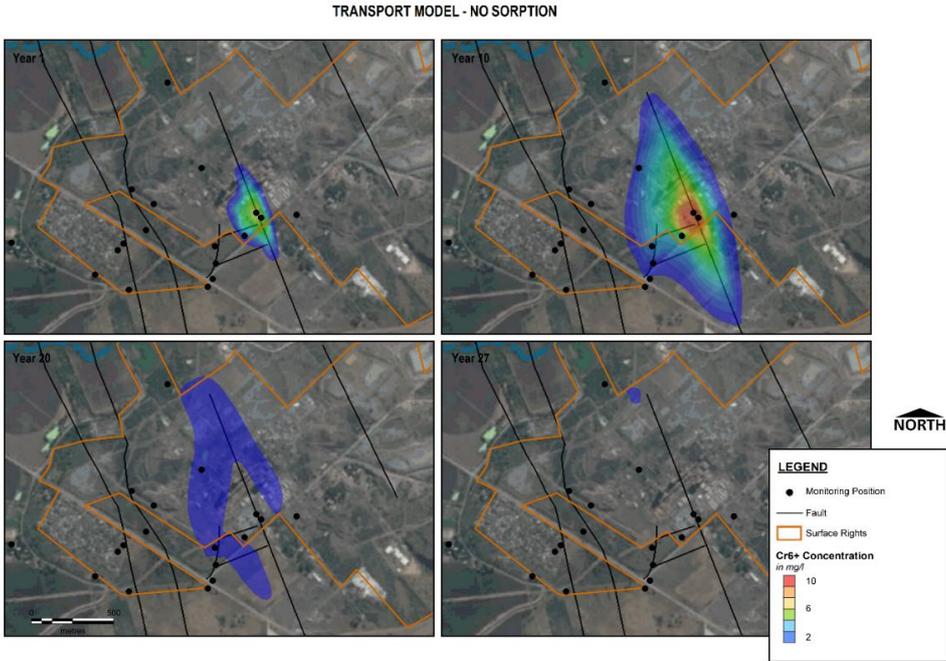


Figure 47: Plume movement without sorption and during active abstraction from 1 year to 27 years

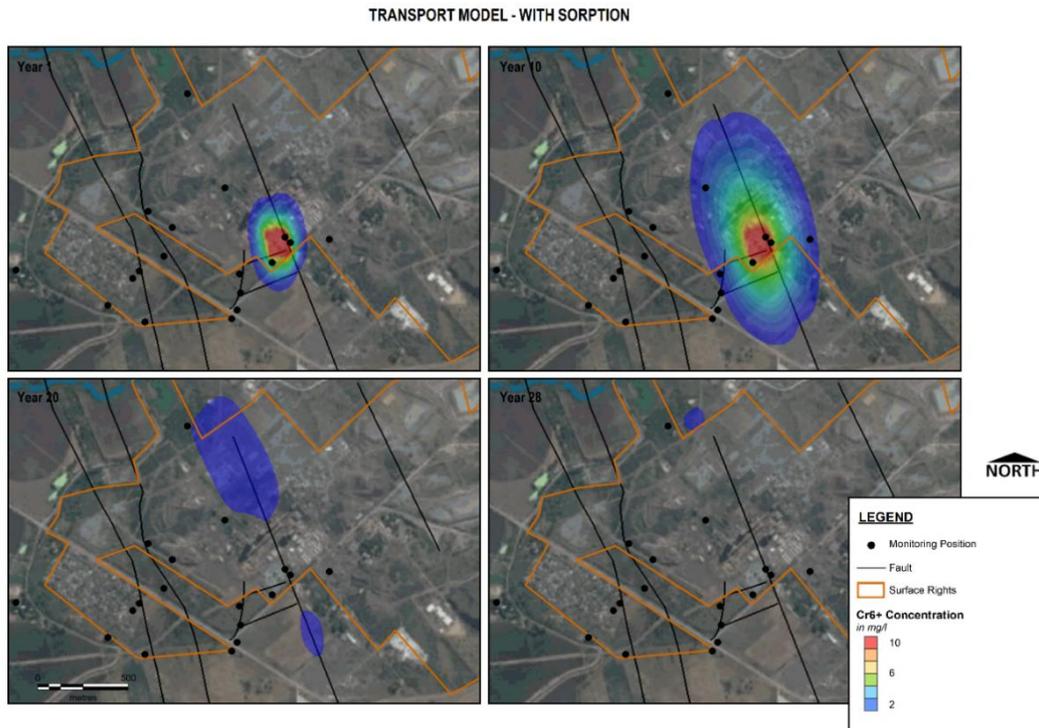


Figure 48: Plume movement with sorption and during active abstraction from 1 year to 28 years

5.4 Mass of Cr(VI)

During the calculation of the mass of Cr(VI), two masses were simulated by means of utilising modflow for flow solution M3TDS concentration and contamination dataset. The mass with retardation and without retardation were simulated. These masses are presented below (Table 11 and Table 12). Based on the tables presented below, an average difference in mass was calculated to be one ton over a 50 year period. This indicates that the retardation has a significant role in quantifying the mass and movement of the plume in the aquifer.

Table 11: Mass of Cr(VI) over time without retardation

Years	Days	Mass (mg)	Mass (kg)	Tons
1	365	2 010 426	2 010	2
2	730	3 325 337	3 325	3
3	1 095	4 396 762	4 397	4
4	1 460	5 330 667	5 331	5
5	1 825	6 172 326	6 172	6
6	2 190	6 935 958	6 936	7
7	2 555	7 644 912	7 645	8

Years	Days	Mass (mg)	Mass (kg)	Tons
8	2 920	8 308 025	8 308	8
9	3 285	8 934 717	8 935	9
10	3 650	9 529 524	9 530	10
11	4 015	8 029 144	8 029	8
12	4 380	7 277 781	7 278	7
13	4 745	6 772 899	6 773	7
14	5 110	6 391 463	6 391	6
15	5 475	6 075 864	6 076	6
16	5 840	5 816 234	5 816	6
17	6 205	5 592 136	5 592	6
18	6 570	5 385 605	5 386	5
19	6 935	5 207 674	5 208	5
20	7 300	5 048 681	5 049	5
21	7 665	4 898 410	4 898	5
22	8 030	4 764 762	4 765	5
23	8 395	4 636 543	4 637	5
24	8 760	4 520 614	4 521	5
25	9 125	4 411 540	4 412	4
26	9 490	4 313 763	4 314	4
27	9 855	4 222 193	4 222	4
28	10 220	4 133 118	4 133	4
29	10 585	4 049 417	4 049	4
30	10 950	3 972 789	3 973	4
31	11 315	3 895 597	3 896	4
32	11 680	3 820 894	3 821	4
33	12 045	3 752 606	3 753	4
34	12 410	3 682 687	3 683	4
35	12 775	3 618 208	3 618	4
36	13 140	3 559 943	3 560	4
37	13 505	3 499 755	3 500	3
38	13 870	3 446 075	3 446	3
39	14 235	3 391 314	3 391	3

Years	Days	Mass (mg)	Mass (kg)	Tons
40	14 600	3 338 717	3 339	3
41	14 965	3 288 420	3 288	3
42	15 330	3 237 496	3 237	3
43	15 695	3 188 166	3 188	3
44	16 060	3 144 671	3 145	3
45	16 425	3 100 400	3 100	3
46	16 790	3 057 401	3 057	3
47	17 155	3 018 965	3 019	3
48	17 520	2 975 744	2 976	3
49	17 885	2 936 010	2 936	3
50	18 250	2 896 077	2 896	3

Table 12: Mass of Cr(VI) over time with retardation

Years	Days	Mass (mg)	Mass (kg)	Tons	Difference in mass (Tons)
1	365	1 631 257.691	1 631	2	0
2	730	2 793 277.516	2 793	3	0
3	1 095	3 756 188.208	3 756	4	0
4	1 460	4 620 284.899	4 620	5	0
5	1 825	5 414 983.704	5 415	5	-1
6	2 190	6 165 694.084	6 166	6	-1
7	2 555	6 878 421.04	6 878	7	-1
8	2 920	7 565 412.915	7 565	8	0
9	3 285	8 228 349.21	8 228	8	-1
10	3 650	8 871 122.383	8 871	9	-1
11	4 015	7 997 919.872	7 998	8	0
12	4 380	7 438 436.276	7 438	7	0
13	4 745	7 056 361.834	7 056	7	0
14	5 110	6 774 346.012	6 774	7	1
15	5 475	6 561 828.576	6 562	7	1
16	5 840	6 381 354.653	6 381	6	0
17	6 205	6 228 983.032	6 229	6	0

Years	Days	Mass (mg)	Mass (kg)	Tons	Difference in mass (Tons)
18	6 570	6 101 921.482	6 102	6	1
19	6 935	5 989 679.17	5 990	6	1
20	7 300	5 892 188.369	5 892	6	1
21	7 665	5 814 972.51	5 815	6	1
22	8 030	5 704 385.761	5 704	6	1
23	8 395	5 630 054.494	5 630	6	1
24	8 760	5 552 828.821	5 553	6	1
25	9 125	5 488 407.863	5 488	5	1
26	9 490	5 424 306.545	5 424	5	1
27	9 855	5 364 542.705	5 365	5	1
28	10 220	5 323 635.078	5 324	5	1
29	10 585	5 279 543.094	5 280	5	1
30	10 950	5 231 705.5	5 232	5	1
31	11 315	5 181 123.875	5 181	5	1
32	11 680	5 131 388.936	5 131	5	1
33	12 045	5 085 797.552	5 086	5	1
34	12 410	5 041 024.668	5 041	5	1
35	12 775	4 998 747.27	4 999	5	1
36	13 140	4 963 498.519	4 963	5	1
37	13 505	4 930 002.373	4 930	5	2
38	13 870	4 901 569.11	4 902	5	2
39	14 235	4 865 622.92	4 866	5	2
40	14 600	4 829 462.172	4 829	5	2
41	14 965	4 794 380.079	4 794	5	2
42	15 330	4 760 348.417	4 760	5	2
43	15 695	4 725 833.371	4 726	5	2
44	16 060	4 691 398.506	4 691	5	2
45	16 425	4 661 611.661	4 662	5	2
46	16 790	4 636 030.181	4 636	5	2
47	17 155	4 602 428.79	4 602	5	2
48	17 520	4 573 661.24	4 574	5	2

Years	Days	Mass (mg)	Mass (kg)	Tons	Difference in mass (Tons)
49	17 885	4 547 575.395	4 548	5	2
50	18 250	4 520 416.978	4 520	5	2

5.5 Numerical Modelling

Based on the calculated capture zone, the rate at which the boreholes are pumped are capable of capturing the plume, as referenced in Figure 49. Based on model results the plume is controlled and contained within the study area, and the transport model indicates that the plume can be fully captured after 27 years, provided no interruptions occur on the pumping system. Major faults at the study area act as the preferential pathway and are pulling the contamination away from the remediation abstraction boreholes leading to more years before the plume is fully captured.

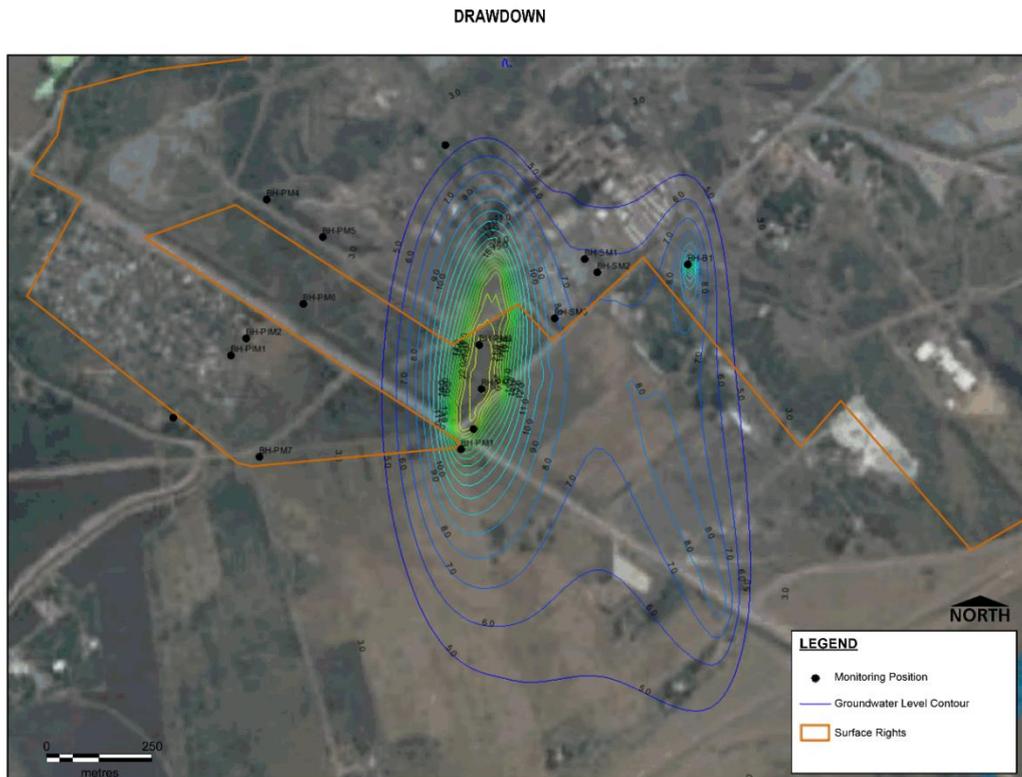


Figure 49: Capture zone due to pumping

CHAPTER 6

6. INTERPRETATION

The trend analyses for Cr(VI) concentrations for source, plume and impact monitoring boreholes were calculated by means of using the Mann-Kendall programme. Based on the calculated values, it was established that the Cr(VI) concentrations in the majority of the boreholes decrease and fluctuate. Few monitoring boreholes indicate an increasing trend. The monitoring boreholes which indicate the fluctuating values are located in the same vicinity and in the proximity of the geological features or within the area where abstraction of Cr(VI) contaminated water is taking place. Monitoring boreholes SM1, SM3, PM2 and PM3 are located in the vicinity where abstraction is occurring and within the fault zone or contact zone. Monitoring borehole PM7 is located within the area of the lower chromite ore. Monitoring borehole PIM3 is located down-gradient of the source area. A similar pattern of trend for the above monitoring boreholes indicate the potential of gradual release of Cr(VI) contamination from the geological features into the aquifer. The abstraction that is taking place in the vicinity of these boreholes also has the potential to contribute to Cr(VI) fluctuation.

The increasing trend in the two monitoring boreholes (PIM1 and PIM5) stipulate that the plume is localised within that area and the Cr(VI) concentrations trend indicate a potential gradual decrease. The decreasing Cr(VI) concentrations in the majority of the monitoring boreholes confirm that the installed liner has ceased the recharge in the slimes dam and the chromium oxidation is minimized. Based on the trend analyses results, the installed liner has proved to be effective on the seepage water quality.

However, this does not mean the liner is the permanent solution, given that the integrity of the liner can be compromised by unforeseen conditions and this can result in possible leakages, which can increase the recharge and chromium oxidation. Consideration of the operational effectiveness of the remediation systems should not be ignored. The dissolved plume is controlled by means of utilising the pump and treat system and the electrochemical reduction system. Based on the treated water chemistry, the observed hydrochemistry showed that the remediation systems (dosing and electrochemical reduction systems) are effective in treating the Cr(VI) contaminated water with related hazardous by-products. However, these systems should work concurrently given that the electrochemical system has mechanical glitches and the dosing system generates hazardous by-products that are harmful to the environment and problematic in plant operations. These systems should be closely monitored given that they operate on a continuous basis.

Treating Cr(VI) contaminated water requires an understanding of the movement of the plume, the mass of the plume and factors affecting the movement, such as retardation. This can assist in revising or improving the remediation systems and planning the costs related to the treatment of the contaminant. The Cr(VI) contamination is migrating towards the impact monitoring boreholes and can be captured within 27 years when sorption is not considered and 28 years when sorption is considered. Furthermore, an average difference of one ton mass was calculated for the plume over time. The difference in one year of capturing the plume and one ton of the mass, indicate that when sorption and the mass of the plume are taken into account for transport models, savings can be made when planning the time when the treatment operations will cease.

CHAPTER 7

7. CONCLUSIONS

The main objective of this study was to address the technical effectiveness of lining the slimes dam. A report based on studies conducted by the US Environmental Protection Agency (EPA), and documented in the 1985 and 1986 Reports to Congress on Wastes from the Extraction and Beneficiation of Ores and Minerals (1985 and 1986 RTC), ((USEPA), 1997), showed that liners can be cost-effective and beneficial in preventing leachate of hazardous compounds into the aquifer for both small and large-scale mine waste. However, the EPA report accentuated that large-scale mine waste units are rarely lined, because when these liners fail it is infeasible to repair them. In reaction to this report, information was later made widely available to the EPA to make the distinction that it is practical to line certain types of mining waste units. This information indicated that certain units currently use liners depending on circumstances. The EPA now indicates that the United States has moved in the direction of requiring mine waste units to be lined.

In the current project circumstances, it was found to be practical to decommission the slimes dam and cover it with polyethylene thermoplastic liner to prevent leaching by rain water and Cr oxidation. Furthermore, the effectiveness of the employed remediation systems is dependent on the integrity of the polyethylene thermoplastic liner, and as a result it is essential to determine if the liner is effective in preventing the recharge into the slimes dam.

The water chemistry data was used to achieve the objective of the study. The definite decreasing Cr(VI) concentrations in the majority of the monitoring boreholes confirm that the installed liner has ceased the recharge in the slimes dam and that chromium oxidation is minimized. Based on the trend analyses results, the installed liner is proved to be effective on the seepage water quality.

The plume movement from the source area to the impact monitoring boreholes was modelled in order to ascertain the plume mass, plume movement during abstraction, and the plume capture zone. Given that the plume has reached the impact boreholes, it was deemed necessary to ascertain plume movement, plume mass and the plume capture zone via a transport and numerical model using the Groundwater Modelling System (GMS10.0).

Based on the modelling results, the movement of the plume is controlled by transport mechanism such as sorption. The plume was characterised by means of considering sorption and ignoring sorption. This exercise proved that the plume moves rapidly when sorption is not considered. The plume mass was also calculated with and without retardation

and a difference in mass was observed. When retardation is considered the mass over time is larger than when it is not considered. This proved that when retardation is not considered in the transport model incorrect plume predictions can be calculated and this can have an impact on the financial planning of the mine.

Sustainable management of the Cr(VI) contaminated water is essential. To effectively manage this contaminated water, remediation methods were put in place that aim at transforming, controlling and minimizing Cr(VI) contaminated water. The implemented remediation methods proved to be effective in managing the contaminated water. However, the remediation methods are proven not to be effective when working independently from each other. As a result, monitoring of these systems is essential and continuously seeking innovative, scientifically sound options is of importance.

The following are recommendations emanating from the present study:

In order to reduce the timeframe of capturing the plume, the abstraction system should be expanded by means of drilling additional abstraction boreholes in the direction of the geological features (fault location); and groundwater abstraction should be increased closer to the permitted volumes.

Based on the sampling data, the two existing monitoring boreholes (PIM5 and IM1), were last sampled in 2015, given that the boreholes were recorded to be blocked. The monitoring network should be expanded, by means of re-instating the two blocked monitoring boreholes, in order to establish the off-site groundwater impacts.

CHAPTER 8

8. REFERENCES

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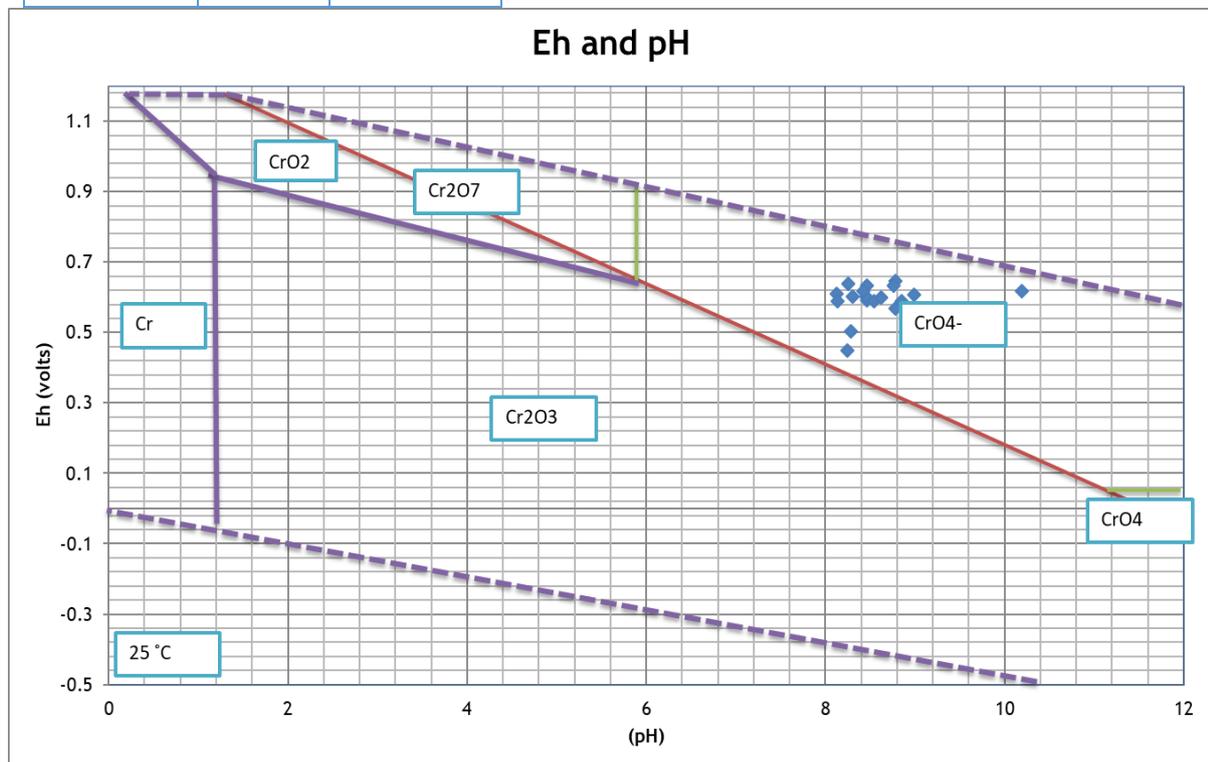
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APPENDIX I

Potential Energy VS pH

ID	pH	Eh
Groundwater		
BH-B1	8.13	0.61
BH-IM1	10.19	0.617
BH-IM2	8.46	0.632
BH-PIM1	8.46	0.591
BH-PIM2	8.28	0.504
BH-PIM3	8.99	0.607
BH-PIM4	8.45	0.602
BH-PIM5	8.78	0.645
BH-PM1	8.85	0.589
BH-PM2	8.42	0.618
BH-PM3	8.76	0.633
BH-PM4	8.24	0.449
BH-PM5	8.14	0.59
BH-PM6	8.78	0.568
BH-PM7	8.54	0.588
BH-SM1	8.25	0.639
BH-SM2	8.3	0.601
BH-SM3	8.62	0.6



Input data to Calculate Recharge

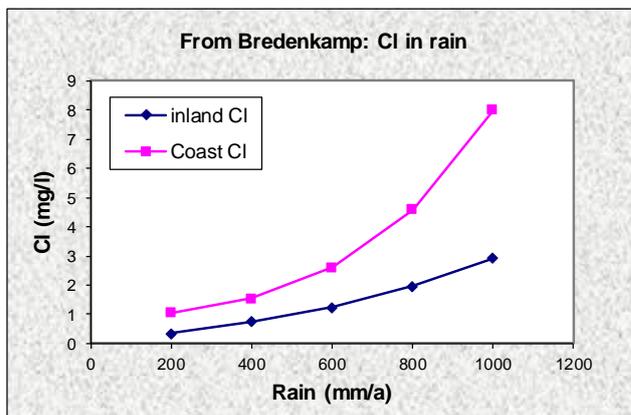
Average annual rainfall (mm)=	668.5
CI in rain (mg/l) =	1.3
Dry deposition CI (mg/l) =	0.02
CI in gw or unsat. zone (mg/l) =	35

Average annual recharge (mm) =	25
Percentage recharge =	5.2

MAIN

If CI rain unknown use = 1.313548 for inland
2.29904 for coast

if dry depo CI unknown Use:
0.1*(CI of rain) for inland if no forest exist
2.5*(CI of rain) if forest exist
0.8*(CI of rain) if spray of mist/dust is a factor at coas



rain	inland CI	Coast CI
200	0.35	1.05
400	0.76	1.55
600	1.25	2.6
800	1.96	4.6
1000	2.93	8

Mannkendall Summary

Hole number	Farm Name	Min Date	Max date	S Statistic	COV	Confidence Factor	Trend Outcome
BH-BH1	Unknown	8/1/2003	1/20/2017	-53	3.12	0.93	Probably decreasing
BH-IM2	Unknown	2/23/1998	2/9/2017	-434	3.7	1	Decreasing
BH-IM3	Unknown	8/31/1998	2/9/2017	-141	2.95	0.99	Decreasing
BH-PIM1	Unknown	10/1/1997	1/20/2017	304	1.43	0.96	Increasing
BH-PIM2	Unknown	5/31/2001	1/20/2017	-784	2.77	1	Decreasing
BH-PIM3	Unknown	2/28/1999	2/9/2017	-19	2.58	0.58	No trend
BH-PIM4	Unknown	10/31/1995	1/20/2017	-189	1.59	0.98	Decreasing
BH-PM1	Unknown	2/28/1998	1/20/2017	-345	1.91	1	Decreasing
BH-PM2	Unknown	8/1/2003	1/20/2017	43	1.16	0.88	No trend
BH-PM3	Unknown	8/1/2003	1/20/2017	25	0.76	0.77	No trend
BH-PM4	Unknown	5/31/1998	2/9/2017	-107	2.41	0.96	Decreasing
BH-PM5	Unknown	5/31/1998	2/9/2017	107	1.62	0.9	Probably increasing
BH-PM6	Unknown	11/30/1998	1/20/2017	-104	1.52	1	Decreasing
BH-PM7	Unknown	7/30/2011	1/20/2017	21	0.6	0.73	No trend
BH-SM1	Unknown	1/31/2001	1/20/2017	95	0.88	0.87	No trend
BH-SM2	Unknown	2/28/1998	1/20/2017	-275	1.89	1	Decreasing
BH-SM3	Unknown	1/30/1996	1/29/2015	81	1.6	0.84	No trend

Pump Test Data Summary

Borehole Number	Transmissivity (m2/d)	Sustainable Yield (L/s)	Sustainable Yield (m3/day)	Sustainable Yield (m3/week)	Sustainable Yield (m3/month)
HER-MB	130.0	0.2	17.3	121.0	3628.8
HER-MA	62.9	0.5	43.2	302.4	9072.0
HER-BH1	79.1	0.5	67.4	471.7	14152.3
Total		1.2	127.9	895.1	26853.1

Cr6 Remediation Data Summary (Settlement Ponds)

Constituent	Cr6+		
Average of Value	Column Labels		
Row Labels	PAT Boreholes (Untreated)	Settling Pond A (Elec treated)	Settling Pond B (Treated)
2/11/2015			0
3/25/2015		2.05	0
4/1/2015		4.59	0
4/9/2015		4.23	0
4/14/2015		4.05	0
4/23/2015		4.38	0
5/4/2015		3.2	0
5/7/2015		1.49	0.012
5/13/2015		1.33	0.01
5/29/2015		3.03	2.47
6/9/2015		2.43	0.01
6/18/2015		2.51	0.01
6/25/2015		2.63	0
7/3/2015		2.04	0.01
7/16/2015		2.1	0.01
8/6/2015		1.48	0.98
8/12/2015		4.56	0
9/23/2015		1.16	0
10/9/2015		1.4	0.01
10/20/2015		1.35	0.01
10/29/2015		1.3	0
1/26/2016		5.4	0
5/18/2016		0.028	0
5/26/2016		1.32	0.01
6/2/2016		1.45	0.01
6/14/2016		5.49	0.017
6/17/2016		4.29	0
6/23/2016		6.74	
6/24/2016			0.027
6/30/2016		8.1	0
7/8/2016		2.3	0.016
7/14/2016		0	0
8/12/2016		0.822	0.024
8/18/2016	3.4	0	0
8/31/2016	1.7	1.45	0
9/12/2016	2.54	0	0
9/16/2016	2.21	0.193	0
9/23/2016	0	0	0
9/30/2016	2.1	0	0
10/5/2016	1.44	0	0
10/12/2016	2.2	0	0

10/21/2016	1.89	1.3	0
10/27/2016	1.11	0.704	0
11/2/2016		1.61	0
11/9/2016	1.9	0	0
11/18/2016	3.9	1.9	0.014
11/24/2016	4.2	0	0
11/30/2016	4.5	0	0
12/7/2016	1.33	0	0
12/14/2016	6.91	1.23	0
1/12/2017	3.8	0.02	0.01
1/20/2017		0.013	0
3/3/2017	1.54	1.85	0
3/8/2017	11	2.2	1.8
3/17/2017	7.81	0	0
3/23/2017	0	0	0
3/29/2017	1.05	0	0
4/7/2017	1.08	0.015	0
4/12/2017	1.28	0.725	0
5/4/2017	1.32	1.15	0
5/17/2017	1.37	0	0
5/26/2017	4.69	1.09	0.013
5/30/2017	2.35	0.012	0

Cr6 Contamination January 2015 and January 2017

Borehole Label	Cr6+ in mg/l (January 2015)
BH-B1	0
Potable Water D	0
BH-SM1	1.6
BH-SM2	0.013
BH-SM3	0
BH-PM1	0
BH-PM2	1.59
BH-PM3	1.59
BH-PM4	0
BH-PM5	0.647
BH-PM6	0.211
BH-PM7	0.296
BH-PIM1	0.851
BH-PIM2	0
BH-PIM3	0.016
BH-PIM4	0
BH-PIM5	0
BH-IM1	0
BH-IM2	0
BH-IM3	0

Borehole Label	Cr6+ mg/l (January 2017)
BH-PM1	0.134
BH-IM2	0.012
BH-PIM4	0.073
BH-PM2	2.36
BH-PM3	2.36
BH-IM3	0.011
BH-PIM3	0.024
BH-PM1	0.134
BH-PM7	0.237
BH-PIM1	1.27
BH-PIM2	0.404
BH-SM1	2.36
BH-SM2	0
BH-PM4	0
BH-PM5	0.496
BH-PM6	0.027
BH-BH1	0
BH-IM2	0.011
BH-IM3	0.011
BH-PIM3	0.029
BH-PM4	0
BH-PM5	0.324