REACTIVE TRANSPORT MODELLING OF FERTILIZER WASTE IN A DUAL POROSITY AQUIFER

By

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Declaration

I, Brendon John Bredenkamp, declare that this thesis hereby submitted by me for the Master of Science degree at the University of the Free State, is my own independent work and has not previously been submitted by me at another university/faculty. I furthermore cede copyright of the thesis in favour of the University of the Free State.

Brendon John Bredenkamp
(2007126267)

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LIST OF ABBREVIATIONS

Bicarbonate – HCO_3

Ammonia - NH_4

Nitrate - NO_3

Nitrite – NO_2

Chloride – Cl

Sulphate - SO_4

Fluoride - F

Sodium - Na

Potassium – K

Ortho-Phosphate – PO_4

Calcium - Ca

Magnesium - Mg

Iron - Fe

Manganese - Mn

Silica - Si

Dissolved Oxygen - DO

Total Dissolved Solids - TDS

Electrical Conductivity – EC

Oxidation Reduction Potential – ORP

Cation/anion balancing error - Cat/an bal%

Ionic Strength – IS

Metres above mean sea level – mamsl

Metres below ground level – mbgl.

Metres above ground level – magl.

Electromagnetic - EM

1 INTRODUCTION

During a hydrogeological investigation it was found that groundwater pollution was present at a production facility which manufactures fertilizer. The plant and the surrounding buildings are here on further referred to as 'the site'. A further study found boreholes located 250m downstream of the site to be polluted with fertilizer related contaminants. The purpose of this investigation is to determine whether the site is responsible for the contamination. Furthermore, this study predicts the future potential impacts which the contaminated groundwater may have on the receiving environment by using the data collected.

2 TERMS OF REFERENCE

A systematic approach was followed during this study as envisaged below:

- A comprehensive desktop study was undertaken to obtain relevant information from topographical maps, geological maps and previous investigations conducted on site.
- The data collected during the previous monitoring events were captured in a groundwater database.
- A hydrocensus was conducted around the site to identify potential receptors which may be impacted on by groundwater contamination. Some of the boreholes identified during the hydrocensus were incorporated in the groundwater monitoring network.
- A geophysical survey using a magnetometer and EM34 was conducted to identify potential preferential flow paths around the site.
- Percussion boreholes were drilled to serve as groundwater monitoring wells and to comply with the design of a groundwater monitoring system for the site within the framework of ISO 14001.
- An short pump test was conducted on one of the boreholes in order to estimate the aquifer parameters. Some of the surrounding boreholes were used as observation wells.
- Water samples were collected from existing and newly drilled monitoring boreholes and some surface water bodies. The static water levels in the boreholes were measured and the water quality of the groundwater and surface water was determined. The groundwater quality was compared to the 241 SANS standard for drinking water (SANS, 2006) and the DWAF Water Quality Guidelines, (where applicable).
- The data collected from the study was interpreted to form a site conceptual model.

- The site conceptual model was used to construct a numerical flow and contaminant transport model. The numerical model was used as a tool to predict the fate of the contaminant plume under different scenarios.

- Relevant deductions were made regarding the fate of the contaminant plume and the future potential impact on receptors.

3 BACKGROUND INFORMATION

3.1 CLIMATE, TOPOGRAPHY AND DRAINAGE

The site is situated in a summer rainfall area, with most of the precipitation occurring between October and April as seen in Figure 1. The average rainfall of the area for the period 1957 to 2007 is 674 mm/annum (DWAE, 2009). The average E-pan evaporation calculated for the period 1957 to 2007 is 1628 mm/annum (DWAE, 2009). The period for high potential evaporation coincides with the summer months (Figure 2) as can be expected.

An illustration of the surface drainage of the area can be seen in Figure 3. The illustration represents a perspective view towards the north east. As can be seen the regional surface drainage of the area is in a south-western direction. The site however drains locally in a southerly direction.
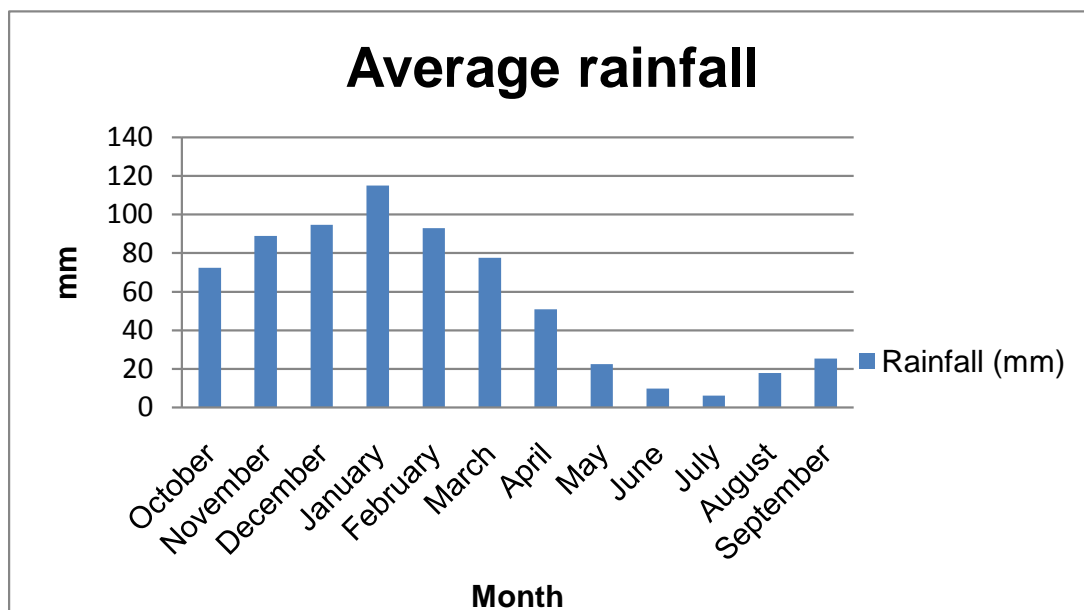
Figure 1: Average rainfall for the area for the period 1957-2007
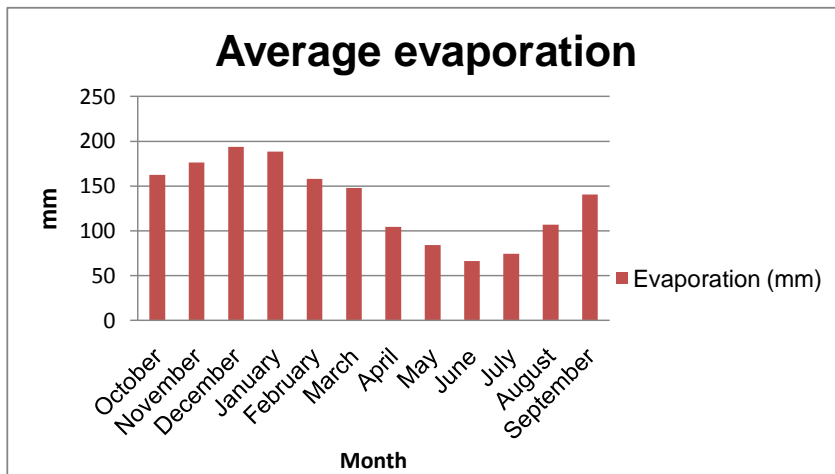
Figure 2: Average evaporation for the period 1957-2007
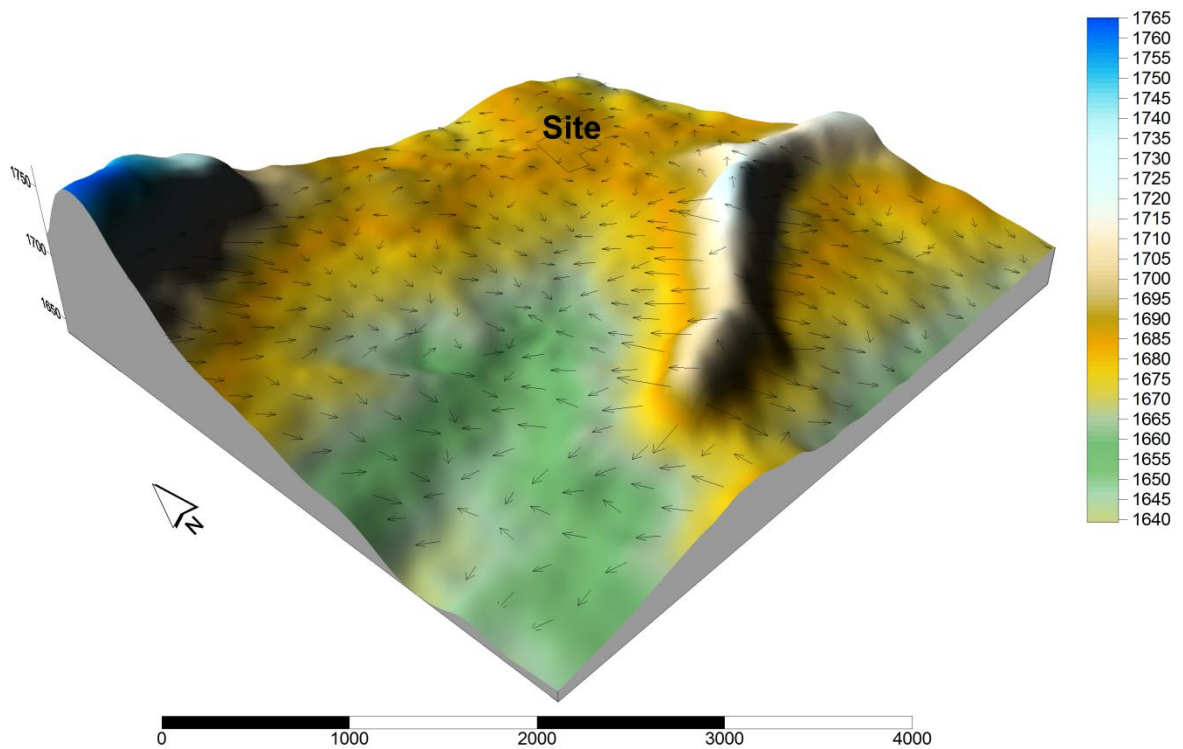
Figure 3: Surface elevation and drainage (elevations are in mamsl)

3.2   REGIONAL GEOLOGY AND HYDROGEOLOGY

According to a geological map, the site is situated on the Tarkastad Formation of the Beaufort Group which forms part of the Karoo Supergroup. This formation consists of an assemblage of sandstone and mudstone (Visser, et al., 1989). Dolerite intrusions are associated with the formation and occur sporadically. The sandstone is likely to act as dual porosity aquifer where flow and storage is governed by the fractures and the matrix. The mudstone tends to act as a fractured aquifer whereby flow and storage is mainly governed by fractures. Boreholes in the Tarkastad Subgroup are generally low yielding with the median borehole yield range of 0.1-0.5 l/s. More than 50% of boreholes yield below 0.5 l/s and 33% yielding between 0.5 to 2.0 l/s (Baran, 2003).

3.3   SOIL DESCRIPTION

The soil horizon underlying the site (plant area) has been described in detail during a previous study. Soil samples were collected for profiling by means of a geoprobe direct push drill. The following soil forms were observed during the soil profiling: Witbank, Katspruit, Rensburg soil forms (A-horizon), G-horizon, weathered mudstone (shattered with high clay content), weathered mudstone (brittle) and un-weathered mudstone.

The depth of competent horizons (mudstone) was shallow on site viz. 0.95-2.4 mbgl; while downstream of the site (slope and topographic low areas) the depth to competent horizons was deeper, but still less than 2.4 mbgl.

Witbank soil form is a disturbed soil formed as a result of man-made activities; as can be expected this soil form is mainly confined to the plant area (on the hill crest), where soil was disturbed due to construction of the plant (Soil Classification Working Group, 1991).

Both the Katspruit and the Rensburg soil forms are clay soil management units and mostly found in areas where clays have accumulated to such an extent that the majority of the soil matrix is clay. These soils are usually indicative of seasonal or permanent wetland conditions (Soil Classification Working Group, 1991).

The Katspruit soil form is found more down-gradient in the lower lying areas. This soil form is most commonly found in areas of semi-permanent wetness. Rensburg soils are characterised by shrinking and swelling of the soils and also found down gradient of the site.

The G-horizon is developed in certain parts of the area of investigation and can be characterised by the following criteria (Soil Classification Working Group, 1991):

- It is saturated with water for long periods unless drained;
- Is dominated by grey, low chroma matrix colours, often with blue or green tints, with or without mottling;.
- Has not undergone marked removal of colloid matter, accumulation of colloid matter is usually found in the horizon;
- Has a consistency at least one grade firmer than that of the overlying horizon;
- Lacks saprolitic and plinthic character.

The Witbank soil form was found on average at a depth of 0.65 mbgl., while the Rensburg and Katspruit soil forms are thinner and developed to a depth of 0.3 mbgl. The G-horizon underlying these soils was developed in places with a thickness of about 0.3 to 0.7m.

Weathered mudstone is developed across the whole investigation area at depths ranging from 0.15 to 2.4 mbgl. The weathered mudstone grades into un-weathered mudstone at relative shallow depth ranging from 0.95 to 2.4 mbgl. The weathered mudstone is brittle and relatively incompetent. Seepage was identified in certain areas (especially near the plant area).

The top horizons have a high clay content, large cracks were observed on the surface across the study area. The weathered mudstone also contains varying percentages of clay depending on the degree of weathering.

Although the primary permeability of the weathered horizon (soil forms, G-horizon, weathered mudstone) can be considered low (due to high clay content), the secondary permeability induced by fissures (desiccation cracking) could result in seepage through the overlying clayey material towards the fractured bedrock. This is however unlikely if the weathered/soil horizon is saturated. The clay is likely to be dominated by montmorillonite type clay minerals.

3.4   HISTORIC SITE INFORMATION

The facility started producing fertilizer related products in the late 1970's. The layout of the site has remained relatively unchanged. As such it can be deduced that no historic contamination activities at the site had occurred in areas other than that which occurs presently (Figure 4). A related source of contamination was found off-site near Dam1 and

BH10 where fertilizer was stored on the ground in the past (Figure 5). The period during which the off-site fertilizer heap was found near Dam1 is not known. The fertilizer has since been removed.

It is likely that the integrity of the hard standing on site has been compromised with time and as such deteriorated to date. Maintenance of the infrastructure (holding tanks, pumps etc.) has occurred and can be regarded as being well managed. The production volumes has increased since the 1970's, therefore some of the containment cannot accommodate the increased production and its related activities. Due to the design constraints of the infrastructure, the probability of contamination has increased since the commissioning of the site. The boreholes (Boer1 and BH4) found approximately 250m downstream of the site were pumped in the past, abstraction from these boreholes stopped approximately 5 years ago (2004).

3.5   POTENTIAL POLLUTION SOURCES AND POLLUTANTS

The following raw materials were and are currently used in the operations at the site and have the potential to contaminate:

- Urea - $(NH_2)_2CO$
- Mono Ammonium Phosphate (MAP) $NH_4 \cdot H_2PO_4$
- Potassium Chloride - KCl
- Phosphoric Acid - H_3PO_4
- Ammonium Nitrate solution (21%. Vol) - NH_4NO_3
- Ammonium Sulphate - NH_4SO_4
- Defluorinated Phosphoric acid
- Zinc oxide - ZnO
- Boron - B
- TSPP - $Na_4P_2O_7$
- Calcium Nitrate $Ca(NO_3)_2$

The products mixed and produced from these raw materials also pose as pollutants.

3.5.1   Potential Sources of Fertilizer Related Contaminants

The following areas are potential sources of soil, groundwater and surface water pollution, these areas can be seen depicted in Figure 4:

- Loading areas at the railway line and loading of liquid fertilizers.
- Dry/raw storage area (urea, ammonium sulphate, potassium chloride).
- Storage tanks phosphoric acid, ammonium nitrate, UAN (solution of urea and ammonium nitrate), magnesium nitrate and calcium nitrate).
- Sump (located in plant area near the liquid fertilizer loading bay
- Dust

The historic off-site contaminant source near Dam1 can be seen in Figure 5.

3.5.2 Potential Contaminant Mobilising Mediums/Pathways

The following mobilising mechanisms were found which are likely to transport contaminants

- Infiltration and run-off of spillages from loading and overfills,
- Infiltration and run-off of process water
- Infiltration and run-off of water used to wash plant
- General surface water run-off
- Infiltration of water/product collected in sump

Reactive transport modelling of fertilizer waste in a dual porosity aquifer
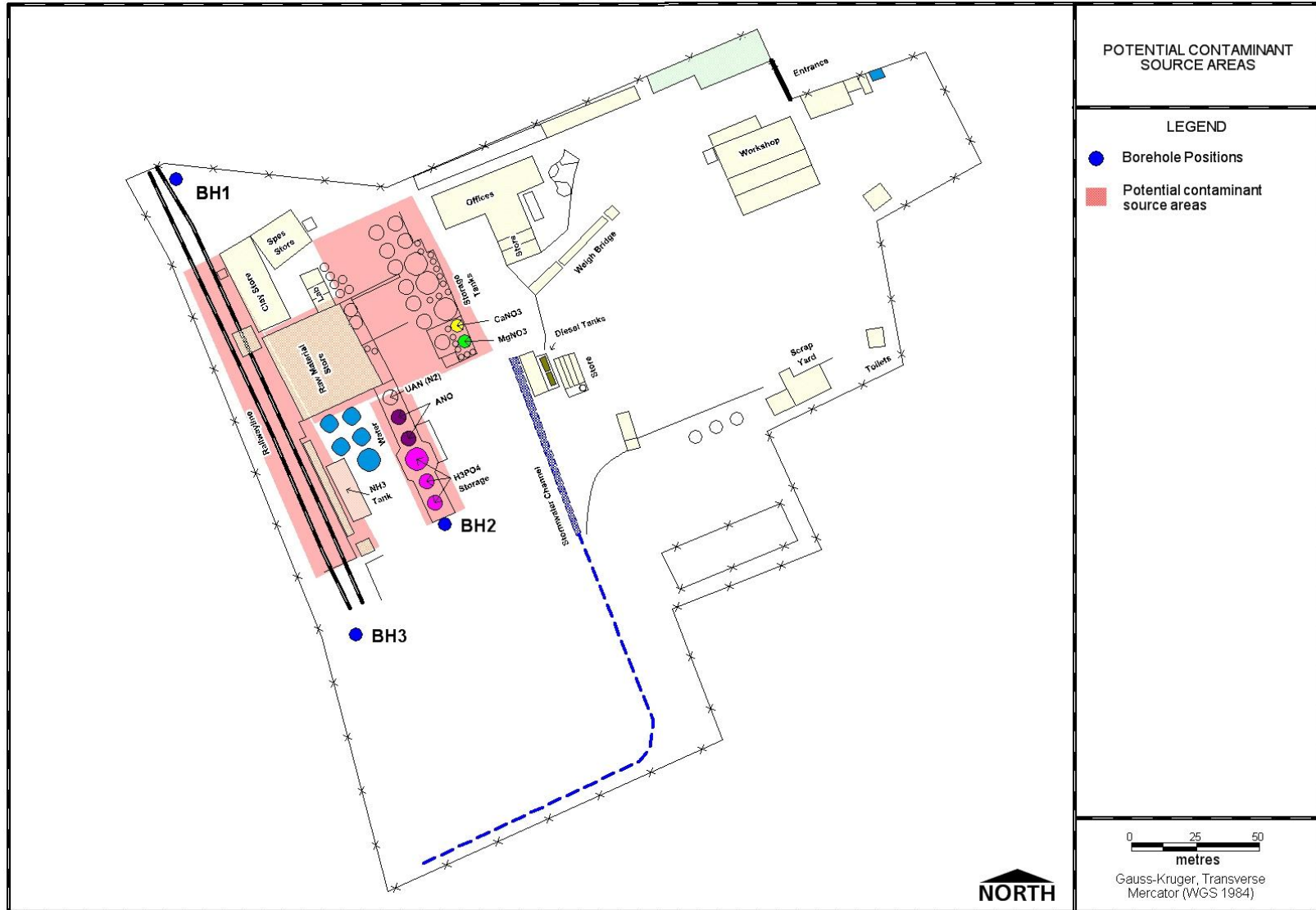
Figure 4: Potential contaminant source areas on-site

Area of investigation

On-site and off-site contaminant sources
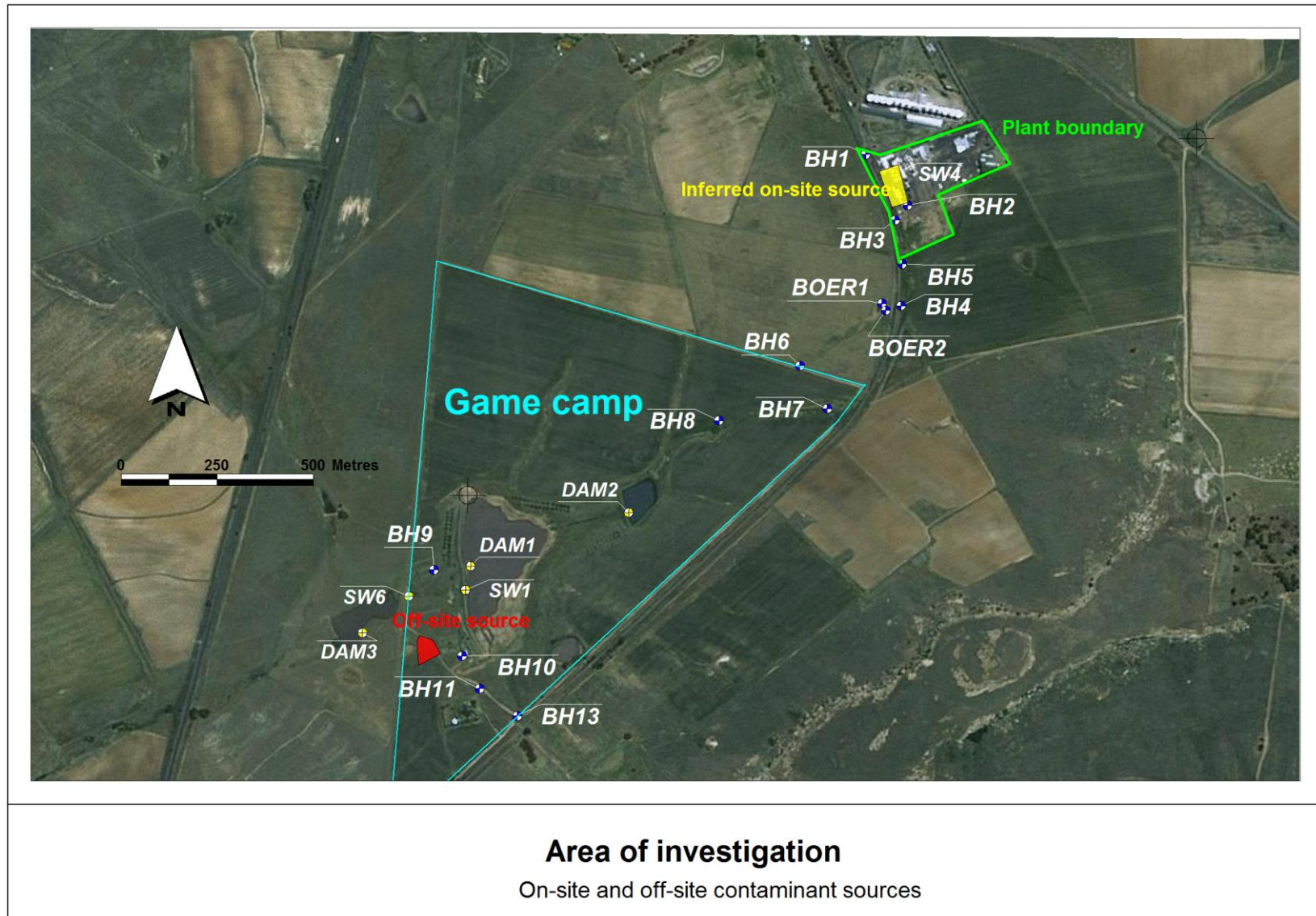
Figure 5: Potential contaminant source areas found in the area of investigation

4   STUDY METHODOLOGY

4.1   HYDROCENSUS (RECEPTOR IDENTIFICATION)

An extended hydrocensus was conducted downstream of the site to a distance of about 1.5 kilometres. The purpose of the hydrocensus was to identify groundwater and surface water users which may be potentially affected by contamination emanating from the site. The following information was gathered at each borehole/water body (where applicable):

- Geographic position

- Depth of the borehole

- Depth of the water strike

- Water level depth

- Yield

- Lithology

- Use of the borehole

- Details of ownership

4.2   GEOPHYSICS

Electromagnetic (EM) and Magnetic methods were employed during the geophysical survey to map preferential flow paths. While the magnetic method is used to detect basic intrusions like dolerite dykes and sills, which is normally associated with groundwater occurrence, the electromagnetic method detects changes in electrical conductance of the subsurface. As water is normally a conducting substance in the rock, the method is thus sensitive for the presence of groundwater. The combination of the two methods lends itself to the identification and preliminary quantification of groundwater occurrences.

4.2.1   Magnetic method

Due to the presence of minerals with a high magnetic susceptibility (mainly magnetite) the earth's magnetic field induces a magnetic field in some rock bodies. The magnitude of the induced magnetic field is dependent on the concentration and magnetic susceptibility of these minerals. Thus, where there is a difference in magnetic susceptibility of rocks, measuring the total magnetic field can give an indication of subsurface structures, especially

dolerite dykes and sills. A proton magnetometer was used to measure the total magnetic field at intervals of 10m along the profile lines.

4.2.2 Electomagnetic method

The electromagnetic survey consists of profiling the subsurface with two connected electrically conductive loops, one being an electromagnetic transmitter and the other a receiver. By means of an alternating current in the transmitter loop, secondary currents are induced in the subsurface. These induced currents are observed with the receiver loop. The instrument is calibrated to give an apparent conductivity reading. The depth of investigation is a function of the transmitter frequency and subsurface conductivity, as well as the orientation of the loops. The skin depth of the subsurface determines the depth of investigation. As both the above methods rely on measurement of magnetic and electromagnetic signals, it is evident that metallic structures and power lines will induce artificial noise on the natural signal. Measurements therefore cannot be taken closer than the loop separation from such structures.

4.3 PERCUSSION BOREHOLE DRILLING

Three boreholes (BH1, BH2, BH3) were drilled on site during a baseline hydrogeological study in 2004. The three boreholes were equipped to serve as groundwater monitoring wells. In July 2008 the groundwater monitoring network was further extended, four percussion boreholes were drilled downstream of the site (BH5, BH6, BH7 and BH8). The boreholes were sited following the geophysical investigation. The locations of all the boreholes are illustrated in Figure 7.

4.4 AQUIFER TEST

An aquifer test was conducted on borehole Boer1 during April 2008 in order to determine the aquifer parameters from the borehole. The purpose for the aquifer parameter estimation, was to calibrate the numerical model. Three boreholes Boer2, BH4 and BH3 were used as observation wells during the test. The test was conducted for a period of 392 minutes. The pump rate ranged from ~0.87 l/s to 0.57l/s at the end of the test. The change in pump rate was noted and the data was analysed accordingly. The water levels in the observation boreholes were measured periodically to identify any response to the abstraction.

4.4.1 Aquifer Parameter Estimation

The aquifer parameters were determined from the aquifer test. The transmissivity and storativity was estimated by curve fitting in Pump Test Pro (Waterloo, 2005) and by calculation in FC-Method (van Tonder, et al., 2000).

Transmissivity is the rate of water flow through a unit width of an aquifer under a unit hydraulic gradient over the saturated thickness of the aquifer (Kruseman, et al., 1990). While storativity is the volume of water per volume of aquifer released from storage per unit surface area of the aquifer as a result of a change in head (Kruseman, et al., 1990).

Curve fitting of the aquifer data was used to determine the transmissivity, the fracture flow double porosity (uniformly fractured aquifers) method by Warren and Root (1963) presented the best fit. This method stipulates flow from the blocks (porous medium) to the fractures. The fractured rock mass is assumed to consist of two interacting and overlapping continua: a continuum of low-permeability primary porosity blocks, and a continuum of high permeability, secondary porosity fissures or fractures (Warren, et al., 1963).

The assumptions and conditions underlying this method are:
- The aquifer is isotropic and confined
- The thickness of the aquifer is uniform over the area of influence.
- The extent of the aquifer is infinite (no barriers causing preferential flow paths),
- Constant discharge rate
- The well fully penetrates a fracture (matrix and fracture is considered as two overlapping continuous media),
- Horizontal piezometric surface prior to pumping
- Pseudo-steady state conditions (Warren, et al., 1963)

4.5 GROUNDWATER RECHARGE ESTIMATION

The groundwater recharge was estimated using the RECHARGE program (van Tonder, et al., 2000), which includes using qualified guesses as guided by various schematic maps. The following methods/sources were used to estimate the recharge.
- Soil information
- Geology
- Groundwater Recharge Map (Vegter)
- Acru Recharge Map (Schulze)

- Harvest Potential Map
- Chloride (Cl) method (van Tonder, G.; Xu, Y., 2000)

The above-mentioned programme incorporates all the different methods to calculate recharge. The following assumptions are necessary for successful application of the Cl Method:

- There is no source of chloride in the soil water or groundwater other than that from precipitation
- Chloride is conservative in the system
- Steady-state conditions are maintained with respect to long-term precipitation and chloride concentration in that precipitation, and in the case of the unsaturated zone
- A piston flow regime is assumed, defined as the downward vertical diffuse flow of soil moisture.
- The type of geology also dictates the validity of the Cl Method.

4.6 ELECTRICAL CONDUCTIVITY (EC) PROFILING

Down the hole electrical conductivity (EC) profiling was conducted on the boreholes to detect changes in EC. A Solinst TLC meter was used to profile each accessible borehole by measuring EC at 1 metre intervals. EC profiles, compared with the construction logs of monitoring wells can be used to determine the optimum sampling depth of each borehole.

4.7 WATER SAMPLING

Groundwater was sampled by low-flow pumping and bailing where possible. The groundwater levels were measured before introducing any equipment in the borehole.

All the boreholes were purged with a low-flow pump (were applicable) until the field parameters measurements (EC, Temp., pH, DO, ORP) stabilised (ensures that a representative sample of the aquifer system is obtained) after which samples were taken. The field parameters were measured in a flow-through cell. Where sampling by means of purging was not possible, discrete sampling was conducted by means of sampling at pre determined depths aided by the EC profile of the borehole The surface water samples were taken directly from the surface of the water bodies.

The water samples were collected in one litre plastic bottles. All samples were kept on ice or in a refrigerator until delivered to a laboratory. The groundwater samples were submitted to a

laboratory for major cation/anion analyses, including some constituents associated with fertilizer contaminants. These chemical constituents were selected to adhere to the SANS Standard for Drinking Water (SANS, 2006).

5   RESULTS OF THE INVESTIGATION

5.1   HYDROCENSUS

Five existing boreholes were identified in the game camp (see Figure 5), near the farmstead (house) located ~1.5 km south of the site. The borehole which supplies the community (BH Background) with water can be assumed to be representative of the background water quality, as it is found ~1km north of the site (up-gradient and not likely to be impacted). The positions of the boreholes can be seen in Figure 7. Furthermore Dam1, Dam2 and Dam3 were identified as potential surface water receptors as seen in Figure 9. Borehole BH9 was found below Dam1 and is strategically situated to determine the quality of the groundwater leaving the property of the site owner (impact monitoring borehole). BH10 is situated 170m south of BH9; this borehole is blocked at a depth of 11m. Boreholes BH11, BH12, BH13 are found around the farmstead and may be potential receptors. Three boreholes were identified 250m down stream of the site (Boer1, Boer2 and BH4), all three of these boreholes are artesian in nature, they are not in use. Only borehole BH13 and BH11 are used for potable water located 1.6 km downstream of the site.

5.2   AQUIFER TEST

The aquifer parameters were determined by means of calculation in FC (van Tonder, et al., 2000) and by curve fitting in Aquifer Test Pro (Waterloo, 2005). The estimated transmissivity (T) of boreholes Boer1, Boer2, BH3 and BH4 can be seen summarised in Table 1 and Table 2. The borehole Boer1 was the pump well while Boer2, BH3 and BH4 were used as observation wells.

With reference to Table 1 and Table 2, it can be seen that the transmissivities of the boreholes are similar, further more these transmissivities are typical of the hydrostatigraphic setting. Both the transmissivities estimated from derivates in FC and from curve fitting in Aquifer Test Pro can be regarded in the same order of magnitude. It can therefore be said that the transmissivity of the tested aquifer ranges from 0.9 to 3.3 m^2/d. It is likely that similar fracture systems had been intersected during drilling of the boreholes.

Table 1: Transmissivity of boreholes estimated in FC (estimates from derivatives)

Borehole	Distance to pump well	Early Transmissivity (m^2/d)	Late Transmissivity (m^2/d)
Boer1	-	0.46	0.92
Boer2	20.45	0.46	3.13
BH3	220.28	Insufficient data	
BH4	50.46	0.46	1.05

Table 2: Transmissivity and storativity of boreholes estimated in Aquifer Test Pro

Borehole	Distance to pump well	Transmissivity (m^2/d)	Storativity
Boer1	-	1.1	4.75×10^{-2}
Boer2	20.45	3.3	1.54×10^{-3}
BH3	220.28	3.31	1.35×10^{-4}
BH4	50.46	0.992	2.24×10^{-5}

5.3   GEOPHYSICS

The position of the traverses can be seen in Figure 6. A total of thirteen profiles were traversed across the study area downstream of the site. The survey was conducted to identify whether any identifiable preferential flow paths exists on which the boreholes may be targeted. Additionally the survey was conducted to verify whether any geological structures occurs near the boreholes (Boer1, Boer2) and BH4, as these boreholes are artesian in nature. A summary of the traverses can be seen in Figure 6, while the findings of each traverse can be seen below. The results of the geophysical survey is appended under Appendix A.

Table 3:Summary of traverse information

Traverse no.	Traverse direction	Length (m)	Observations
Traverse 1	N-S	400	No major anomalies can be identified in this traverse, a minor EM vertical dipole anomaly can be seen at 90m, but cannot be substantiated by the magnetic profile. The effects of the fence can be seen at 60m on the magnetic profile.
Traverse 2	W-E	200	No anomalies discernable, conductivity increased gradually towards the east (power lines).
Traverse 3	W-E	210	A minor anomaly may be seen at 90m, possibly identified as zone of deeper weathering
Traverse 4	W-E	180	No significant anomaly was identified
Traverse 5	W-E	210	No significant anomaly was identified
Traverse 6	NE-SW	200	Both an EM and magnetic anomaly was identified at 80m, most likely dolerite material used to fill an erosion gully
Traverse 7	NE-SW	180	No significant anomaly was identified
Traverse 8	W-E	200	Effects of the power lines can be seen at 200m
Traverse 9	W-E	150	No significant anomaly was identified
Traverse 10	W-E	150	No significant anomaly was identified; conductivity appears to decrease gradually to the east.
Traverse 11	W-E	150	No significant anomaly was identified, conductivity appears to decrease gradually to the east.
Traverse 12	N-S	180	No significant anomaly was identified
Traverse 13	N-S	85	Only a magnetic profile was done, an anomaly was identified at 70m, most likely the same dolerite identified in traverse 6.

From the geophysical survey it can be seen that no major structures or preferential flow paths were discernable in the survey area. The geophysical survey did not identify major vertical or sub-vertical geological structures which influence groundwater flow (in the area of the investigation). The geophysical survey conducted was limited, as the geophysical methods used cannot identify any horizontal fractures such as bedding plane and pressure

release (caused by removal of overburden over time) fractures. It can therefore be concluded that no major vertical or sub-vertical geological structures are likely to act as preferential flow paths in the immediate area downstream of the site.

Reactive transport modelling of fertilizer waste in a dual porosity aquifer

Figure 6: Position of the geophysics traverses

5.4 PERCUSSION BOREHOLE DRILLING

The results of the geophysical survey did not identify any major anomalies or geological structures. As a result, drilling targets were not derived from the geophysical survey. The boreholes were sited taking into consideration the inferred groundwater flow direction. Table 4 below summarises the borehole construction and blow yields.

Table 4: Borehole construction

Borehole no.	Date drilled	Depth (mbgl.)	Well construction (casing depth m)		Blow Yield
			Solid	Perforated	
BH1	August 2004	40	0-3	3-40	0
BH2	August 2004	40	0-3	3-40	0
BH3	August 2004	32	0-3	3-32	0.25 l/s
BH4	unknown	>90	unknown		
BH5	July 2008	40	0-3.5	-	0
BH6	July 2008	36	0-3.5	-	0.33 l/s
BH7	July 2008	40	0-3.5	-	0
BH8	July 2008	40	0-3.5	-	0
BH9	unknown	>44	unknown		
BH10	unknown	22	unknown		
BH11	unknown	unknown	unknown		
BH12	unknown	unknown	unknown		
BH13	unknown	unknown	unknown		
BH Background	unknown	unknown	unknown		
Boer1	unknown	36	unknown		
Boer2	unknown	9	unknown		

The boreholes drilled for monitoring purposes as seen in Figure 7 were positioned in the following areas:

- **BH1:** Situated on the north western boundary of the site and upstream of all of the potential pollution sources on the plant.
- **BH2:** Situated south and downstream of the liquid bulk storage tank.

- **BH3:** Situated on the south-western boundary of the site, downstream of all potential contamination sources and specifically the road and rail loading area,
- **BH5:** Situated to the south of the plant outside the plant borders,
- **BH6:** This borehole is situated approximately ~500 m south west of the site. The borehole was sited downstream of the contaminated boreholes (Boer1 and Boer2).
- **BH7:** This borehole was drilled ~550 m south south west of the site along a natural drainage line in the game camp.
- **BH8:** Located ~700m south west downstream of the site along a natural drainage line in the game camp.

The observations made during the drilling in 2004 and 2008 indicated that no major water yielding structures were intersected in the boreholes, except in BH3 and BH6 which had blow yields of 0.25 l/s and 0.33 l/s, respectively. Seepage was absent in most of the wells except BH3, BH5 and BH6. Seepage was observed at an average depth of 18-20 mbgl.

The geological logs of the drilled monitoring boreholes are similar, as can expected given the geological setting. The table below shows a simplified log of the geological units. A colluvial layer (discussed in section 3.3 above) overlies highly weathered to un-weathered mudstone, this is underlain by sandstone with subordinate mudstone lenses.

Table 5: Simplified geological log

Depth (mbgl.)	Description
0-2	Brown red, sandy silty clay, colluviums and residual mudstone
2-10	Brown red, highly to slightly weathered mudstone
10-40	Grey, weathered to un-weathered sandstone with subordinate mudstone lenses in places

Borehole Positions
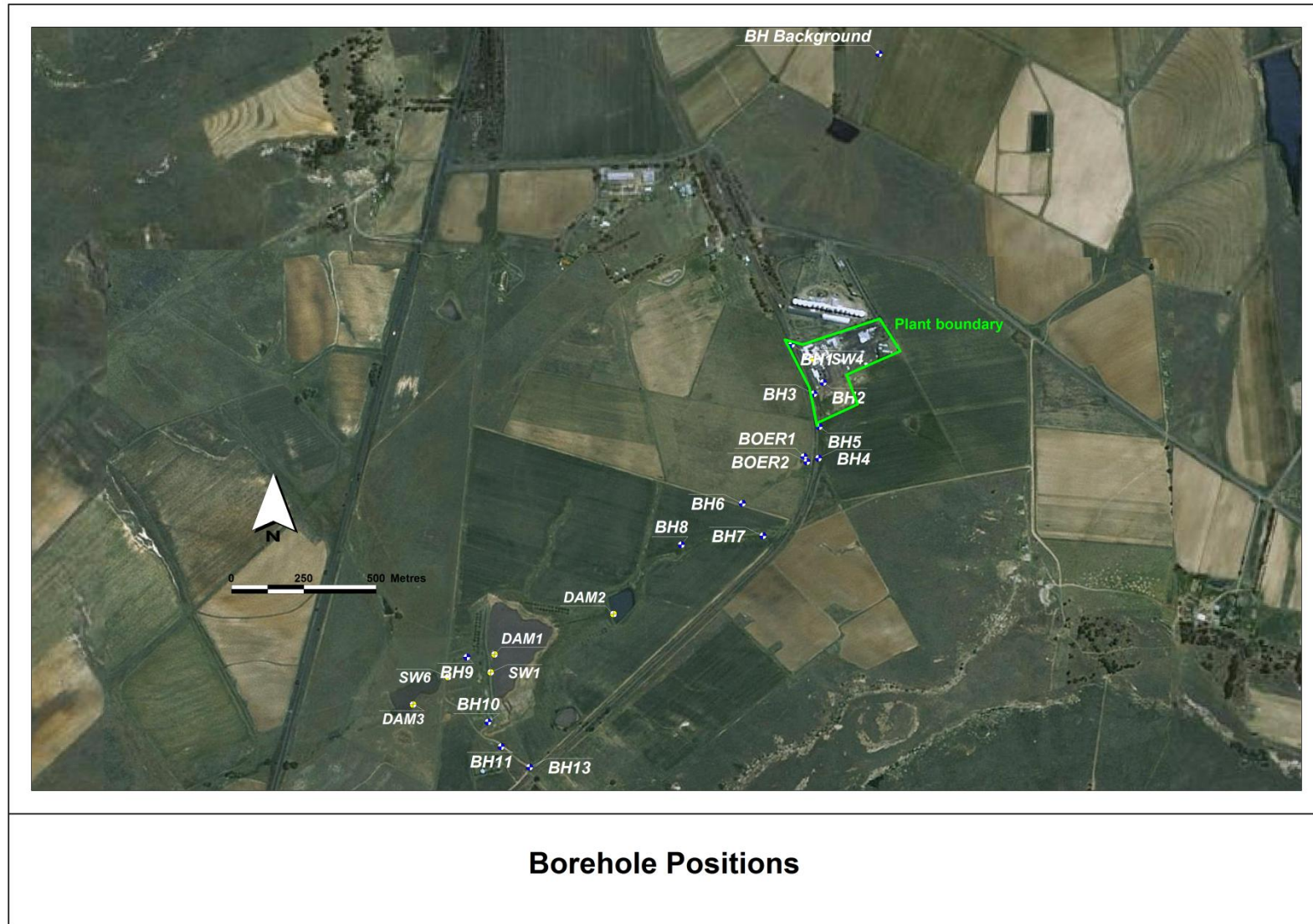
Figure 7: Borehole Positions

5.5 GROUNDWATER LEVELS

The groundwater levels can be seen in Table 6. The water levels are relatively shallow, with the piezometric levels ranging from ~0.7 magl. (above ground level) to ~5 mbgl. (below ground level). The boreholes Boer1, Boer2, BH4 and BH9 are artesian in nature i.e. the water level (piezometric level) is above the ground level. In Figure 8, the correlation between the borehole elevation and the static water level can be seen, there appears to be a good correlation. Therefore it can be said that the groundwater flow direction emulates the topography and flows towards the south west.

Table 6: Groundwater levels (April 2009)

Borehole No:	Z	Collar heights (mm)	Current borehole depth (m)	Water level*
BH1	1683	320	40	4.31
BH2	1682	220	40	3.54
BH3	1682	240	29	4.16
BH4	1677	1630	>50	0.03
BH5	1679	590	37	1.89
BH6	1671	440	30	0.41
BH7	1672	170	29	1.1
BH8	1668	560	40	1.36
BH9	1655	300	>44	0.3 (above ground level)
BH10	1658	0	22	5.55
BH11	1662	0	n/a	n/a
BH13	1665	0	n/m	12.75
BOER 1	1677	1860	36	0.69 (above ground level)
BOER 2	1677	1400	9	0.32 (above ground level)
BH Background		0	n/m	0

*- water levels are measured in metres below ground level (bgl.), except where specified otherwise.
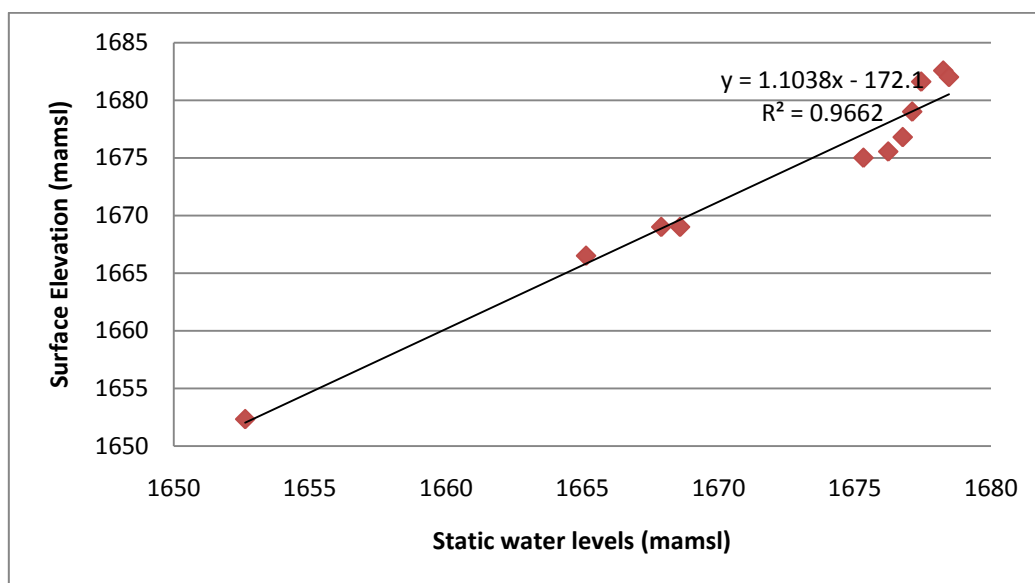
Figure 8: Correlation between borehole elevation and static water level

Surface Water Sample Positions
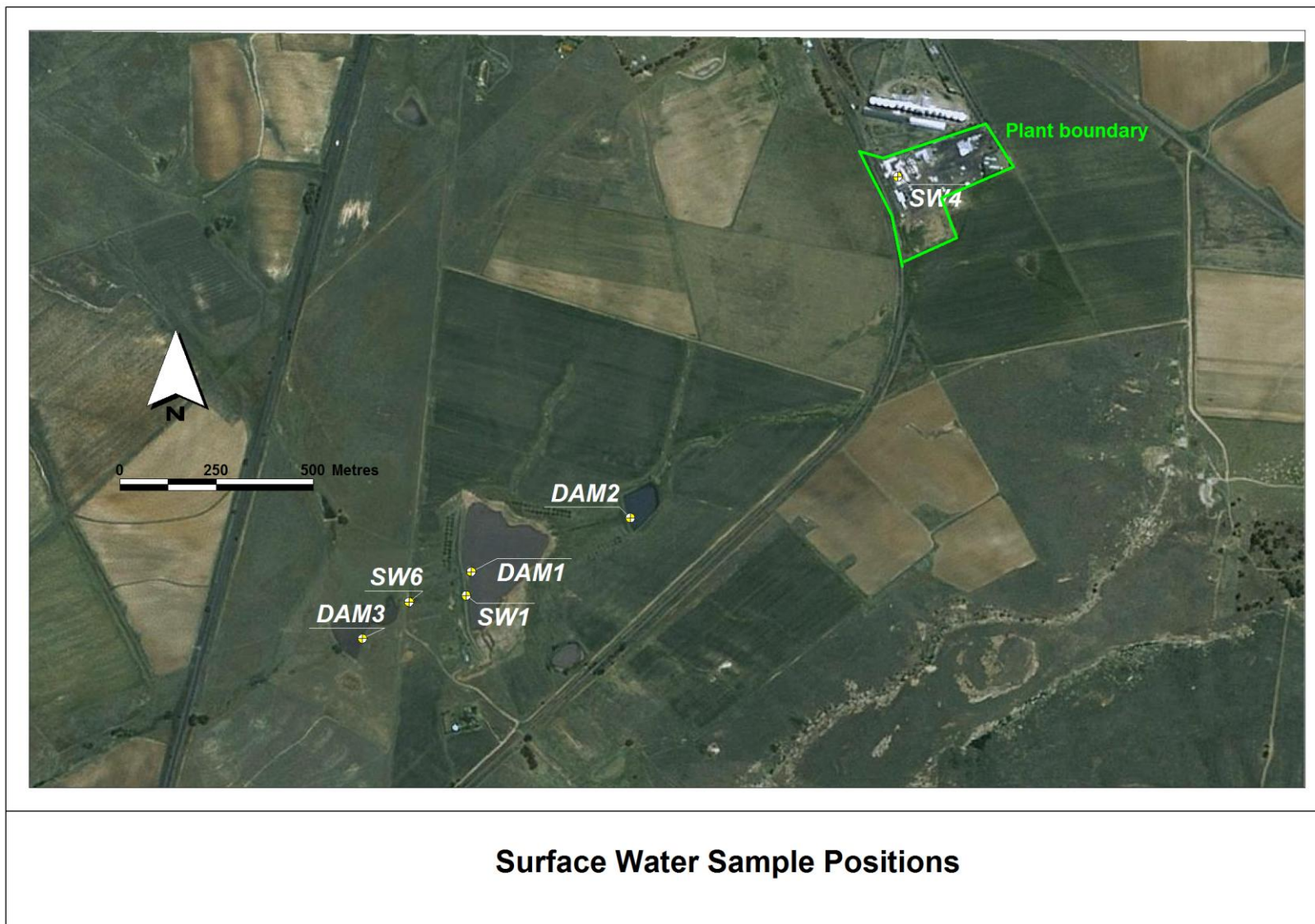
Figure 9: Surface water sampling positions

5.6 GROUNDWATER RECHARGE ESTIMATION

According to the rainfall data the average rainfall of the area is 674 mm/year (DWAE, 2009). A Cl concentration of 20 mg/l was used in the Cl method estimation. The concentration was derived by averaging (harmonic mean) the Cl concentrations in boreholes BH11, BH13 and BH background during the monitoring period. The other methods used to estimate the recharge are qualified guesses derived from certain thematic maps and equations (van Tonder, G. and Xu, Y., 2000).

The result of the estimations including the Cl method can be seen in Table 7. It can be seen that the Cl method estimates a much larger recharge than the qualified guesses. It can be seen that the groundwater recharge is averaged at 4.18% percent of the rainfall.

If a more conservative approach is used and the Cl method is not taken into account then the recharge decreases to 2.8%. Therefore as accurate estimation of recharge is not possible given the collected data; the groundwater recharge of the area of interest is likely to range between ~2.8 and ~4%. Furthermore recharge does not occur uniformly across the area, as a result this estimated recharge can be regarded an average value for the area.

Table 7: Summary of recharge including the Cl method

Method	mm/a	% of rainfall	Certainty (Very High=5 ; Low=1)
Cl	48.27	7.16	4
Qualified Guesses :			
Soil	20.23	3.00	3
Geology	13.48	2.00	3
Vegter	45.00	6.67	3
Acru	15.00	2.22	3
Harvest Potential	20.00	2.97	3
Expert's guesses			3
Base Flow (minimum Re)	30.00	4.45	1
Average recharge	**28.21**	**4.18**	

5.7 EC PROFILING

The EC (electrical conductivity) profiling was conducted on 12 boreholes. Borehole BH11, BH13 and BH Background were not profiled as they were sealed. The EC profiles were incorporated into the geological logs as the geology may have an influence to the EC profile in the boreholes. No geological logs were available for the boreholes BH4, BH9, BH10, Boer1 and Boer2 as they were drilled for water supply in the past and consequently no

information is available for the boreholes. In the majority of the boreholes the EC increased with depth. The boreholes which are artesian in nature (BH4, BH9, Boer1 and Boer2) show an EC profile which remains relatively constant with depth, however a slight increase with depth could be discerned.

5.8 WATER QUALITY RESULTS

5.8.1 Water quality standard

A total of 15 boreholes and 5 surface water bodies/positions were sampled. The water sampling results were compared with the maximum recommended concentrations for domestic use as defined by the SANS 241 standards (SANS, 2006). This standard classifies domestic water in two classes, namely:

- Class I is considered as acceptable domestic water for lifetime consumption (SANS, 2006)
- Class II, which can be tolerated for a limited period only (SANS, 2006)

All the sampled boreholes, except the background borehole and BH13, contain contaminants associated with fertilizer i.e. elevated cations and anions (Table 8). Surface water sample SW1 taken below Dam1 showed a relation to fertilizer related contaminants, while SW4 taken from a storm water furrow at the liquid fertilizer decanting area contains highly elevated concentrations of certain constituents. Both water samples taken from Dam1 and Dam2 show no signs of significant contamination, it must be noted that these samples were taken from the surface of the water bodies.

Although the sampled surface water bodies may not be used for drinking water, they were compared to the SANS 241 standard in order to create a baseline standard for the site (Table 9). The DWAF standards for drinking water (DWAF a, 1996) and stock watering (DWAF b, 1996) were used to assess the health risk which the contaminants in the water pose to human and livestock health (see section 7).

5.8.2 Statistical summary of water quality

A correlation coefficient matrix in Table 10 illustrated the relationship between certain parameters in the groundwater viz. EC correlated well with TDS, Ca, Mg and NO_3 concentrations. Mg and Ca also relates well with NO_3, Mg and Ca concentrations.

A statistical summary of all the groundwater samples can be seen in Table 11, a total of 43 groundwater samples were collected from 2004 until April 2009. NO_3 is the constituent which exceeds the SANS 241 drinking water standard in 81 % of the samples, as a result NO_3 can be regarded as one of the major contaminants of concern. The cations Na, Ca and Mg also exceed the standard in more than half the boreholes, NH_4 and Cl to lesser extent are also associated with the elevated cations. The elevated cations and anion result in the EC and TDS concentrations exceeding the standard in more than a third of the samples. The large standard deviations of the constituents illustrate the large difference in solute loads of the boreholes located at the source and background quality areas.

The surface water samples appear to be less mineralised than the groundwater, NH_4 appears to be the constituent which exceeds the standard in 29% (2 samples) of the samples (Table 12). As seen in the groundwater samples, the contaminants in the surface water samples also deviate largely. One sample (SW4) taken from a furrow in the loading area was not added into the sample population, as it is not representative of the ambient surface water environment. However SW4 can be used to present the signature of the water which infiltrates into the subsurface from the activities on site.

5.8.3 Accuracy of chemical analysis

The accuracy of the chemical analysis was evaluated according to the plausibility of the electro neutrality (ion balance); electro neutrality was calculated according to:

$$\text{E.N.}[\%] = \frac{\sum cations\,[\text{meq/L}] - \left|\sum anions\,[\text{meq/L}]\right|}{\sum cations\,[\text{meq/L}] + \left|\sum anions\,[\text{meq/L}]\right|} \cdot 100\%$$

An error of 5 % is considered as acceptable; interpretations of samples with larger errors in the ion balance should be taken with caution. With reference to Table 13, it can be seen that of the 51 samples (groundwater and surface water) analysed over the monitoring period, 8 samples exceed the error of 5%. Therefore 84% of the samples collected can be considered plausible and accurate. The cause of exceedence of the percentage error might have been caused by analytical errors and/or most probably by undetermined ions in the samples.

Table 8: Representative groundwater chemistry results

Sample No.	BH1	BH2	BH3	BH4	BH5	BH6	BH7	BH8	BH9	BH10	BH11	BH13	BOER1	BOER2	BH background	Class I	Class II
Ca	301.00	762.00	1137.00	692.00	574.00	133.00	145.00	41.00	115.00	95.00	46.00	39.00	1137.00	892.00	46.00	150	300
Mg	49.00	172.00	316.00	153.00	99.00	25.00	47.00	8.00	27.00	37.00	16.00	9.00	267.00	264.00	15.00	70	100
Na	730.00	571.00	584.00	514.00	707.00	277.00	358.00	82.00	108.00	100.00	66.00	76.00	584.00	551.00	64.00	200	400
K	6.20	12.40	16.00	18.90	6.80	3.00	2.50	3.10	2.30	4.20	2.50	2.50	9.80	10.90	8.00	50	100
Mn	0.44	0.41	0.23	3.34	1.07	0.70	0.44	0.34	0.04	0.05	0.00	0.00	0.17	0.44	0.00	0.1	1
Fe	0.00	0.00	0.00	0.06	0.05	0.07	1.57	8.62	0.63	1.03	0.00	0.00	0.44	9.01	0.00	0.2	2
F	0.00	0.20	0.20	0.40	0.30	0.40	0.80	0.70	0.40	0.70	0.30	0.30	0.20	0.20	0.20	1	1.5
NO_2	0.00	24.63	95.25	49.27	2.63	0.00	1.64	0.00	0.00	20.69	0.00	0.00	32.84	27.59	0.00	33	66
NO_3	247.86	3616.04	6311.48	3093.77	2726.42	0.00	849.79	43.37	119.50	318.67	57.54	9.29	5576.76	4603.04	23.46	44	88
NH_3	1.03	33.54	51.60	1.29	1.03	1.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	15.48	0.00	1.29	2.57
Si	4.80	7.60	9.00	5.30	6.20	7.70	5.70	6.60	7.90	3.90	9.00	7.20	7.30	6.10	10.80	-	-
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.20	0.00	0.00	0.00	0.00	0.00	5	10
PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-
HCO_3	262.88	268.14	0.00	224.31	233.79	413.23	218.27	155.55	484.34	160.73	234.60	310.44	321.59	9.32	291.40	-	-
Cl	1358.00	358.00	528.00	471.00	566.00	151.00	210.00	57.00	51.00	90.00	33.00	8.00	10.00	570.00	24.00	200	600
SO_4	289.00	415.00	587.00	208.00	308.00	480.00	263.00	75.00	93.00	98.00	44.00	9.00	305.00	349.00	28.00	400	600
TDS by sum	3123.00	6092.00	9956.00	5277.00	5120.00	1292.00	1985.00	390.00	757.00	824.00	383.00	306.00	8636.00	7385.00	351.00	1000	2400
M-Alk($CaCO_3$)	216.00	220.00	268.00	184.00	192.00	340.00	180.00	128.00	400.00	132.00	196.00	256.00	264.00	184.00	240.00	-	-
pH	7.40	7.00	6.80	6.90	7.30	7.60	7.80	7.60	7.90	7.30	8.30	7.80	7.20	7.20	7.70	5.0 - 9.5	4.0 - 10.0
EC	518.00	753.00	1154.00	686.00	665.00	183.00	294.00	64.40	122.00	132.00	65.80	55.60	1102.00	1023.00	61.70	150	370
Cat/An Bal. %	4.80	1.80	4.80	1.10	2.10	1.80	3.60	1.50	2.30	0.30	1.20	3.10	5.70	5.20	0.20	-	-

Notes
Yellow = Class I
Tan = Class II
exceeds maximum allowable drinking water standard
na- not analysed
ADL = Above instuments detection limit
NM = not measured
All concentrations are presented in mg/l, EC is presented in mS/m
0 = below detection limit of analytical technique

Table 9: Representative surface water chemistry results

Sample No.	DAM1	DAM2	SW1	SW4	SW6		Class I	Class II
Ca	24.000	52.000	98.000	150.000	127.000		150	300
Mg	10.000	19.000	137.000	78.000	47.000		70	100
Na	19.000	19.000	1775.000	334.000	285.000		200	400
K	14.800	38.000	25.000	16560.000	12.100		50	100
Mn	0.248	0.190	2.830	2.250	0.357		0.1	1
Fe	1.500	0.414	2.170	0.329	0.360		0.2	2
F	0.500	0.700	1.500	37.000	0.400		1	1.5
NO_2	0.000	0.000	0.000	2.956	0.000		33	66
NO_3	1.320	0.000	0.884	31558.800	0.884		44	88
NH_4	2.451	4.773	2.451	20640.000	1.032		1.29	2.57
Si	1.900	4.100	17.300	20.000	4.700		-	-
Zn	0.000	0.000	0.039	3.210	0.000		5	10
PO_4	0.000	3.302	55.880	3759.200	5.588		-	-
HCO_3	106.300	165.682	2533.361	7025.110	879.836		-	-
Cl	22.000	55.000	400.000	16498.000	140.000		200	600
SO_4	55.000	102.000	1703.000	18103.000	272.000		400	600
TDS by sum	219.000	407.000	4730.000	115575.000	1286.000		1000	2400
M-Alk($CaCO_3$)	88.000	140.000	2200.000	5760.000	732.000		-	-
pH	8.000	8.500	8.800	6.500	8.200		5.0 - 9.5	4.0 - 10.0
EC	32.700	60.800	706.000	17250.000	192.000		150	370
Cat/An Bal. %	3.00	3.20	0.60	0.60	3.20		-	-

Notes

Yellow = Class I

Tan = Class II

 exceeds maximum allowable drinking water standard

na- not analysed

All concentrations are presented in mg/l, EC is presented in mS/m

0 = below detection limit of analytical technique

Table 10: Correlation coefficient matrix of selected parameters in groundwater

Total Number of Samples: 43											
Correlation coefficient											
		Cond	TDS	pH	K	Ca	Na	Mg	NH4	Cl	SO4	NO3
Cond	mS/m	1	0.971	-0.615	0.789	0.978	0.839	0.956	0.301	0.370	0.788	0.909
TDS	mg/L		1.000	-0.622	0.851	0.975	0.789	0.947	0.416	0.306	0.801	0.888
pH				1.000	-0.486	-0.611	-0.511	-0.580	-0.324	-0.214	-0.519	-0.523
K	mg/L				1.000	0.795	0.624	0.736	0.537	0.287	0.650	0.735
Ca	mg/L					1.000	0.758	0.979	0.383	0.224	0.759	0.935
Na	mg/L						1.000	0.687	0.306	0.726	0.741	0.629
Mg	mg/L							1.000	0.254	0.156	0.746	0.926
NH4	mg/L								1.000	0.008	0.375	0.384
Cl	mg/L									1.000	0.380	0.082
SO4	mg/L										1.000	0.783
NO3	mg/L											1
r > 0.9												

Table 11: Statistical summary of groundwater chemical analyses

Parameter	Unit	No of Samples	Max	Min	AM	Q25	Q50	Q75	No of Exceedences*	Percent of Exceedences*	Standard deviation
Default											
Ca	mg/l	43	1333.7	39	579	118	574	999.5	24	56	458.4
Na	mg/l	43	746.8	64	483	247	591.8	648	29	67	241.8
K	mg/l	43	26.6	2	9.6	4.55	7.9	13.6	0	0	6.64
Mg	mg/l	43	332.4	3.84	136.2	27.2	127	250	22	51	114.7
Cl	mg/l	43	1358	8	456.8	154.5	471	579.9	9	21	358.2
SO4	mg/l	43	587	9	293.4	216.9	291.5	371	0	0	157.2
HCO3	mg/l	43	485.1	9.3	256.7	220.7	260.9	306.3	0	0	95.7
pH		43	8.6	6.7	7.5	7.2	7.5	7.8	0	0	0.47
Cond	mS/m	40	1206	55.6	581.4	153.8	591.5	1023.5	26	65	399.4
TDS	mg/L	43	11060	306	4615.5	1106	5120	7078.5	28	65	3400
NH4	mg/L	43	384	0	19.3	0	1	6.7	17	40	65.1
NO3	mg/L	43	7410.1	0	2461.3	172.1	1648	4684	35	81	2452.6
NO2	mg/L	28	95.3	0	11.1	0	1.62	14.6	1	4	20.7

* Exceedence of SANS 241 Class II drinking water (maximum allowable)

AM- Arithmetic mean

Q25- 25th percentile

Table 12: Statistical summary of surface water chemical analyses

Parameter	Unit	No of samples	Max	Min	AM	Q25	Q50	Q75	Number of Exceedences	Percent of Exceedences	Standard deviation
Ca	mg/l	7	127	24	69.6	32.5	52	109.5	0	0	44.7
Na	mg/l	7	1775	14	342.9	19	24	274.5	1	14	642.9
K	mg/l	7	38	12.1	20.8	14.3	18.7	24	0	0	9
Mg	mg/l	7	137	10	40.7	12	19	47.5	1	14	45.5
Cl	mg/l	7	400	21	110	24.5	55	122.5	0	0	135.8
SO4	mg/l	7	1703	17	322	49.5	61	187	1	14	614.8
HCO3	mg/l	7	2533.4	106.3	715	126.5	165.7	973.5	0	0	896.6
pH		7	8.8	7.2	7.96	7.5	8	8.35	0	0	0.59
Cond	mS/m	7	706	32.7	180.8	41.1	60.8	192	1	14	242
TDS	mg/L	7	4730	219	1176	234	407	1204	1	14	1629.3
NH4	mg/L	7	18	0	4.25	1.03	2.45	3.6	2	29	6.26
NO3	mg/L	7	7.1	0	1.96	0.88	0.89	1.99	0	0	2.4
NO2	mg/L	7	0.33	0	0.047	0	0	0	0	0	0.125

* Exceedence of SANS 241 Class II drinking water (maximum allowable)

AM- Arithmetic mean

Q25- 25th percentile

Table 13: Electro neutrality of the groundwater and surface water samples

Station Name	Sampling Date	E.N.
		%
BH1	2004/11/01	-1.481372
BH1	2005/11/01	-0.8782343
BH1	2007/01/07	-6.104104
BH1	2008/01/08	-1.167357
BH1	2008/07/15	-4.237815
BH1	2009/04/29	1.138415
BH10	2008/07/15	-2.517778
BH10	2009/04/29	-0.4470475
BH11	2009/04/29	-0.6719397
BH13	2009/04/29	3.325476
BH Background	2008/04/18	4.685675
BH Background	2009/04/29	0.7169061
Boer1	2008/04/17	3.826184
Boer1	2008/07/15	-4.48406
Boer1	2009/04/29	1.214102
Boer2	2008/04/17	5.232391
Boer2	2008/07/15	-4.141941
Boer2	2009/04/29	-3.381407
DAM1	2008/07/15	-2.67869
DAM1	2009/04/29	-1.910706
DAM2	2008/07/15	-1.580041
DAM2	2009/04/29	2.704478
SW1	2008/07/15	3.218547
BH2	2004/11/01	31.74953
BH2	2005/11/01	1.781049
BH2	2007/01/07	-14.68548
BH2	2008/01/08	2.466363
BH2	2008/07/15	-5.202346
BH2	2009/04/29	-1.408954
SW4	2008/07/15	4.205994
SW6	2008/07/15	-2.313735
SW6	2009/04/29	4.68056
BH3	2004/11/01	34.23927
BH3	2005/11/01	2.18E-02
BH3	2007/01/07	-8.810574
BH3	2008/01/08	4.098499
BH3	2008/07/15	-2.970781
BH3	2009/04/29	-10.56738
BH4	2008/04/17	4.468704
BH4	2008/07/15	-3.686355
BH4	2009/04/29	-0.7485661
BH5	2008/07/15	-4.7166
BH5	2009/04/29	-1.732653
BH6	2008/07/15	-2.087208
BH6	2009/04/29	-0.3220358
BH7	2008/07/15	-0.77767
BH7	2009/04/29	-3.555801
BH8	2008/07/15	1.070294
BH8	2009/04/29	-0.7302358
BH9	2008/07/15	1.077255
BH9	2009/04/29	-2.092899
Minimum		-14.7
Maximum		34.2
Arithmetic Mean		0.27
Error >5%		

5.9 GEOCHEMICAL CHARACTERISATION

The water types and ionic strengths of the water samples can be seen in Table 14. Boreholes BH9, BH11, BH13 and BH background are classified as $Na-Ca-HCO_3$ type water, which is typical of the background water quality . As can be expected the ionic strength of the background waters are analogous with geogenic water (<0.02 mol/kg). The remainder of the samples are dominated by $Ca-Na-NO_3$ type water facie with minor variations including other ions such as Mg, Cl, SO_4 and NH_4. The ionic strength of these samples are orders of magnitude higher than the background and range from 0.02 to 1.7 mol/kg. These elevated ionic strengths indicate an external influence on the groundwater chemistry. SW4 taken from the plant area (ionic strength 1.7 mol/kg) is the only sample which has an ionic strength higher than that of sea water.

With reference to the piper and durov diagram of all the water samples (Figure 10 and Figure 11), the background borehole is represented by the blue triangle, the red symbols represent the source monitoring boreholes (BH1, BH2 and BH3). The plume monitoring boreholes (BH4, BH5, Boer1 ands Boer2) are represented by the purple symbols, while the impact monitoring boreholes (BH6, BH7, BH8, BH9, BH10, BH11 and BH13) are represented by green. The surface water samples (Dam1, Dam2, SW1, SW4 and SW6) are represented by the yellow symbols.

In the Durov diagram (Figure 11) the samples were grouped according to similar milli-equivalents. In group 1 the background borehole including BH11, BH9 and BH13 are found; these waters are $Na-Ca-HCO_3$ which represent relatively fresh recharged waters. In group 2 the impact monitoring boreholes are found (BH6, BH7, BH8 and BH10), these waters are more mineralised than group 1 and can be regarded as been affected by anthropogenic activities. The major anions in the waters are Cl, SO_4, NO_3 and to lesser extent HCO_3. Group 3 has a signature significantly different from the norm, the source and plume monitoring boreholes (BH2, BH3, BH4, BH5, Boer1 and Boer2) are represented in this group. The major anion in this group is NO_3. Even though the dominant anion in BH1 is Cl it may be grouped together with group 1 as the groundwater chemistry differs from the background group. BH1 is likely to be affected by a different contaminant source than represented by BH2 and BH3.

It can be seen that the geochemistry of all the on-site boreholes (BH1, BH2, BH3) and plume monitoring boreholes (BH4, BH5, Boer1 and Boer2) have been influenced by contaminants. Borehole BH6 appears to be slightly affected (elevated SO_4 and EC when compared to background borehole), BH7 and BH8 are impacted and relatively similar in nature. BH9

located below Dam1 has a similar signature to the background borehole (BH Background) although it contains certain elevated fertilizer related contaminants (especially NO_3); together with BH10 the boreholes have been affected by the secondary off-site source.

Table 14: Water types and ionic strengths of the water samples

Sample no.	Sampling Date	Water Type	Ionic Strength
			mol/kg
BH1	2004/11/01	Na-Cl	0.0405812
BH1	2005/11/01	Na-Ca-Cl	0.0494613
BH1	2007/01/07	Na-Ca-Cl	0.0538872
BH1	2008/01/08	Na-Ca-Cl	0.0507476
BH1	2008/07/15	Na-Ca-Cl	0.0523615
BH1	2009/04/29	Na-Ca-Cl	0.0623576
Boer1	2008/04/17	Ca-Na-Mg-NO3	0.132902
Boer1	2008/07/15	Ca-Na-Mg-NO3	0.15636
Boer1	2009/04/29	Ca-Na-Mg-NO3	0.139323
Boer2	2008/04/17	Ca-Na-Mg-NO3	0.124085
Boer2	2008/07/15	Ca-Na-NO3	0.149622
Boer2	2009/04/29	Ca-Na-Mg-NO3	0.125995
BH2	2004/11/01	Ca-Na-Cl-NO3	0.0799872
BH2	2005/11/01	Ca-Na-NO3	0.167908
BH2	2007/01/07	Ca-Na-NO3	0.153177
BH2	2008/01/08	Ca-Na-NO3	0.0908264
BH2	2008/07/15	Ca-Na-NO3	0.128101
BH2	2009/04/29	Ca-Na-NO3	0.103435
BH3	2004/11/01	Ca-Na-Mg-NO3	0.124985
BH3	2005/11/01	Ca-Na-Mg-NO3	0.17406
BH3	2007/01/07	Ca-Na-Mg-NO3	0.181797
BH3	2008/01/08	Ca-Na-Mg-NO3	0.141871
BH3	2008/07/15	Ca-Na-Mg-NO3	0.130922
BH3	2009/04/29	Ca-Mg-Na-NO3	0.157917
BH4	2008/04/17	Ca-Na-NO3	0.0984132
BH4	2008/07/15	Ca-Na-NO3	0.119404
BH4	2009/04/29	Ca-Na-NO3	0.0926853
BH5	2008/07/15	Ca-Na-NO3-Cl	0.0878898
BH5	2009/04/29	Na-Ca-NO3-Cl	0.0858585
BH6	2008/07/15	Na-Ca-SO4-HCO3-Cl	0.0241171
BH6	2009/04/29	Na-Ca-SO4-HCO3-Cl	0.0264878
BH7	2008/07/15	Na-Cl-HCO3-SO4-NO3	0.0176436
BH7	2009/04/29	Na-Ca-NO3-Cl	0.0334419
BH8	2008/07/15	Na-Ca-SO4-Cl-NO3	0.0196381
BH8	2009/04/29	Na-Ca-HCO3-Cl-SO4	8.15E-03
BH9	2008/07/15	Ca-Na-HCO3	0.0177163
BH9	2009/04/29	Ca-Na-HCO3	0.0165877
BH10	2008/07/15	Ca-Na-Mg-NO3-Cl	0.0188373
BH10	2009/04/29	Ca-Na-Mg-NO3-HCO3-Cl	0.0162553
BH11	2009/04/29	Na-Ca-HCO3	8.42E-03
BH13	2009/04/29	Na-Ca-HCO3	7.12E-03
BH Background	2008/04/18	Na-Ca-Mg-HCO3	9.39E-03
BH Background	2009/04/29	Na-Ca-HCO3	8.21E-03
SW4	2008/07/15	NH4-K-NO3-Cl-SO4	1.70188
SW6	2008/07/15	Na-Ca-HCO3-SO4	0.0280635
SW6	2009/04/29	Na-Ca-HCO3	0.0257679
DAM1	2008/07/15	Ca-Na-Mg-HCO3-SO4	4.78E-03
DAM1	2009/04/29	Ca-Na-Mg-HCO3-SO4-Cl	5.24E-03
DAM2	2008/07/15	Ca-Mg-HCO3-SO4-Cl	0.0086652
DAM2	2009/04/29	Ca-Mg-HCO3-SO4	5.83E-03
SW1	2008/07/15	Na-HCO3-SO4	0.102848
Minimum			0.0048
Maximum			1.7
Range (Max-Min)			1.7
Arithmetic Mean			0.105
Ionic strenght <0.02 (geogenic groundwater)			
Ionic strenght >0.02 and <0.7			
Ionic strenght >0.7 (estimated IS of sea water)			

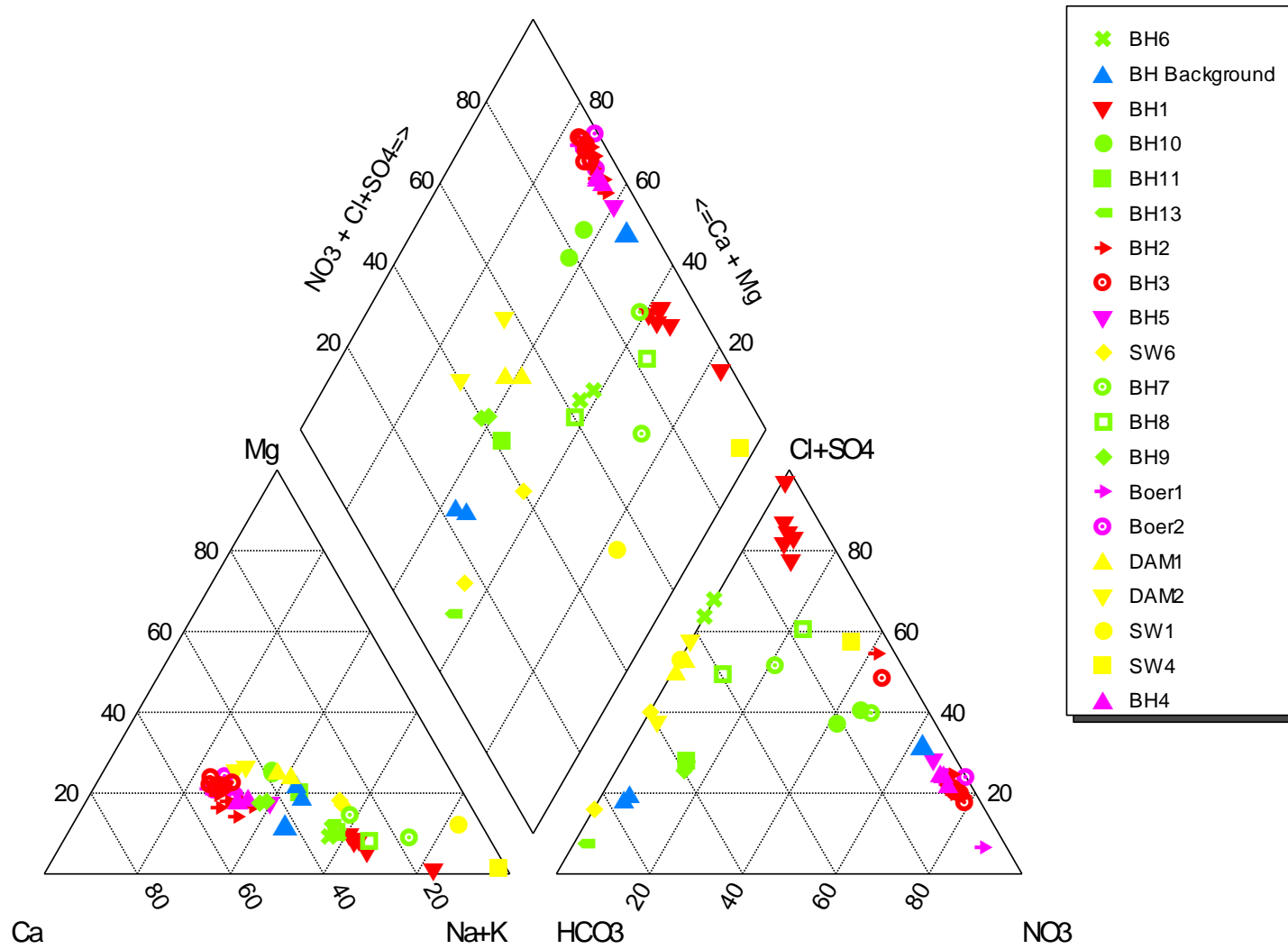Reactive transport modelling of fertilizer waste in a dual porosity aquifer

Figure 10: Piper diagram of water samples

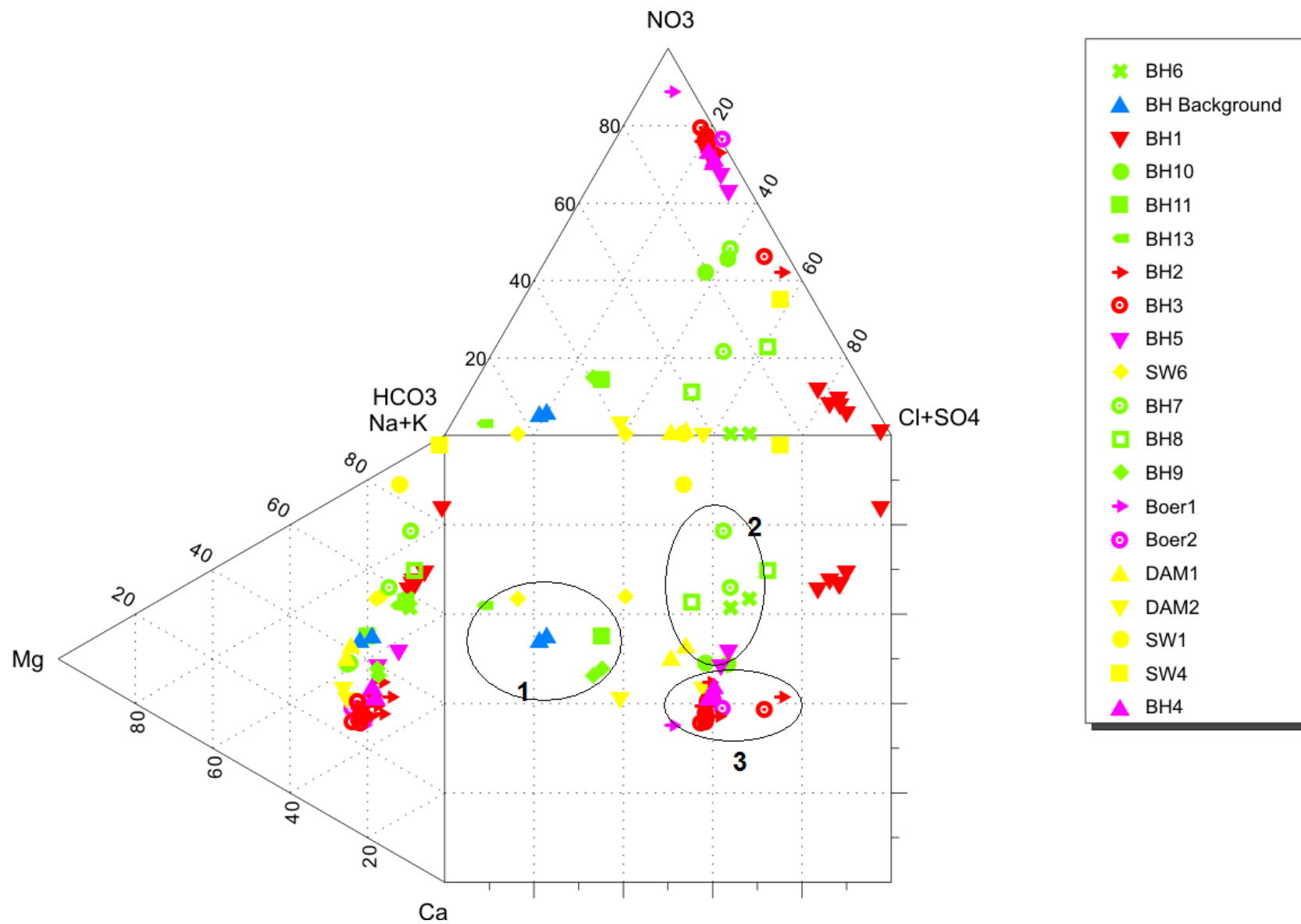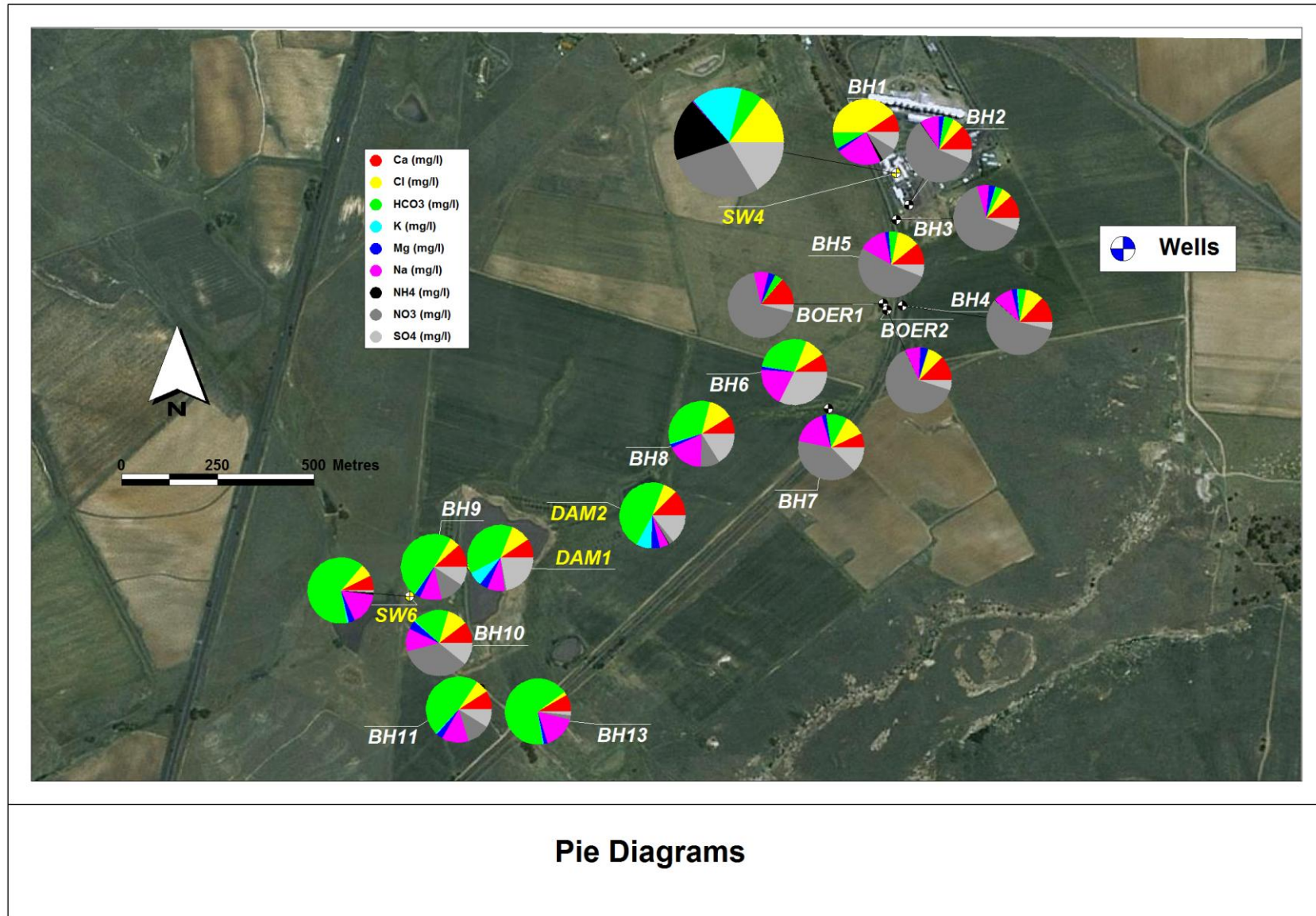Reactive transport modelling of fertilizer waste in a dual porosity aquifer

Figure 11: Durov Diagram of water samples

Pie Diagrams
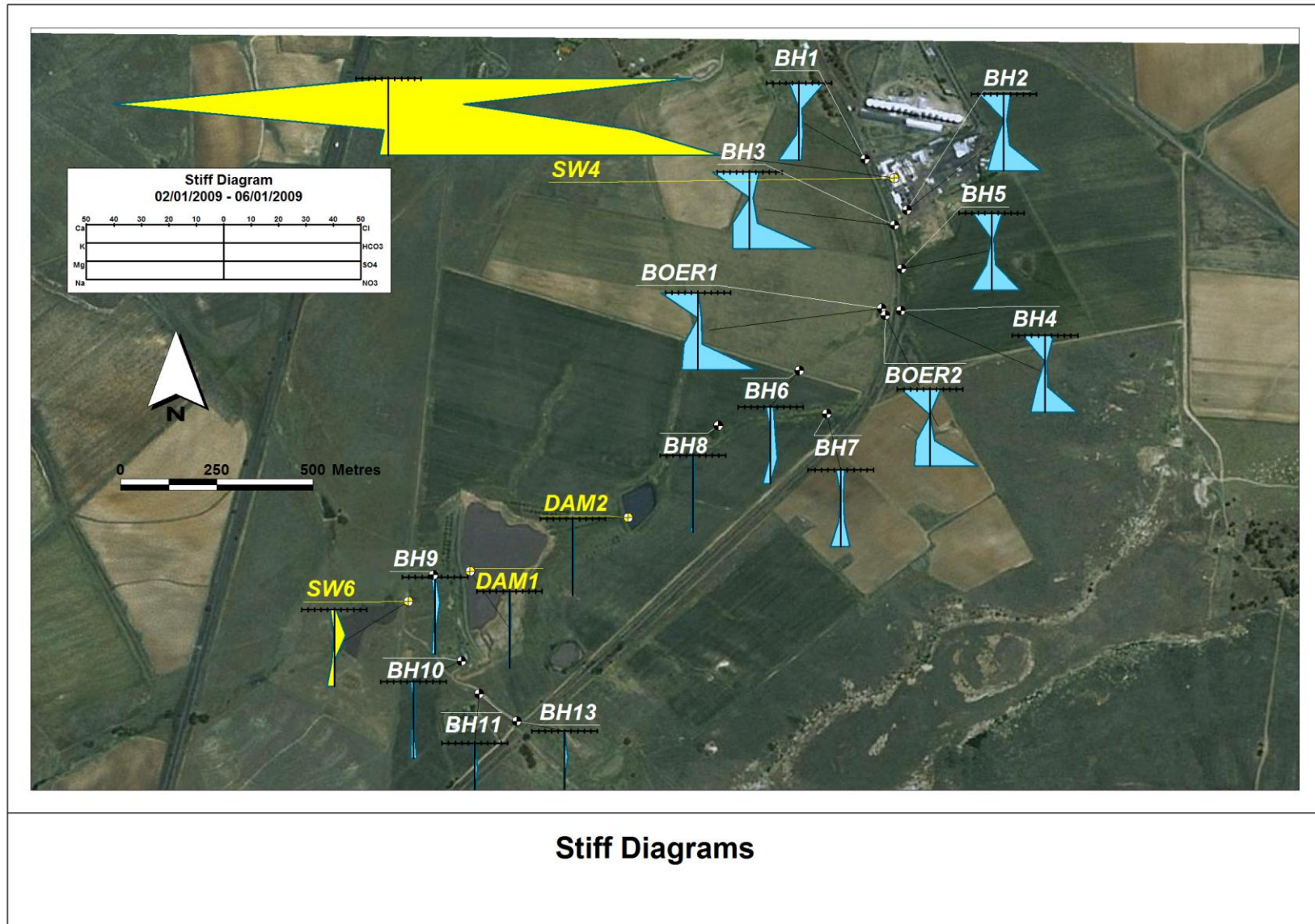
Figure 12: Pie diagram of Groundwater chemistry

Figure 13: Stiff diagrams of the groundwater chemistry

6 DISCUSSION OF GEOCHEMISTRY

6.1 IMPACTS

6.1.1 Groundwater

The chemistry results indicate that all the sampled boreholes downstream of the site are likely to be affected by contaminants emanating from the site (Figure 12 and Figure 13). Boreholes BH1 to BH5 and boreholes Boer1 and Boer2 have been negatively impacted (exceeds maximum allowable limit) by the fertilizer contamination; the geochemistry of these boreholes are similar in nature. Furthermore the boreholes downstream of these boreholes also show signs of been impacted. BH6 contains elevated Cl, SO_4, NH_4, EC, TDS, Na and Ca when compared to the background water quality, although none of the constituents found in this borehole exceed their maximum allowable concentration for drinking water. Similar to BH6, boreholes BH7 and BH8 also contain elevated Cl, SO_4, EC, TDS, Na. However, NO_3 concentrations in these boreholes exceed allowable concentrations. Borehole BH9 found below Dam1 near the boundary fence of the game camp, has a signature similar to the background geochemistry, however Ca, Na, SO_4, NO_3 are found in levels above the background, with NO_3 exceeding the maximum allowable limit. BH10, below the Dam1 to the south, contains elevated Ca, Na, Cl, SO_4 and NO_3 concentrations with NO_3 found in unacceptable levels. Mn and Fe are found in elevated concentrations in most of the boreholes.

6.1.2 Surface water

The samples taken from Dam1 and Dam2 are similar in nature with NH_4 being the only constituent exceeding the allowable limit for drinking water. These samples were taken at surface and may not be representative of the water quality at the bottom of the dams.

SW1 taken below Dam1 is most likely to be seepage from the dam, contains elevated Mg, Na, NH_4, Cl, SO_4, Fe, Mn, TDS and EC; most of these constituents exceed the drinking water limit. The solute load of SW1 may be high due to evaporation. It may also be possible for stratification to take place in the dams caused by temperature and density differences in the water body, resulting in the contamination (mineralised water) to sink to the bottom resulting in the type of seepage represented by SW1.

SW6 was taken at the inlet of Dam3 (the first immediate downstream surface water receptor below the game camp); elevated Ca, Na, Mn, Fe, Cl, SO_4, TDS and EC levels were identified, similar to SW1. However none of these constituents exceed the limit for drinking water. The sample taken at the time of the investigation does not indicate that a negative impact was made. It may be likely that down stream surface water bodies may be affected by contaminants during a flood event.

Water sample SW4 taken from a drainage channel at the liquid fertilizer loading area, is highly mineralised, with most constituent found in unacceptable levels, elevated K, Mn, F, Cl SO_4, NO_3 NH_4 ,EC and TDS concentrations were found. The purpose of this sample was to identify the geochemical signature of the standing water which may potentially seep into the subsurface and reach the groundwater table.

6.2   TEMPORAL TREND ANALYSIS

Only the onsite (source) boreholes (BH1, BH2 and BH3) have historic data for which temporal trend analysis can be done, as illustrated in Figure 14 to Figure 16. Due to the absence of historical data of the boreholes found off-site, trends can not be established with confidence as data only available from 2008, nevertheless certain deductions were made.

The Ca and Na concentrations in BH1, BH5 and BH7 show a slight increasing trend, while a slight decreasing trend can be seen in BH2, BH3, BH4, BH6, Boer1 and Boer2 (Figure 14). The minor changes in concentrations of Ca and Na in the boreholes do not indicate any significant change in the groundwater chemistry.

NO_3 in BH3 and BH7 is increasing while the level in BH1, BH9 and BH10 remained constant. Boreholes BH2, BH4, Boer1 and Boer2 showed a decrease in NO_3 levels since July 2008 (Figure 15). The EC concentrations in the boreholes follow the same trend as the NO_3 levels.

SO_4 levels are on the rise in the three on-site (source) boreholes (BH1, BH2 and BH3), as well as in boreholes BH6, BH5 and BH7. In BH2 and BH3, Cl has a shown a fluctuating trend since 2004. BH1 is the borehole containing the highest concentration of Cl, the levels show an upward trend with some minor fluctuations. Cl has decreased in most of the boreholes except BH7 where a slight increase in visible.

The trends can be interpreted as follows: The contaminant levels in the on-site boreholes are likely to fluctuate as contaminants enter (leach) to the subsurface from the product handling

facilities, therefore the source is likely to change depending on the quantity and chemical nature of the leachate reaching the groundwater. The seepage from the handling facilities transports a number of constituents used at the specific time, as a result the chemical composition and solute load of the leachate is likely to vary from time to time. Therefore the reason for the fluctuations seen in the BH2 and BH3 may be the result of change in leachate composition or fluctuating water table and not necessarily a reduction of the quantity of leachate entering the subsurface. The migration of the contaminant plume contributes to the fluctuations observed in some of the boreholes.

Time Series
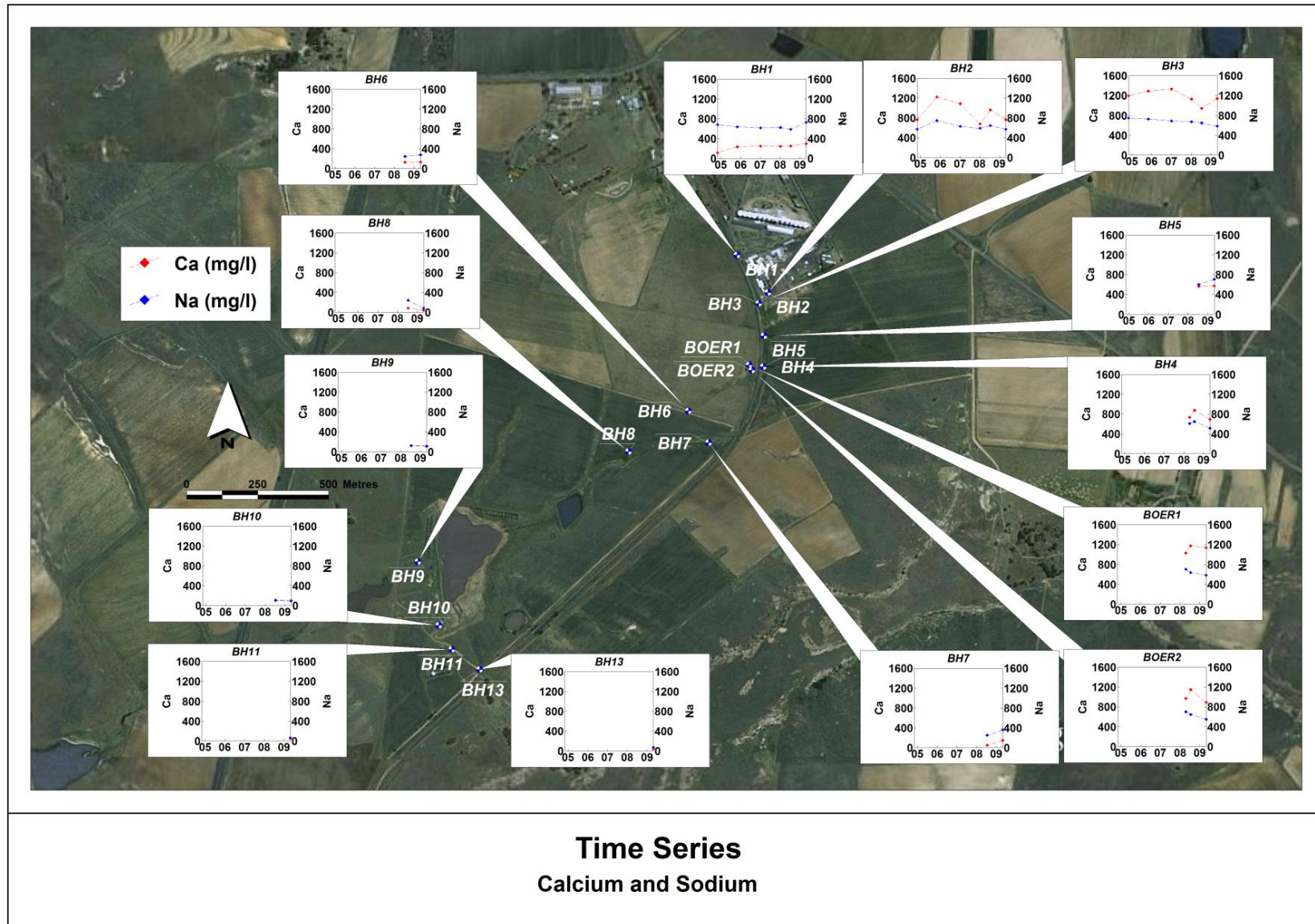
Calcium and Sodium

Figure 14: Calcium and sodium time history of boreholes
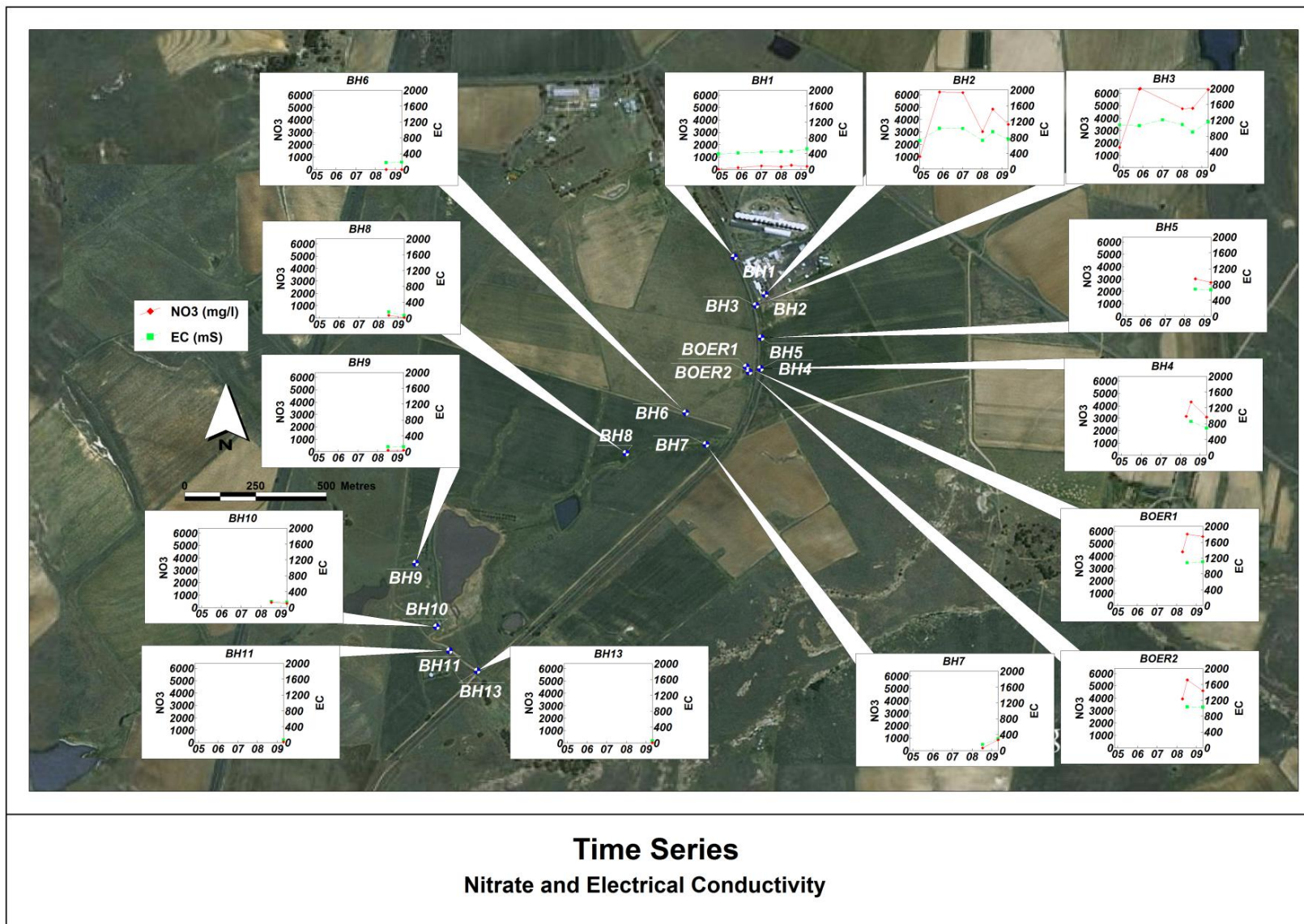
Figure 15: Nitrate and electrical conductivity time history of boreholes

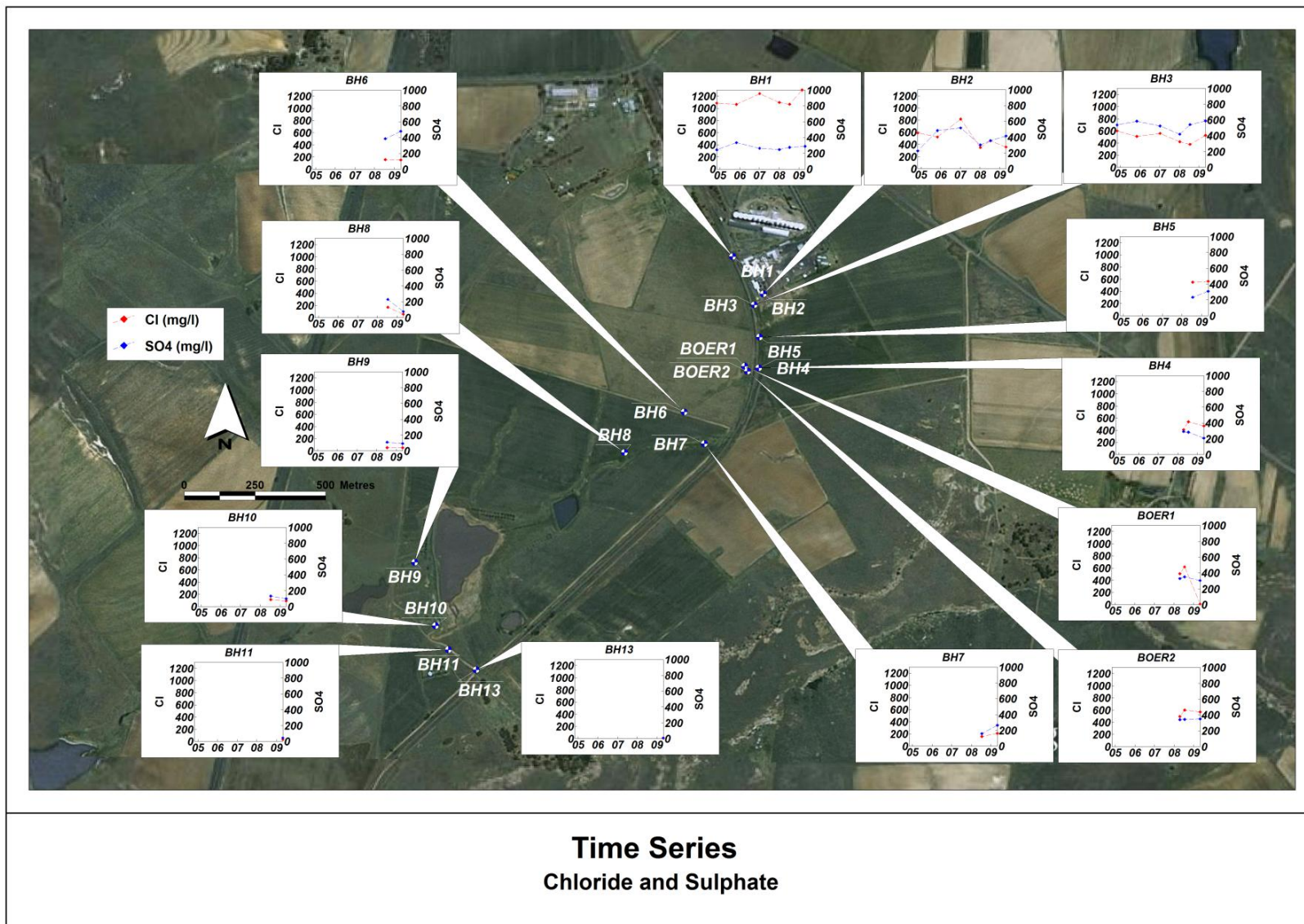**Time Series**
Chloride and Sulphate

Figure 16: Chloride and sulphate time history of on-site boreholes

6.3   SPATIAL TREND ANALYSIS

The contamination emanating from the site appears to be migrating towards the south west, emulating the topography. Boreholes BH1 to BH5 and Boer1 and Boer2 are boreholes which are impacted by the groundwater plume sourced from the site. The nitrate plume front appears to be between Boer1, Boer2 and the newly drilled borehole BH6. The boreholes BH9 and BH10 have been affected by contaminants emanating from the secondary off-site source.

Groundwater reaches the surface near the artesian boreholes (piezometric surface above the ground level) Boer1, Boer2 and BH4. As a result the seepage from this area contributes to surface flow. In other words, the groundwater contaminant plume reaches the surface from where it may possibly contaminate surface water or actually flow along natural drainage downstream. In addition to this, direct surface run-off from site also contributes to surface water pollution, and may even be responsible for the majority of pollution. The contaminated surface water may act as secondary source and leach into the subsurface, contaminating groundwater, evident from elevated NO_3 level in BH7 and BH8

7   HEALTH RISK ASSESSMENT

From the chemistry analysis of the water emanating from the workings of the plant; calcium, magnesium, sodium, manganese, iron, nitrate, ammonium, sulphate and chloride were the chemical substances found not to comply with SANS 241 drinking water standard. Surface water SW4 which is non-compliant did not form part of the assessment as it was found on-site and most likely to be eventually assimilated by the production process. SW1 was also not included into the assessment. A summary of the health risks posed by the reported elevated (none compliant) concentrations of the relevant elements are presented in Table 15 and Table 16. The health risks for both humans (DWAF a, 1996) and livestock (DWAF b, 1996) were obtained from the DWAF water quality guidelines. It can be seen that certain human and animal health effects are likely to occur when the groundwater and/or surface water exceeding the drinking water standards is ingested.

As the contaminated groundwater decants to surface near boreholes Boer1, Boer2 and BH4, it is likely that this water would also have a negative affect if ingested by humans or animals. Nitrates (NO_3) and ammonium appear to be the constituents which would most likely have a negative effect on human and animal health.

Table 15. Summary of the human health risks posed by the relevant constituents

Elevated element	In boreholes/surface water	Human Health effects at current concentrations (DWAF a, 1996)
Magnesium	BH2, BH3, BH4, BH5, Boer1, Boer2	Water aesthetically unacceptable due to a bitter taste and may cause diarrhoea if ingested.
Calcium	BH2, BH3, BH4, BH5, Boer1, Boer2	No known adverse health effects.
Sodium	BH1, BH2, BH3, BH4, BH5, Boer1, Boer2, SW1	Water will have a very salty taste. There is a likelihood of nausea and vomiting and the water is highly undesirable for infants or persons on a sodium restricted diet.
Manganese	BH4, SW6	Extreme staining, likely to be aesthetically unacceptable to a large proportion of users. No health effects
Iron	BH7, BH8, BH10, Boer2	Pronounced aesthetic effects (taste) along with problems with plumbing. Slight health effects expected in young children, and sensitive individuals
Nitrate/Nitrite	BH1, BH2, BH3, BH4, BH5, BH7, BH9, BH10 Boer1, Boer2.	Water does pose a definite health risk, especially in infants causing methaemoglobinaemia, also known as the blue baby syndrome. Nitrate is converted to nitrite in the body. The latter combines with the oxygen-carrying red blood pigment, haemoglobin, to form methaemoglobin, which is incapable of carrying oxygen (DWAF, 1996). Occurrence of mucous membrane irritation in adults.
Ammonium	BH2, BH3, Boer2, SW6	Danger of formation of nitrite. Likelihood of fish deaths in aquaria.
Sulphate	BH2, BH3, BH6	Definite salty and bitter taste. Diarrhoea in most sensitive individuals.
Chloride	BH1	Water will have an unacceptable salty taste and nausea and disturbances of the electrolyte balance may occur.

Table 16: Summary of the animal health risks posed by the relevant constituents

Elevated constituent	In boreholes/surface water	Livestock Health effects at current concentrations
Magnesium	BH1, BH2, BH3, BH4, BH5,BH6, BH7, BH8, BH9, BH10, BH11, BH13, Boer1, Boer2, BH Background, DAM1, DAM2, SW6	No adverse effects
Calcium	BH3, Boer1	Adverse chronic effects such as hypercalcemia and adverse palatability may occur, but it is unlikely if stock have adapted to the water
Sodium	BH1, BH2, BH3, BH4, BH5,BH6, BH7, BH8, BH9, BH10, BH11, BH13, Boer1, Boer2, BH Background, DAM1, DAM2, SW6	No adverse effects
Manganese	BH1, BH2, BH3, BH4, BH5,BH6, BH7, BH8, BH9, BH10, BH11, BH13, Boer1, Boer2, BH Background, DAM1, DAM2, SW6	No adverse effects
Iron	BH1, BH2, BH3, BH4, BH5,BH6, BH7, BH8, BH9, BH10, BH11, BH13, Boer1, Boer2, BH Background, DAM1, DAM2, SW6	No adverse effects
Nitrate	BH2, BH3, BH4, BH5, BH7, Boer1, Boer2	Adverse chronic effects such as restlessness, frequent urination, dyspnoea, Cyanosis and decreased feed and water intake. Acute effects such as severe gastroenteritis in non-ruminants and acute methaemoglobinemia in ruminants (severe dyspnoea and cyanosis).
Sulphate	BH1, BH2, BH3, BH4, BH5,BH6, BH7, BH8, BH9, BH10, BH11, BH13, Boer1, Boer2, BH Background, DAM1, DAM2, SW6	No adverse effects
TDS	BH1, BH2, BH3, BH4, BH5, Boer1, Boer2	Reluctance to drink water which may lead to decline in intake and eventual decline in production.

8   GROUNDWATER MONITORING SYSTEM

The groundwater sampling positions are seen in Figure 7. A groundwater monitoring system has to adhere to the following criteria and the system is developed accordingly.

8.1   GROUNDWATER MONITORING NETWORK

8.1.1   Source, plume, impact and background monitoring

A groundwater monitoring network (see Table 17) should contain monitoring positions which can assess the groundwater status at certain areas viz:

- **Source monitoring** – monitoring boreholes are placed close to or in the source of contamination to evaluate the impact thereof on the groundwater chemistry. ***BH1, BH2 and BH3 comply with this requirement.***
- **Plume monitoring** – monitoring boreholes are placed in the primary groundwater plume's migration path to evaluate the migration rates and chemical changes along the pathway. ***BH4, BH5, Boer1, Boer2 comply with requirement***
- **Impact monitoring** – monitoring of possible impacts of contaminated groundwater on sensitive ecosystems or other receptors. These monitoring points are also installed as early warning systems for contamination break-through at areas of concern. ***BH6, BH7, BH8, BH9, BH10, BH11 and BH13 comply with this requirement.***
- **Background monitoring** – background groundwater quality is essential to evaluate the impact of a specific action/pollution source on the groundwater chemistry. ***BH Background complies with this requirement.***

8.1.2   System response monitoring network

Groundwater levels – the response of water levels to rainfall events are monitored for accurate calculation of recharge to the groundwater regime. Static water levels are also used to determine the flow direction and hydraulic gradient within an aquifer. Where possible all of the above mentioned borehole's water levels need to be recorded during each monitoring event.

8.1.3   Monitoring frequency

A monitoring frequency of at least twice a year is a proposed. Monitoring needs to take place before and after the wet season, i.e. during September/October and April.

It is important to note that a groundwater-monitoring network should also be dynamic. This means that the network should be extended over time to accommodate the migration of contaminants through the aquifer as well as the expansion of infrastructure and/or addition of possible pollution sources.

8.1.4   Inadequacies in the monitoring network

The current monitoring network was implemented in July 2008, before this date only BH1, BH2 and BH3 was monitored. The western and south eastern extent of the contaminant plume is currently unknown, therefore additional monitoring wells should be incorporated into the monitoring network.

8.1.5   Surface water monitoring network

The surface water monitoring network was implemented in July 2008, the sampling positions are illustrated in Figure 9. The current status of the surface water monitoring positions can be seen in Table 18. The surface water bodies Dam1 and Dam2 form part of the network. Monitoring points are also positioned in the surface drainage feature between the plant and Dam2, these points may be dry and are dependant on surface water flow. A monitoring point SW4 is positioned at the loading bay on-site, and is likely to represent water infiltrating the subsurface on-site. SW6 is taken at the inlet of Dam3 and represents the quality of water leaving the game camp property.

Table 17: Groundwater Monitoring Status

Borehole No:	Description	Monitoring status	Date installed	Date included in monitoring network	Nov-04	Nov-05	Jan-07	Jan-08	Apr-08	Jul-08	Apr-09
BH1	monitoring well	source monitoring	Nov-04	Nov-04	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled
BH2	monitoring well	source monitoring	Nov-04	Nov-04	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled
BH3	monitoring well	source monitoring	Nov-04	Nov-04	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled	Sampled
BH4	borehole not in use	plume monitoring	unknown	Jun-08	-	-	-	-	Sampled	Sampled	Sampled
BH5	monitoring well	plume monitoring	Jul-08	Jul-08	-	-	-	-	-	Sampled	Sampled
BH6	monitoring well	impact monitoring	Jul-08	Jul-08	-	-	-	-	-	Sampled	Sampled
BH7	monitoring well	impact monitoring	Jul-08	Jul-08	-	-	-	-	-	Sampled	Sampled
BH8	monitoring well	impact monitoring	Jul-08	Jul-08	-	-	-	-	-	Sampled	Sampled
BH9	borehole not in use	impact monitoring	unknown	Jul-08	-	-	-	-	-	Sampled	Sampled
BH10	borehole not in use	impact monitoring	unknown	Jul-08	-	-	-	-	-	Sampled	Sampled
BH11	Windmill	impact monitoring	unknown	Jul-08	-	-	-	-	-	Not sampled	Sampled
BH13	borehole with submersible	impact monitoring	unknown	Jul-08	-	-	-	-	-	Not sampled	Sampled
BOER 1	borehole not in use	plume monitoring	unknown	Jul-08	-	-	-	-	Sampled	Sampled	Sampled
BOER 2	borehole not in use	plume monitoring	unknown	Jul-08	-	-	-	-	Sampled	Sampled	Sampled
BH Background	borehole with submersible	background monitoring	unknown	Jul-08	-	-	-	-	Sampled	Sampled	Sampled

Table 18: Surface water monitoring positions

Surface water positions	Description	Jul-08	Apr-09
DAM1	Earth dam(used for process water)	Sampled	Sampled
DAM2	Earth dam	Sampled	Sampled
SW1	Seepage below DAM1	Sampled	Not sampled dry
SW2	Seepage near BOER1	Not sampled	Not sampled dry
SW3	Surface water drainage below culvert	Not sampled	Not sampled dry
SW4	Wash water on hard standing	Sampled	Not sampled
SW5	Seepage near DAM3	Not sampled	Not sampled
SW6	Surface water exiting property	Sampled	Sampled

9 CONCEPTUAL MODEL

The conceptual model has been developed by taking a number of processes into consideration; the validity of the factors may be substantiated by the numerical modelling.

9.1 GROUNDWATER FLOW

The geophysical survey did not identify any major geological structures such as dykes and vertical/sub vertical fractures in the area as indicated in Figure 6. Groundwater flow and contaminant transport is therefore not likely to be affected by any major vertical/sub vertical geological features in the area. Horizontal and bedding plan fractures are however likely to be present. A simplified conceptual model can be seen in Figure 17.

The soil profiling conducted across most of the study area showed that the soil horizons have a high clay content and vary in thickness across the area of interest (ranging from 0.15-2.4 m thick). Given the high clay content of soil horizons, cracking (fissures) is prevalent under dry conditions (desiccation). The permeability of the soil horizons can therefore be regarded as limited, however under dry conditions secondary permeability is induced and flow in the horizon may increase; until the soil expands and fissures are closed. Underlying the soil forms; brittle and shattered highly weathered mudstone is found. The clay (dominated by montmorillonite) content of this weathered horizon is also high in certain areas and likely to form minor preferential flow paths under dry conditions. The weathered mudstone grades into un-weathered mudstone at depth, competent mudstone (bedrock) is found at depths ranging from 0.95 to 2.4 mbgl. Furthermore it was found that the depth to competent bedrock is shallower at the plant area than in the lower lying areas, as expected given its location on a hill crest. The geological profiles inferred from the geological logs show that the mudstone is underlain by sandstone. The sandstone was encountered on average at 10-12 mbgl.

The soil and weathered horizon is likely to act as an aquitard (confining layers). The mudstone is likely to act as a secondary aquifer where flow and storage is governed by fractures in the rock. The matrix of the mudstone is not likely to contribute significantly to storage. The sandstone acts as secondary porosity aquifer where flow and storage is governed by the fractures and the matrix, the sandstone layer is likely to be semi-confined.

Seepage was observed in the core holes during the soil profiling exercise, especially on site around the plant and production area and the natural drainage feature near the artesian wells. All the other core holes drilled off-site were dry. The maximum depth reached by the

geoprobe during profiling was 2.4 mbgl. due to refusal. The groundwater levels on site range from 3.5-4 mbgl. It can therefore be said that a water table mound was present in and around the plant area and absent in the rest of the study area. The water table mounding formed due to seepage from the process area consequently created a head resulting in flow towards the groundwater table below the plant. The source (on-site) monitoring boreholes are not located in the inferred source areas but on the periphery; may partly explain why the potential mounding of the water table is not discernable in the water levels of these boreholes. The borehole construction of these boreholes is the other likely explanation (cased through weathered horizon and therefore not representative of the shallow aquifer zone).

A response in water levels of BH4, BH3 and Boer2 was observed during the short aquifer test conducted on Boer1. It can therefore be deduced that these boreholes are connected by a fracture system. BH5 was not drilled yet at the time of the test. The observations made during drilling and aquifer testing show that a groundwater yielding fracture system is found at ~18-20 m bgl in the sandstone.

Groundwater recharge is likely to occur laterally and vertically, vertical recharge through infiltration is likely to be higher in the higher lying areas where aquitard layers are less developed than in the lower lying areas. The shallow groundwater levels found down gradient in the vicinity of the artesian wells BH4, Boer1, Boer2 and BH9 can be attributed to a seepage interface of the groundwater table with surface and not as a result of any geological structure. This area in which the boreholes are found is a natural drainage feature. Groundwater therefore reaches the surface and may contribute to the base flow of the catchment (especially in proximity to BH9) depending on seasonality.
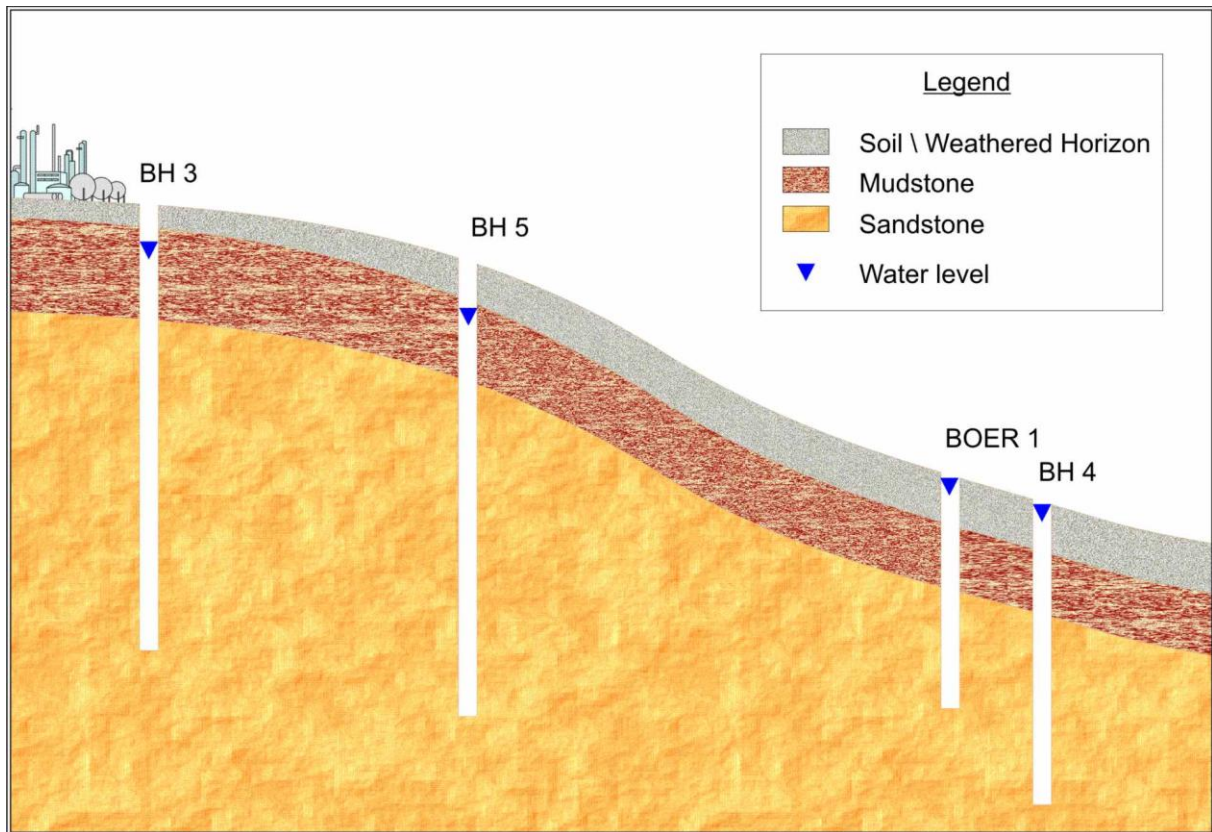
Figure 17: Simplified conceptual model

9.2 CONTAMINANT TRANSPORT

The contaminants which enter the subsurface below the site move through the soil horizon where various sorption, ion exchange and retardation reactions are likely to take place. Generally, clayey soils (montmorillonite) have high cation exchange capacities (CEC) as a result cation exchange partly takes place before the seepage reached the fractured bedrock. The contaminants are most likely transported by seepage water from surface (leaking sump, mineralised water infiltrating through concrete etc.) towards the groundwater table (as observed). The potassium ions which leach are largely accommodated in the clay layer structure, furthermore the phosphates are also sorbed onto the clay particles. As a result of this process relative low or absent potassium and phosphate levels are found in the groundwater.

The contaminants are partly retarded by the weathered soil horizon, it can therefore be said that the thicker the retarding horizon, the less vulnerable the aquifer is to contamination. If the plant area (which sources the majority of contaminated seepage) was underlain homogenously by the soil horizon with the high clay content, then vertical flow and

contaminant transport through the horizon is to occur at such a low rate, that large scale contamination (as found) would not be likely.

However given the presence of disturbed soil below the plant; the relative thin soil horizon (clay layer), the presence of subsurface source areas (sump depth is 1.5 mbgl.) it can be said that the vulnerability of the aquifer below the plant area is high when compared to the lower lying part of area of interest. Therefore it is likely that vertical flow and contaminant transport through a compromised clay layer and brittle mudstone is possible. The occurrence and quality of seepage in the soil profile holes at the plant in contrast to the absence of seepage in the holes found off-site substantiates the presence of contaminated leachate in the soil/weathered horizon. The contaminants are therefore likely to migrate through the subsurface towards the water table.

The contaminants enter the groundwater in solution and are transported mainly through advective forces (in mudstone and sandstone fractures) and mainly by dispersion and diffusion in the sandstone matrix. The contaminants are transported through the aquitard/aquifer medium along fractures and pores in the aquifer. Advective forces (horizontal movement) dominate once the contaminants reach a fracture. The contaminants follow and migrate along the groundwater flow direction.

A connected fracture system was identified during the aquifer test and exists between the site (source borehole BH3) and the plume boreholes Boer1, Boer2 and BH4. The implication of the connectivity is important as the geochemical signature of the on-site boreholes (BH2 and BH3) and the plume monitoring boreholes (BH4, BH5 Boer1 and Boer2) are very similar.

The geochemical signature of these boreholes indicate that retardation of contaminants between the site and the plume boreholes can at the time of sampling can be regarded as minimal. The most likely reason is the fracture system which connects the boreholes allowing for advective dominant flow and consequent low retardation and chemical reaction potential between the site and the plume boreholes. Furthermore groundwater was abstracted from Boer1 until approximately 2004. This groundwater abstraction from the borehole most likely increases the seepage velocity, decreasing the potential for retardation (ion exchange, reduction-oxidation reactions and sorption) of contaminants.

As previously mentioned, the groundwater seeps to surface (under wet seasonal conditions) near BH4, Boer1, and Boer2, therefore the contaminants also reach the surface. The contaminated groundwater reaching the surface is therefore likely to flow along the surface

drainage line. The volume of groundwater seeping is likely to be influenced by the height of piezometric surface, which is likely to be seasonal (winter low, summer high). This contaminated water is expected to impact on any surface water bodies (Dam1 and Dam2) downstream if the flow is sufficient to reach the specific body.

Any storm water run-off emanating from the site also enters the drainage features, which may then transport the potentially contaminated run-off to the surface water bodies. It is speculated that the storm water run-off may have a larger potential impact on the downstream surface water bodies than the seeping contaminated groundwater. Contaminated surface water emanating from the site is also deemed to have a negative impact on the groundwater.

The off-site contaminant source located near BH10 had been removed, the period over whcth this source was present is unknown. Even though the primary off-site source has been removed, the contaminated soil/weathered horizon is likely to continue to act as a secondary source. The concentrations of contaminants in BH9 and BH10 are expected to show a decreasing trend.

10 NUMERICAL MODELLING AND CONTAMINANT TRANSPORT

The aim of this chapter is to assess the modelled hydrogeological impact that the site has on the receiving environment. The model will furthermore be used to validate the conceptual model before predictive modelling is conducted. The current operational stage of the plant will be considered and various scenarios will be simulated.

Numerical groundwater modelling can be considered to be the most reliable method of anticipating and quantifying the likely impacts on the groundwater regime. The model construction will be described in detail in the following paragraph, followed by predicted impacts in terms of groundwater quality and quantity for all the relevant phases. Fetter described modelling as a method "to understand why a system is behaving in a particular observed manner or to predict how it will behave in the future" (Fetter, 2001).

The finite difference numerical model was created using the Processing Modflow (PMWIN) (Chiang, et al., 2001) as Graphical User Interface (GUI) for the well-established MODFLOW (Harbaugh, et al., 1996) and MT3DMS (Zheng, et al., 1999) numerical codes.

MODFLOW is a 3D, cell-centred, finite difference, saturated flow model developed by the United States Geological Survey. MODFLOW can perform both steady state and transient analyses and supports a wide variety of boundary conditions and input options. It was developed by McDonald and Harbaugh of the US Geological Survey in 1984 and has been updated several times since.

MT3DMS is a 3D model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in groundwater systems. MT3DMS uses a modular structure similar to the structure utilized by MODFLOW, and is used in conjunction with MODFLOW in a two-step flow and transport simulation. Heads are computed by MODFLOW during the flow simulation and utilized by MT3DMS as the flow field for the transport portion of the simulation.

The required steps in modelling are as follows:

- *Data collecting and interpreting field data*: Collecting of field data is required to identify the processes and status of the specific area of interest. It is important to follow a thorough quality control/quality assurance program to ensure that collected data can be used with a high level of confidence.
- *Formulation of a site conceptual model:* The site is conceptualised in a manner which simplifies the natural conditions and processes.
- *Computer code and algorithm:* An acceptable computer code should be selected to ensure optimal modelling results and flow model construction.
- *Calibration & model verification:* Model calibration and validation are essential for specific models before any predictions are made. The main aim of calibration is to obtain a degree of correspondence between the model simulation and the groundwater system. Calibration can be performed manually or automatically (by means of inverse modelling). Validation of the model application can be performed by using the parameter values and boundary conditions from a calibrated model to acceptably approximate another set of field measurement. A sensitivity analyses can be conducted on the calibrated model to determine the degree of change if certain parameters are varied
- *Predictive simulations:* Once a model has been calibrated and validated it can be used as a predictive tool to simulate certain scenarios*.*

10.1 FLOW MODEL SET-UP

In this paragraph the setup of the flow model will be discussed in terms of the conceptual model as envisaged for the numerical model, elevation data used, boundaries of the numerical model and assumed initial conditions.

10.1.1 Elevation Data

Elevation data is crucial for developing a credible numerical model, as the groundwater table in its natural state tend to emulate the topography as verified in 5.5. The best currently available elevation data is derived from the SRTM (Shuttle Radar Tomography Mission) DEM (Digital Elevation Model) data. The SRTM consisted of a specially modified radar system that flew onboard the Space Shuttle Endeavour during an 11-day mission in February of 2000, during which elevation data was obtained on a near-global scale to generate the most complete high-resolution digital topographic database of Earth (Farr, 2007). Data is available on a grid of 30 metres in the USA and 90 metres in all other areas. The data points in the study area are shown in Figure 18.

Several studies have been conducted to establish the accuracy of the data, and found that the data is accurate within an absolute error between 2 and 4 metres for Southern Africa (Rodriguez, 2005). Over a small area as in this study, the relative error compared to neighbouring point is expected to be less than one metre. This can be deemed acceptable for the purpose of a numerical groundwater model, especially if compared to other uncertainties.

10.1.2 Boundaries

To simulate the groundwater conditions that occurs at the site, the aquifer as described below has been modelled. Boundaries were chosen to include the area where the groundwater pollution plume could reasonably be expected to migrate and simultaneously be far enough from the site not to affect the local groundwater flow.

Wherever practical, natural topographical water divides are normally used as no-flow boundaries, assuming that the groundwater elevation follows the topography; as a result the boundary west, north and east of the site was classified as a no-flow boundary (Neumann or 2nd type). No-flow (parallel flow) (Neumann or 2nd type) boundaries were represented to the south by a watershed. A 1st type or Dirichlet constant head boundary was defined to the

south west of the modeled area Figure 19: Boundaries of the Numerical Model can be seen in Figure 19.

The site is located ~200m from the nearest boundary (northern upstream boundary), which is considered far enough for the expected groundwater effects not to be influenced by the set boundaries. Initial groundwater levels were derived from Bayes interpolated groundwater levels which uses the relationship between the topography and the measured groundwater levels.

The modelling area was discretizised by a 130 x 130 grid in the x and y direction, resulting in grid cell dimensions of 20m x 20m meters (see Figure 20). All modelled features, like sources, are sizably larger than these dimensions, and the grid is thus adequate for the purpose. The subsurface was modelled in two dimensions (one layer model); the layer thickness is 30m.

10.1.3 Fixed Aquifer Parameters

Although the most relevant aquifer parameters are optimised by the calibration of the model (section 10.2) many parameters have to be calculated and/or judged by conventional means. The following fixed assumptions and input parameters were used for the numerical model of this area:

- Recharge = 0.000055 m/d. The recharge value was estimated in section 4.5 (between the estimated 2.8 and 4%). An estimated recharge of 3% was used for modelling purpose as the well developed clay horizon in the area is perceived to result in a lower recharge. Please note that this is not effective recharge, as evapotranspiration was also modelled as discussed below. The result will thus be high recharge in high topographical areas and lower recharge where the water table is shallow, similar to the conditions in nature.

- Maximum Evapotranspiration = 0.0044 m/d (1606 mm/annum). This value is based on the E-pan evaporation data for this area as discussed in section 3.1. Note that this rate of evapotranspiration is used by the modelling software only if the groundwater should rise to the surface. For the groundwater level between the surface and the extinction depth, the evapotranspiration is calculated proportionally. Below the extinction depth the evapotranspiration is assumed to be zero.

- Evapotranspiration Extinction Depth = 1 m. This depth relates to the expected maximum root depth of plants in this area (grass).

- Horizontal Hydraulic Conductivity of the layer was estimated as 0.74 m/d, this value correlates well with the abbreviated pump test as discussed in section 5.2.
- The effective porosity value of the layer was taken as 0.06. This value could not be determined directly and was taken as estimation of the fractured bedrock.
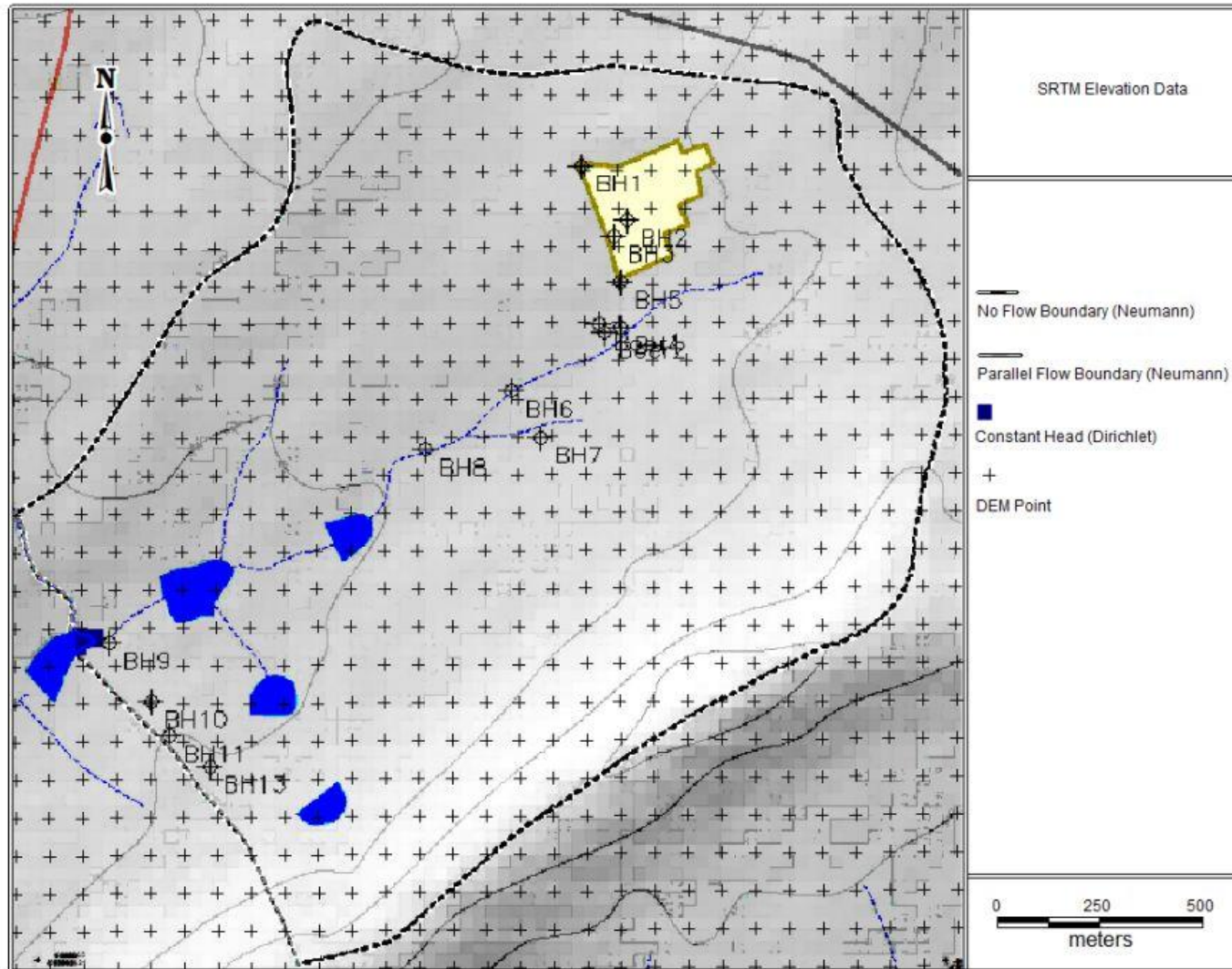
Figure 18: SRTM Elevation Data
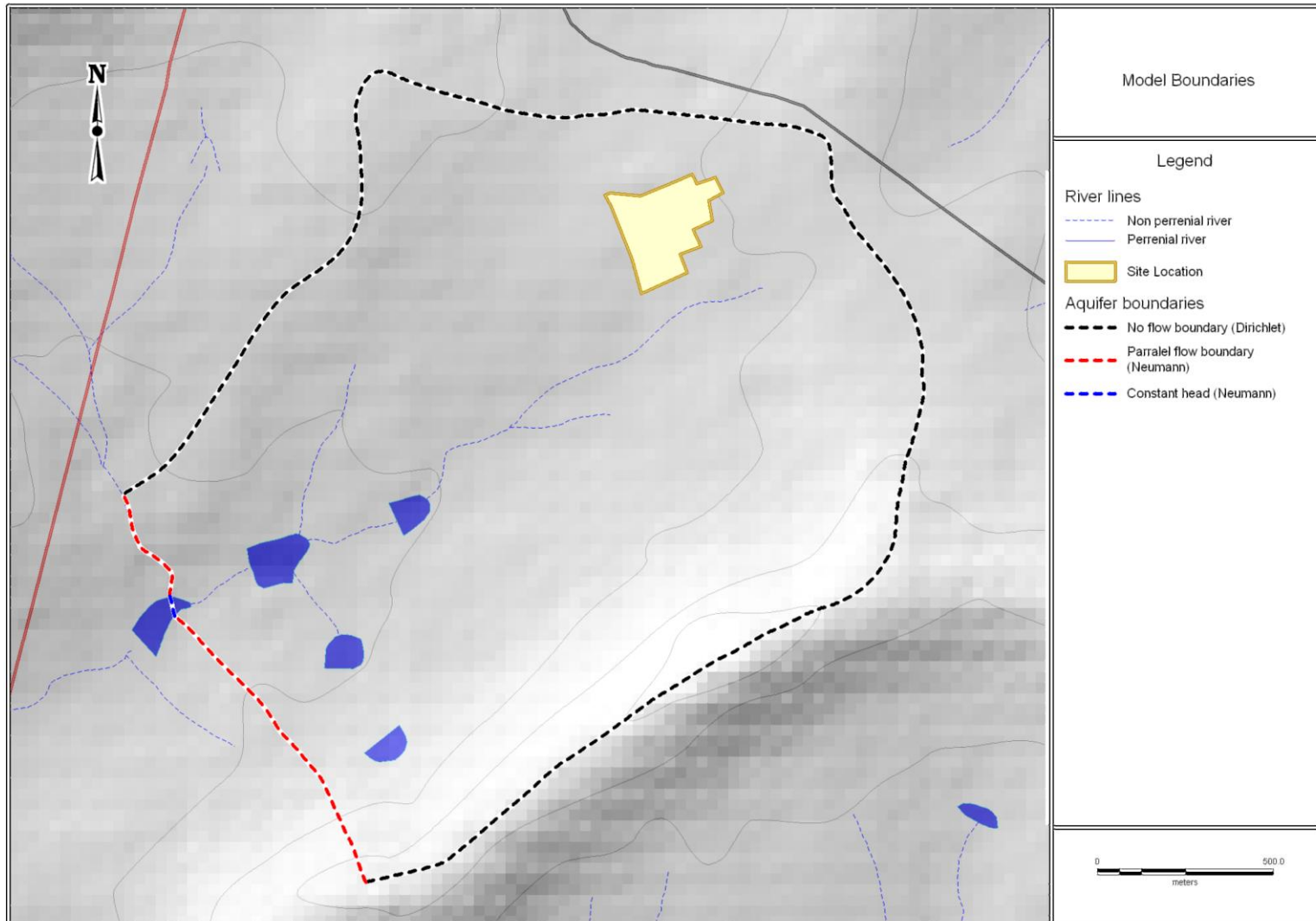
Figure 19: Boundaries of the Numerical Model
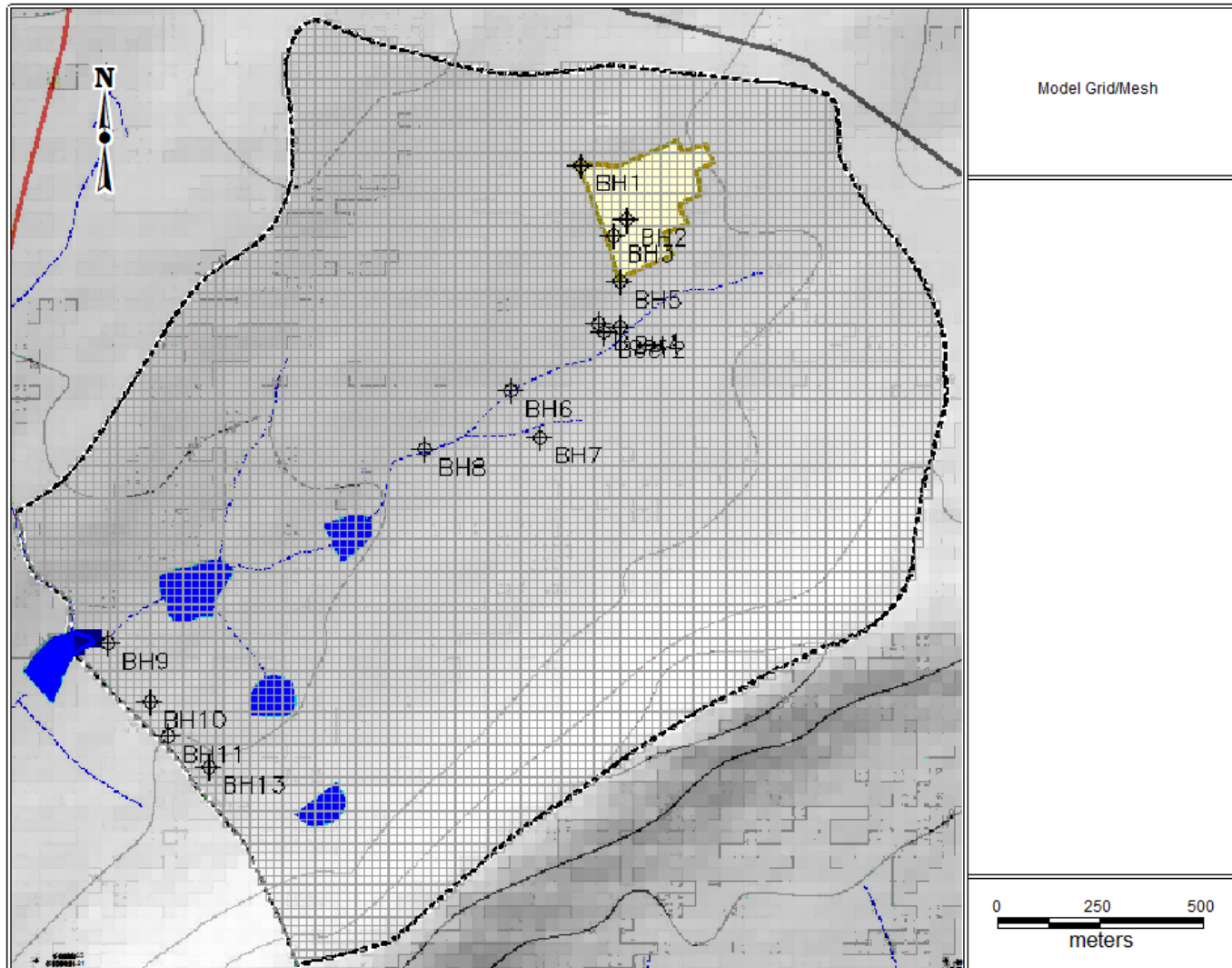
Figure 20: Lateral Delineation of the Modelled Area

10.2 CALIBRATION OF THE MODEL

The depths to groundwater were measured in many boreholes over a large area covering the important sections of the model where the plume could potentially spread to. It thus presented adequate information with which to calibrate the model.

Using this data, a good fit of computed and measured groundwater levels were obtained. A 10% difference (calculated versus observed) of the groundwater level over the modelled area is prescribed in various modelling guidelines as acceptable (Mandle, 2002). In general, the difference between measured and calculated groundwater levels are much less than the 2.5 metre target (a difference of ~25m in groundwater levels was modelled). A 98% correlation was achieved between the modelled and observed heads (Figure 21). Figure 22 below illustrates the comparison of calculated (modelled) and observed heads of the 11 boreholes used to calibrate the steady state conditions.
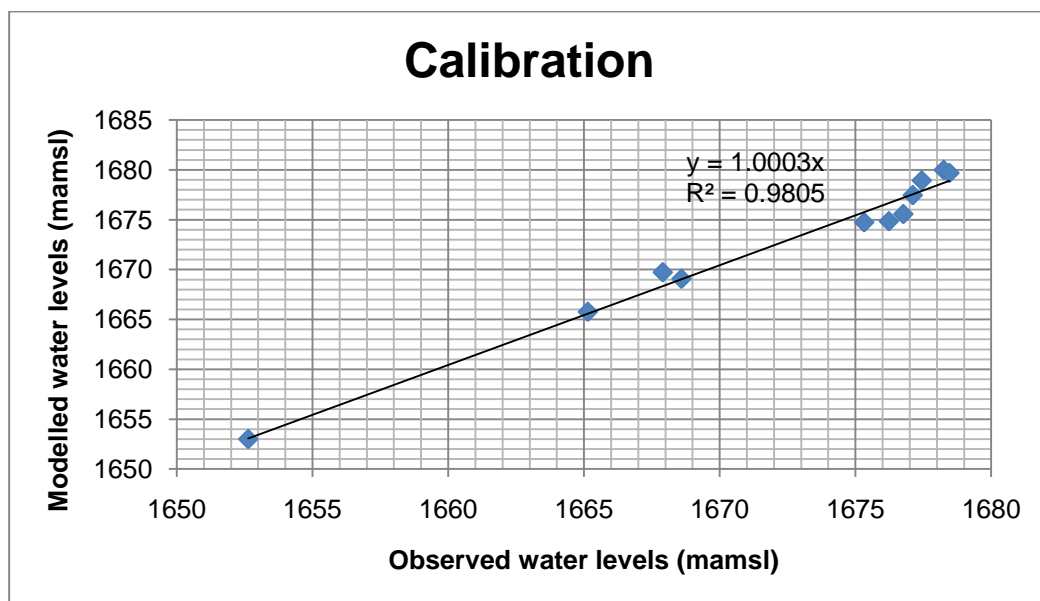
Figure 21: Correlation between modelled and observed heads
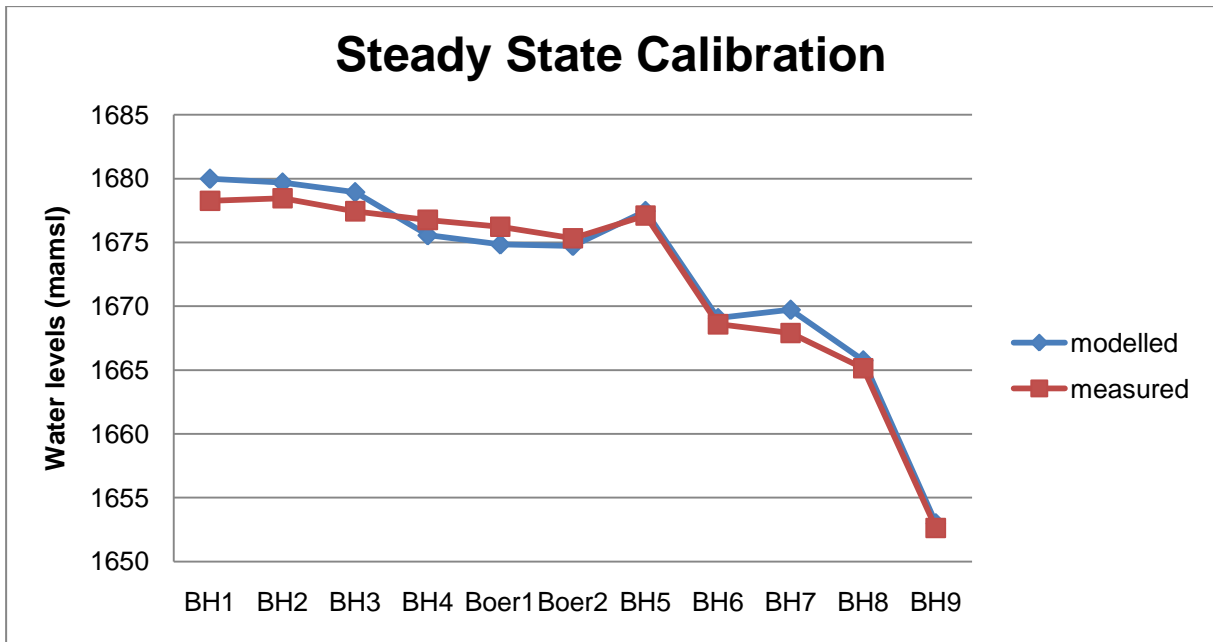
Figure 22: Calibration Graph for the Numerical Model
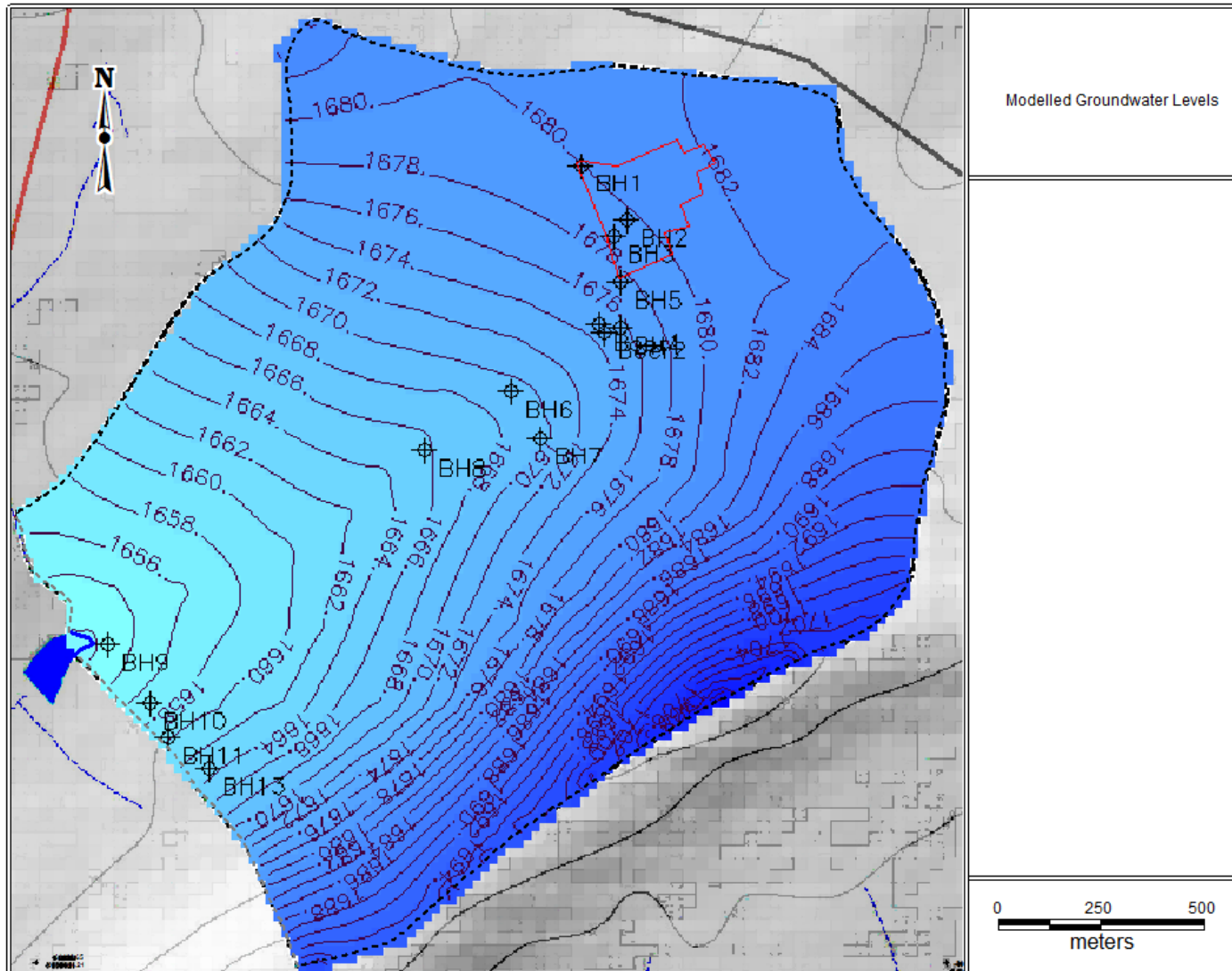
Figure 23: Modelled groundwater levels

10.3 SOLUTE TRANSPORT MODEL

The migration of the contaminant plume was estimated by means of the numerical mass transport model MT3DMS (Zheng, et al., 1999) as described in the introduction to this section. Advection and hydrodynamic dispersion are the two main processes that control contaminant transport through a porous medium. Advection is the lateral flow component, while hydrodynamic dispersion refers to mechanical dispersion and molecular diffusion (Chiang, et al., 2001).

The same input parameters as previously stated for the flow modelling were chosen for the numerical model. In addition, the following assumptions were made for the transport modelling:

- The effective porosity value of the layer was taken as 0.06
- Longitudinal dispersivity was taken as 30 metres. As the inferred primary plume length is 300m.
- The ratio of horizontal transverse dispersivity to longitudinal dispersivity was taken as 0.5 while the effective molecular diffusion coefficient was taken as $0.001m^2/d$.
- Nitrate was considered for solute transport calculations as it is the constituent found in the highest concentrations in the groundwater, and it is inferred to be the main contaminant emanating from the site. Nitrate is also not readily retarded given the current prevailing site conditions
- An initial concentration of 0 mg/l nitrate was assumed for the modelled area, as the natural background levels should approach 0 mg/l nitrate.
- The potential sources were taken as the liquid fertilizer plant, (Figure 4 and Figure 5). The sources areas were calibrated according to the observed contaminant concentrations to approach the best fit.
- The contaminants were introduced into the groundwater through recharge originating from surface. The nitrate was introduced at a concentration of 32000mg/l in the plant area, while the recharge concentration at the secondary (off-site) source was estimated as 18000 mg/l.
- It was assumed that the nitrate will not decay or be retarded while the plume is migrating. This is a worst-case scenario and actual development of the plume will most likely be less.
- The calculated water levels as calibrated were used as hydraulic heads in the mass transport model.

- This methodology was selected to provide worst-case scenario results within the limitations of homogeneous assumptions.

10.4 SCENARIOS USED TO REFINE CONCEPTUAL MODEL

The calibrated model as described above was used to validate the current extent of the groundwater contaminant plume. The following iterative scenarios were simulated:

10.4.1 Current status as modelled

A simulation was run using the initial parameters mentioned above, the scenario was run under steady state conditions for a period of 30 years, (the estimated age of the plant). Therefore the plume in Figure 24 should represent the current status of the contaminant plume if the conceptual model in section 9 is valid. It can be seen that the lateral extent of the plume is well developed as observed. The borehole Boer1, Boer2 and BH4 contain modelled concentrations of 189-427 mg/l compared to the observed 3093mg/l - 5576 mg/l levels. Furthermore BH6 contained NO_3 levels modelled as 54 mg/l while in reality trace levels of NO_3 was found in this borehole. In Figure 25 the correlation between the modelled (initial conditions) and observed nitrate concentrations can be seen, the correlation R^2 is 29%, which can be regarded as poor. It can also be seen that the plume centre of mass is migrating towards the south west. It can therefore be said the current conceptual model is not entirely valid. In order to validate the conceptual model, various potential scenarios will be run to approach the situation found in reality.

10.4.2 Groundwater abstraction of downstream boreholes

It was identified that the boreholes Boer1, Boer2 and BH4 were used in the past as abstraction wells. The volume and duration of abstraction is unknown, it was therefore assumed in this simulation that the boreholes were being pumped for the past 30 years. The pump rate was estimated as 0.3 l/s for 24 hours in Boer1 and BH4. The simulated plume can be seen in Figure 26. Firstly the plume migration appears the be south south-west (as observed). The plume migration has also been retarded beyond the pumped boreholes. The modelled NO_3 levels have increased in borehole Boer1, Boer2 and BH4 to 363-621 mg/l, while the NO_3 level in BH6 is less than 1 mg/l (approaches observed concentrations). Even though the groundwater abstraction scenario from these boreholes have improved the validity of current situation, the relative low modelled NO_3 concentrations in Boer1, Boer2 and BH4 render the conceptual model partly valid.

10.4.3 Surface water as source of contamination.

A storm water / process water management system is not in place at the site, therefore contaminated surface water and/or process water may leave the site especially during the rainy season. This storm water is discharged at the south western part of the site, flow is initially governed by the railway line (located adjacent to the plume boreholes), after which it follows the natural drainage. The surface water was added as a source (32000 mg/l source concentration) in the inferred drainage area (Figure 27). In Figure 28 it can be seen that plume boreholes have shown an increased in NO_3 concentration ranging from 722 to 1018 mg/l, it is however still considerably lower than the observed concentrations (3093 - 5576 mg/l). Various reasons may result in the elevated observed concentrations. Given the underlying fractured aquifer and a fracture connection between the site and plume boreholes, the fracture system is likely to largely account for the NO_3 transport. The influence of the horizontal fractures on the transport of contaminants cannot be modelled with certainty as the spatial location is not known. The concentrations and location of minor sources of contamination is unknown and may have an affect. The recharge may be higher at the source areas (plant).

10.4.4 Increased recharge at loading area and surface water sources

As observed during the drilling of holes into the soil/weathered horizon at the site, seepage water was found in the holes drilled near and around the loading/plant area. It is likely that the surface water leaving the site is also likely to infiltrate along the railway line between the site and the plume boreholes. (BH4, Boer1 and Boer2) (Figure 29). As a result of the observations made the recharge was increased to 10% in these localised areas. The hydraulic conductivity remained the same as initially as no significant changes occurred between the observed and modelled heads due to the slight increase in recharge .

As expected the solute load of the modelled plume increased (Figure 28). A slight over estimation of the on-site NO_3 concentrations were found. The modelled downstream boreholes NO_3 levels ranged from 1103 to 1364 mg/l, while BH6 modelled NO_3 correlated well with the observed levels (<1 mg/l). These under estimated concentrations are likely to be found given the limitations of model (porous homogenous aquifer).

In Figure 31 (no pumping of boreholes), the plume development can be seen if no abstraction took place. The plume has migrated further downstream, with BH6 being

significantly impacted (1304 mg/l NO_3). Concentrations in the plume also appear to be more elevated, however the 'hotspots' may be attributed to artefacts of evapotranspiration.

By assessing both these figures it can be deduced that groundwater abstraction from the boreholes (BH4, Boer1 and Boer2) is likely to have contributed significantly to the NO_3 plume migration in the past.
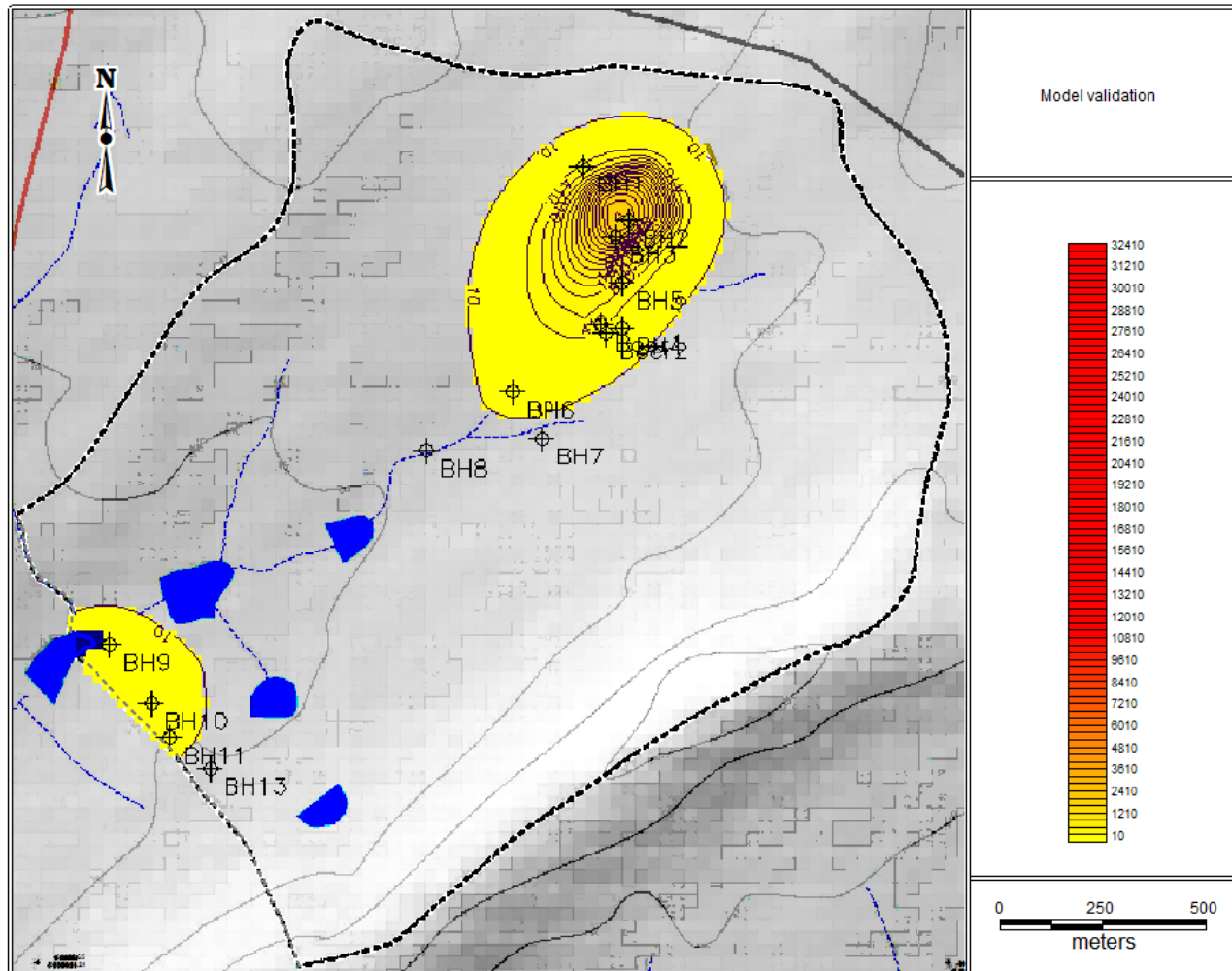
Figure 24: Current status of plume as modelled
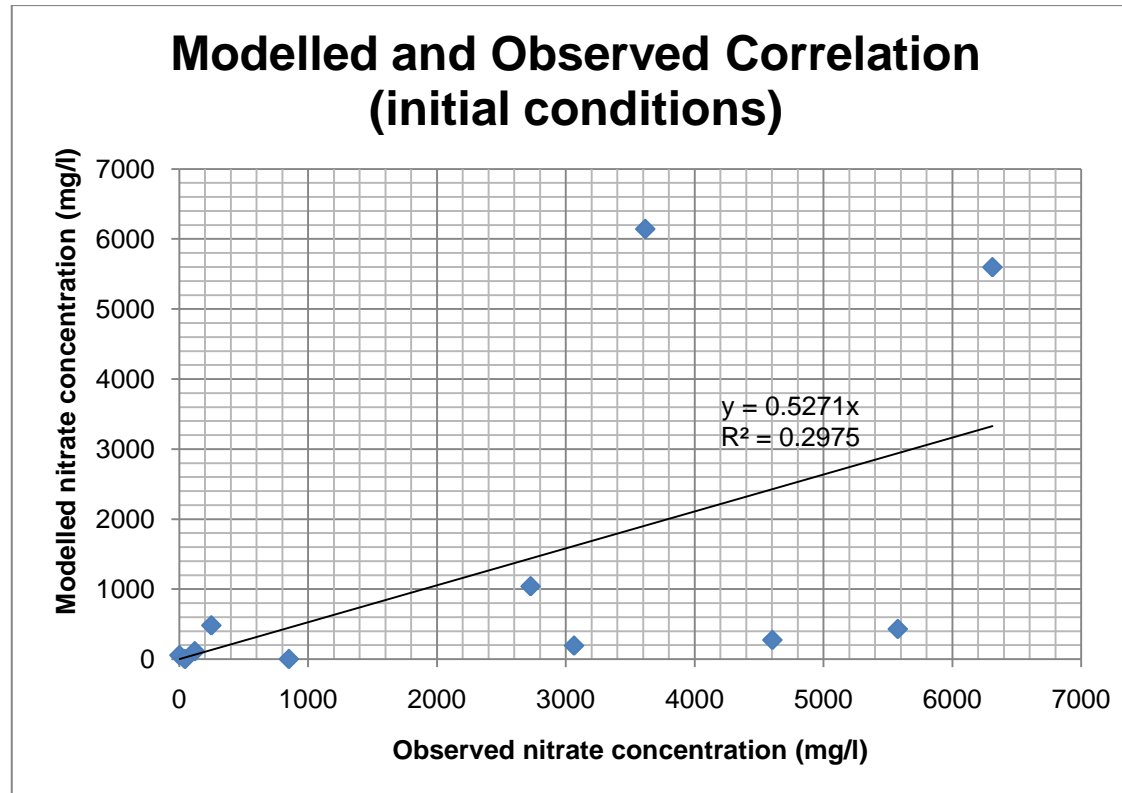
Figure 25: Correlation between modelled and observed nitrate concentrations (initial conceptual model)
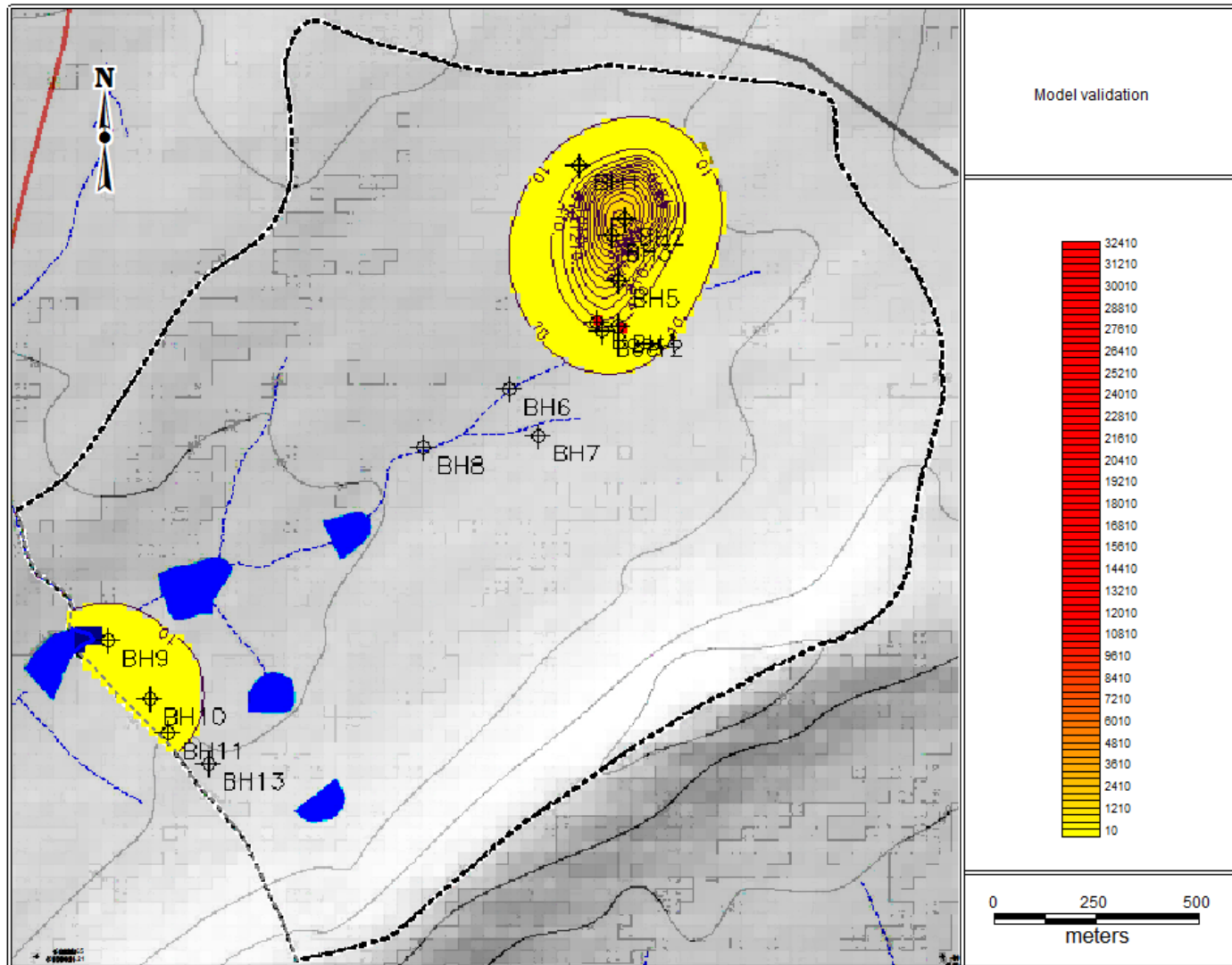
Figure 26: Status of plume assuming abstraction from Boer1 and BH4
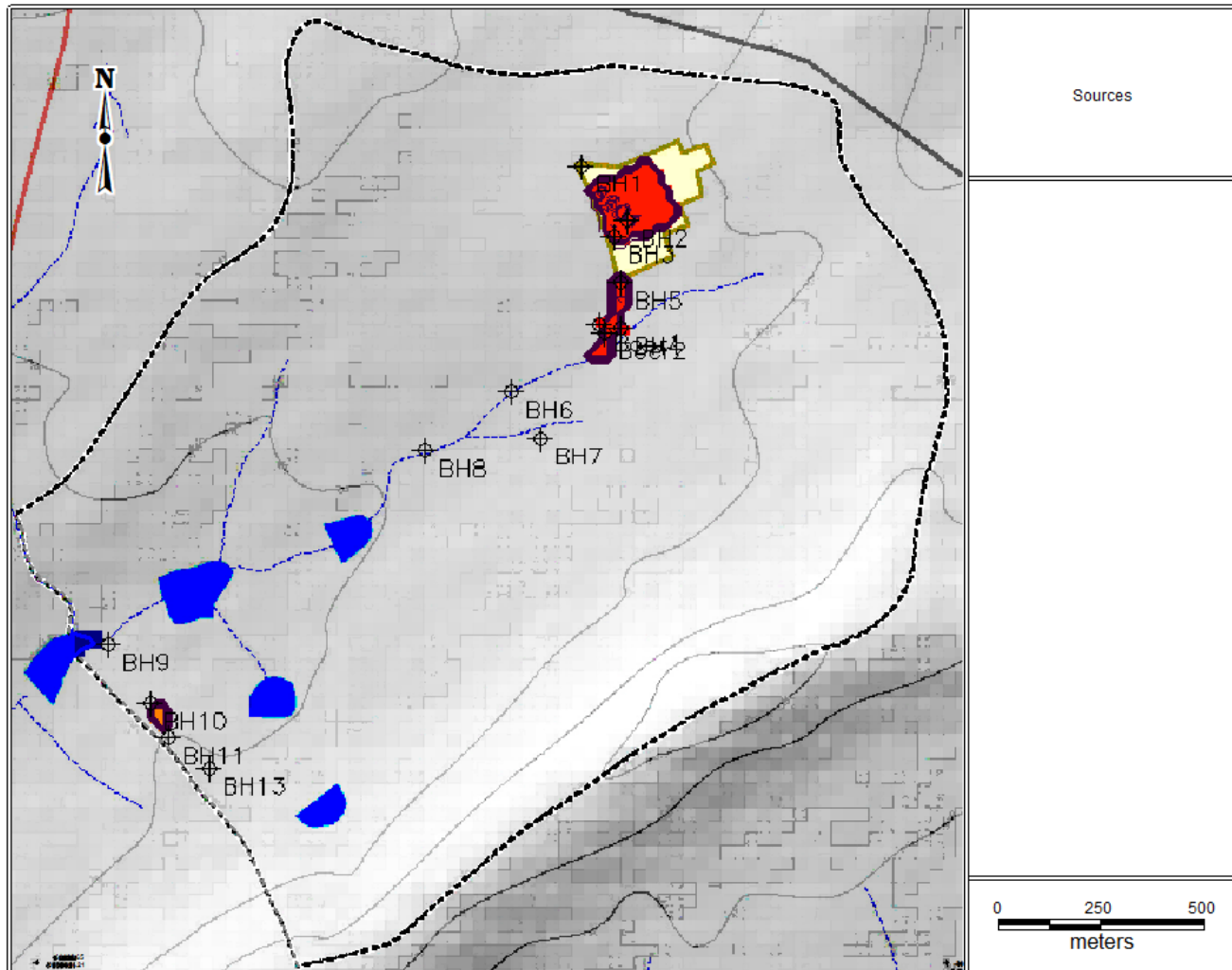
Figure 27: Primary source at plant, surface water and near BH10
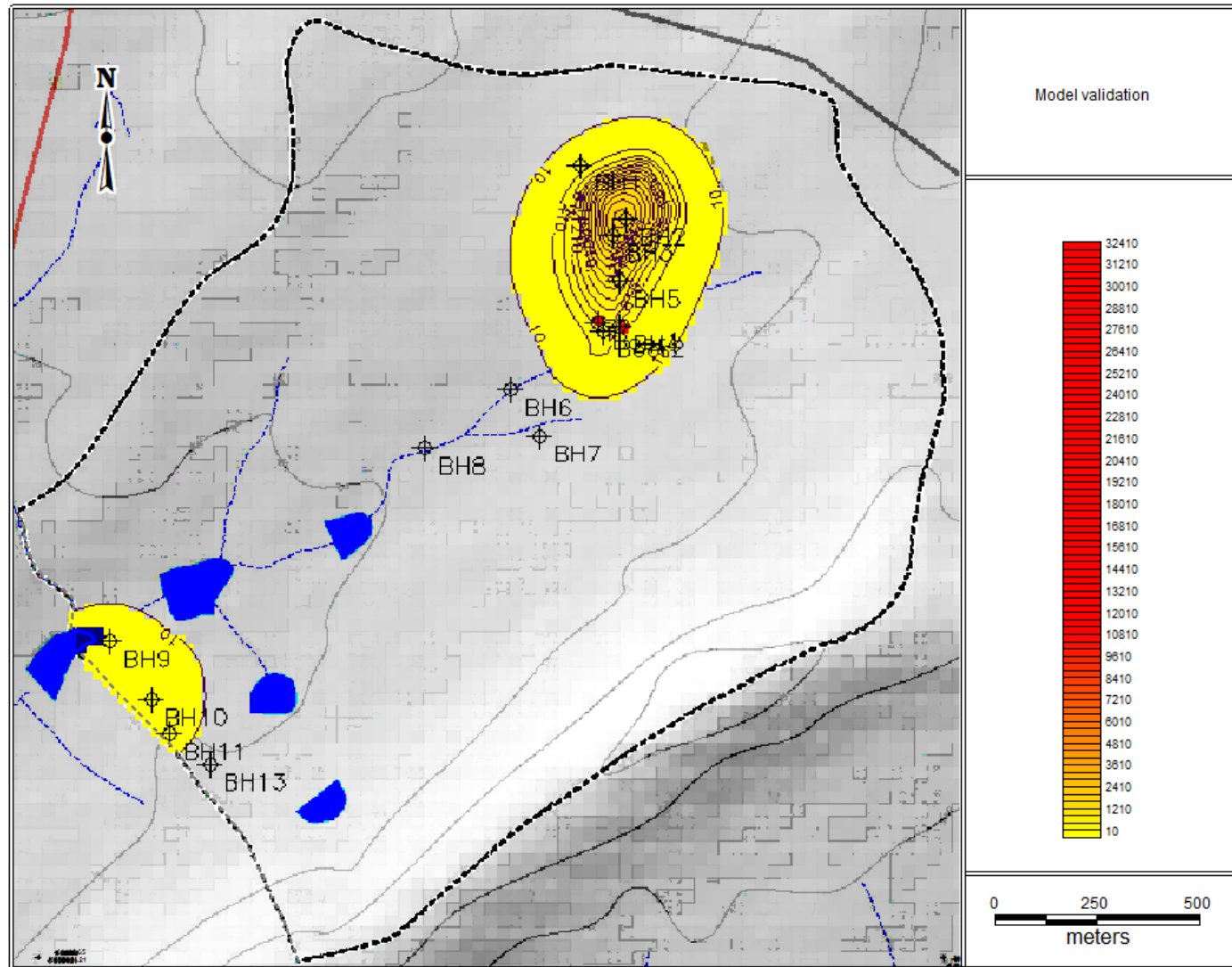
Figure 28: Current status of plume with surface water source and groundwater abstraction.
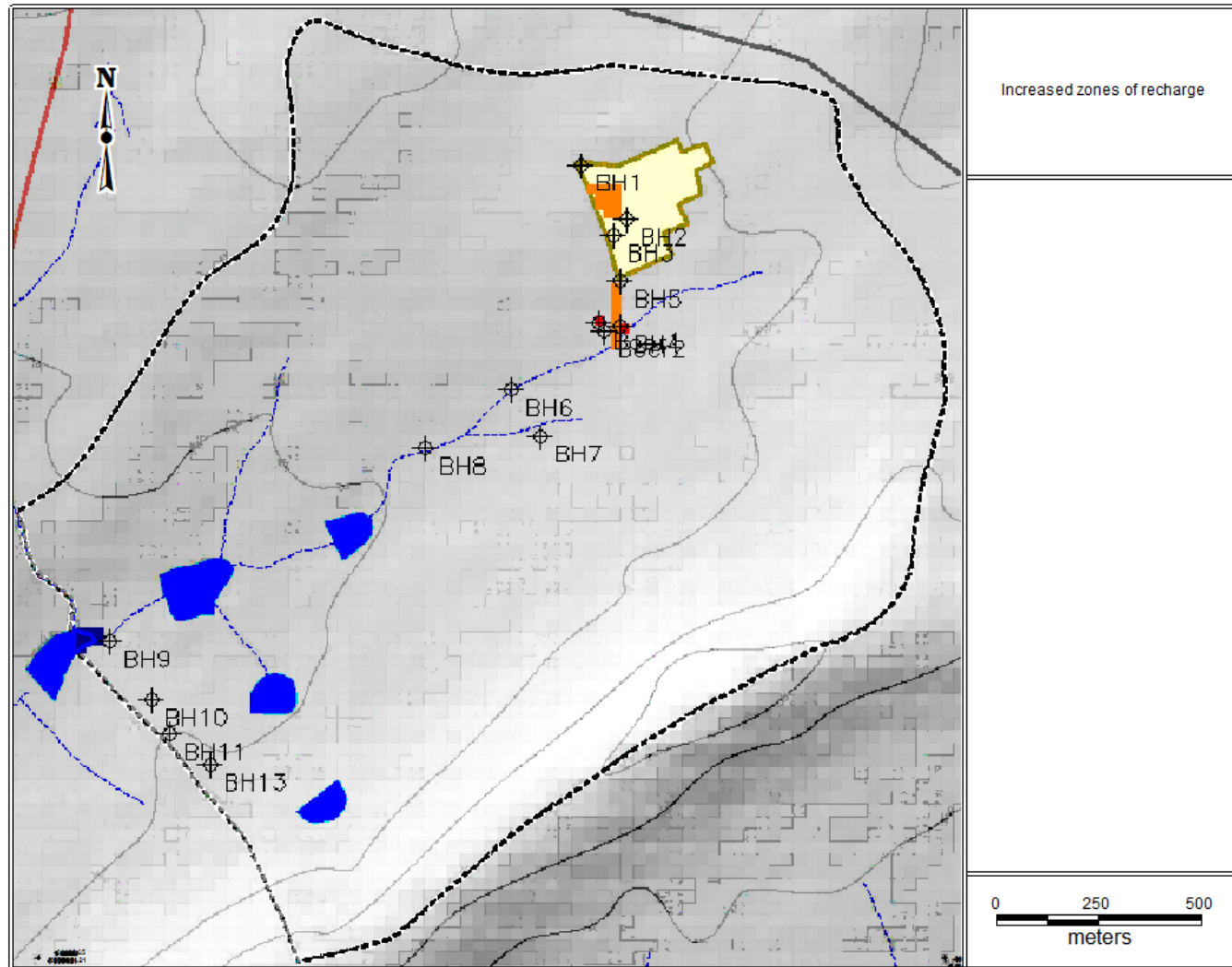
Figure 29: Increased recharge (10%) at loading area and surface water drainage
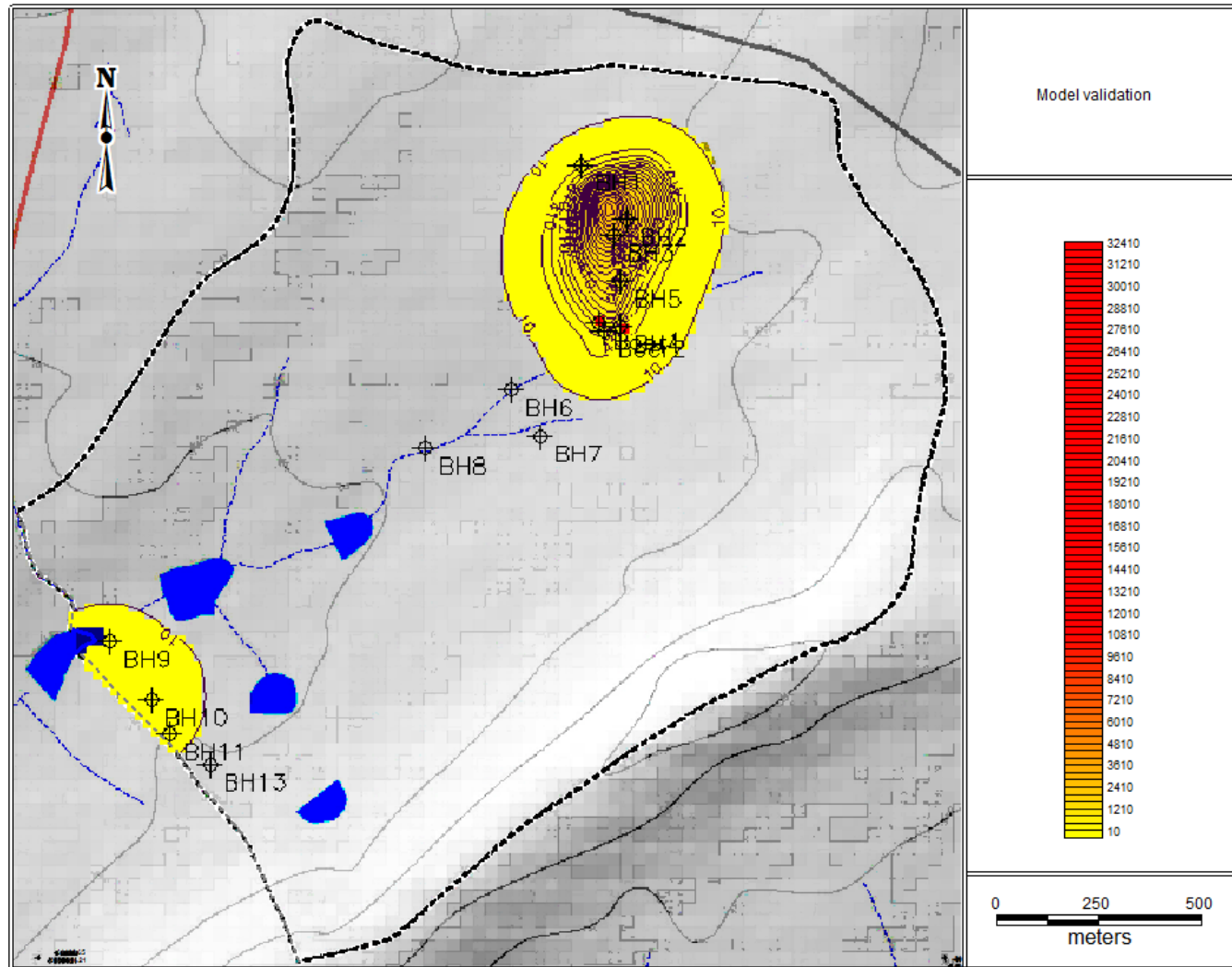
Figure 30: Status of plume assuming 10% recharge at loading area and surface water sources including groundwater abstraction.
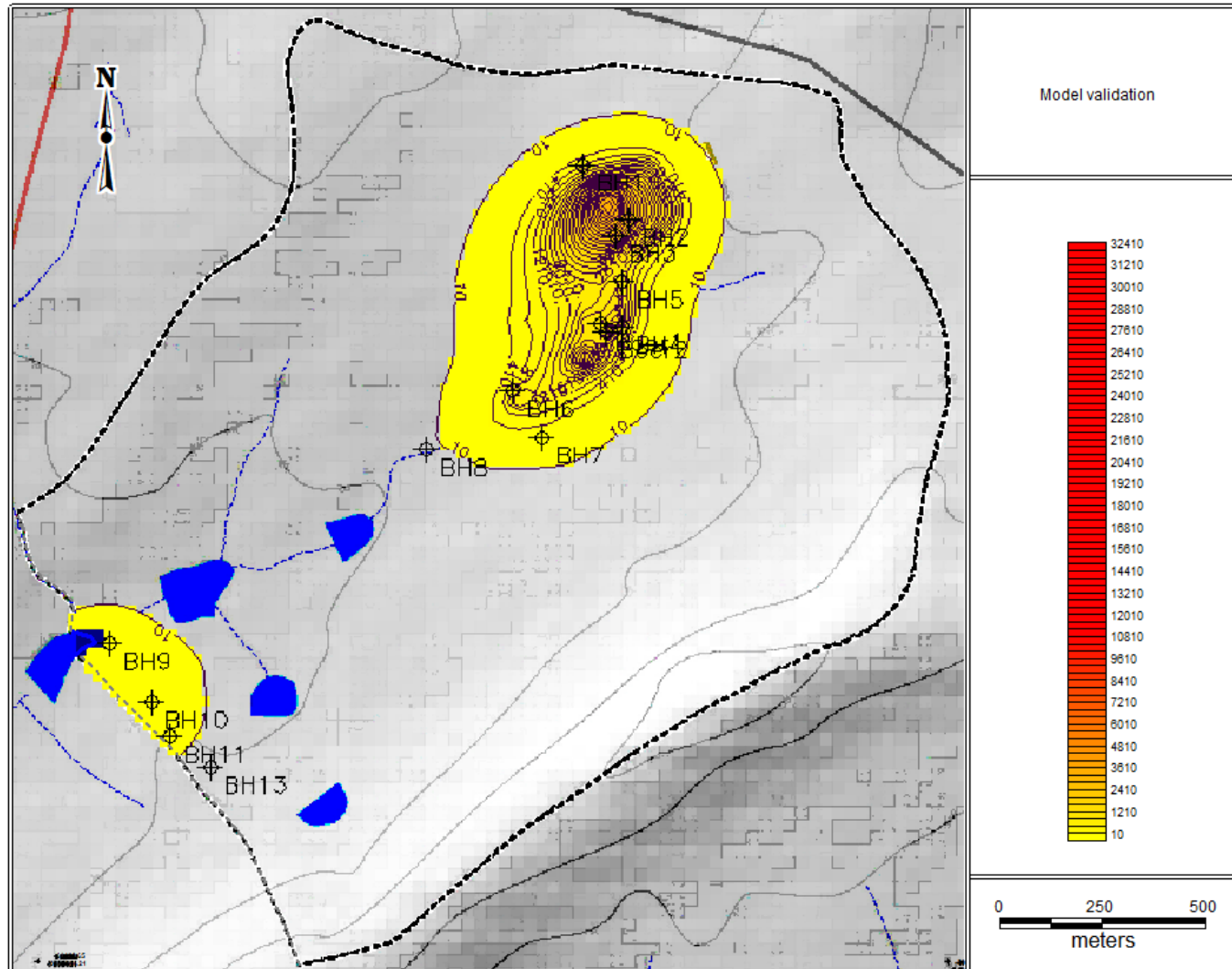
Figure 31: Status of plume assuming 10% recharge at loading area and surface water source, without abstraction

10.5 REFINED CONCEPTUAL MODEL

In addition to the model discussed in section 9, the following comments can be made in order to validate to conceptual model:

- Horizontal and bedding plan fractures are likely to be present and are inferred to play a role in contaminant transport (elevated NO_3 levels in Boer1, Boer2 and BH4), a fracture system was also indentified during the aquifer test. This fracture system was not modelled.

- An increased artificial recharge (seepage and leachate infiltration) is present at the plant area mainly around the loading bay as substantiated by the observations during soil core drilling. The increased recharge in the localised areas did not have a significant effect on the groundwater flow, a 98% correlation was still found between the modelled and calibrated heads.

- The groundwater abstraction from Boer1 and BH4 has influenced the plume movement, furthermore the plume may have been larger if the abstraction did not occur. No major volumes of groundwater was abstracted from the boreholes Boer1, Boer and BH4 in at least the past five years. These boreholes were however perceived to be pumped prior to 2004.

- Surface water contamination contributed to the current plume geometry and therefore partly responsible for the current plume extent.

- A secondary groundwater contaminant found in proximity to BH9 and BH10 was present and substantiated by the modelled NO_3 levels in those boreholes.

- Although an exact solution was not reached and uncertainties are still found, the current conceptual model allows the numerical model to approach reality.

Therefore the current status of the contaminant plume as modelled by taking into account various assumptions can be seen in Figure 32. The model approaches the observed concentrations found. A correlation between the observed and modelled nitrate concentrations can be seen in Figure 33, a correlation R^2 of ~64 % was obtained, given the assumptions and limitations of the model this correlation can be regarded as acceptable, especially for predictive modelling purposes. The correlation of the refined model improved significantly from the model using the inferred initial conditions. With reference to Figure 34, it can be seen that the largest discrepancy between the modelled and observed nitrate concentrations are found in boreholes BH2, Boer1, Boer2, BH7.
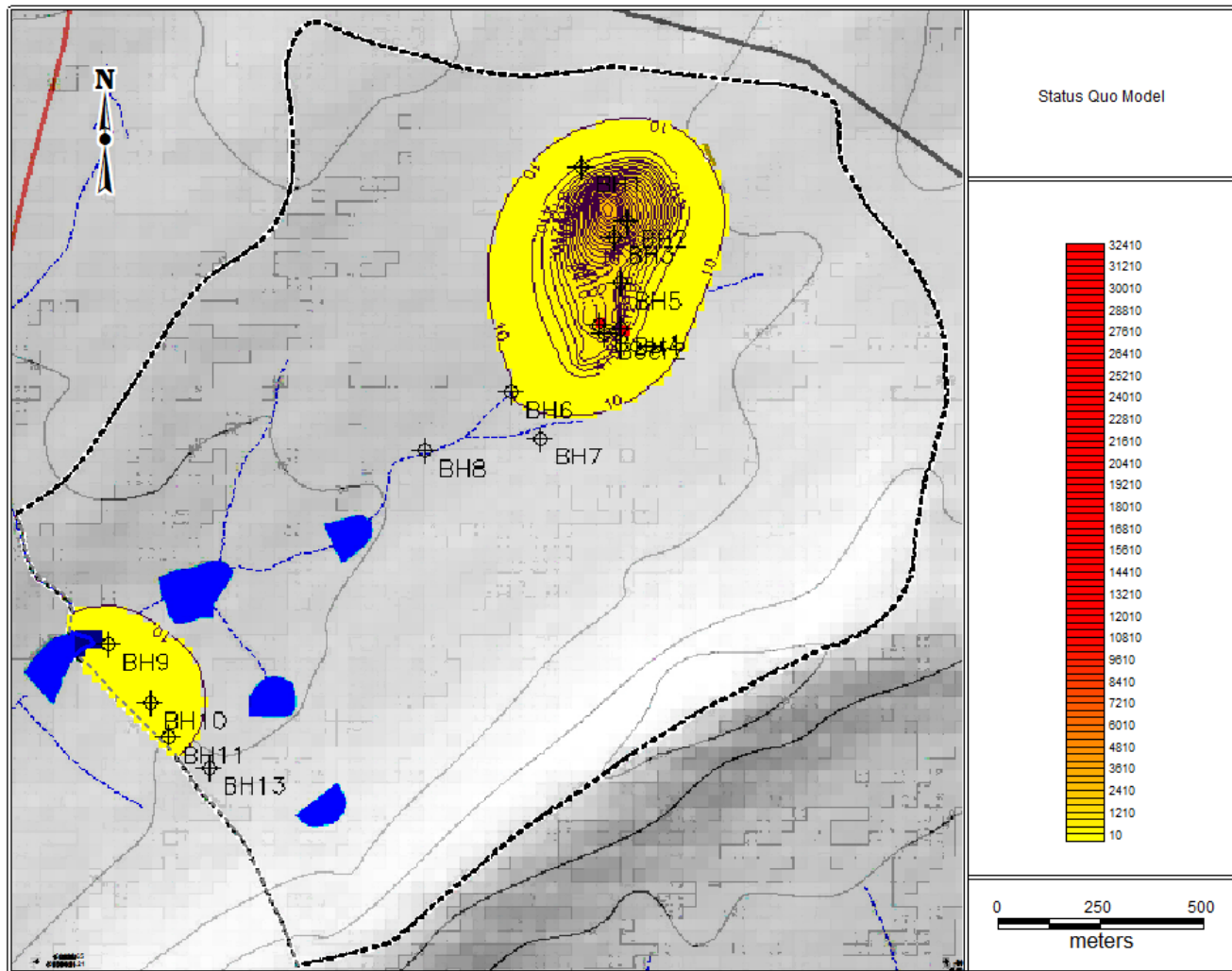
Figure 32: Modelled contaminant plumes at present
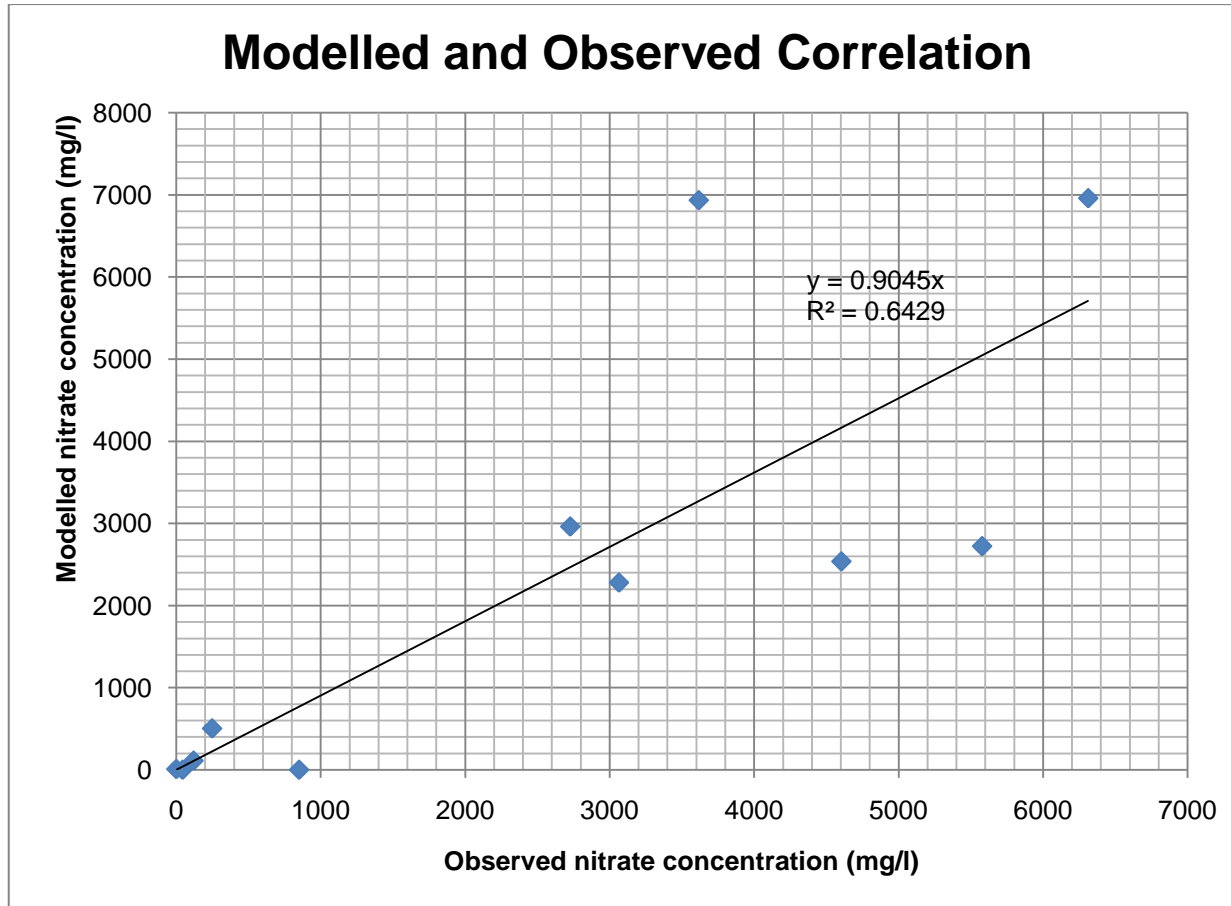
Figure 33: Correlation between modelled and observed nitrate concentrations (refined conceptual model)
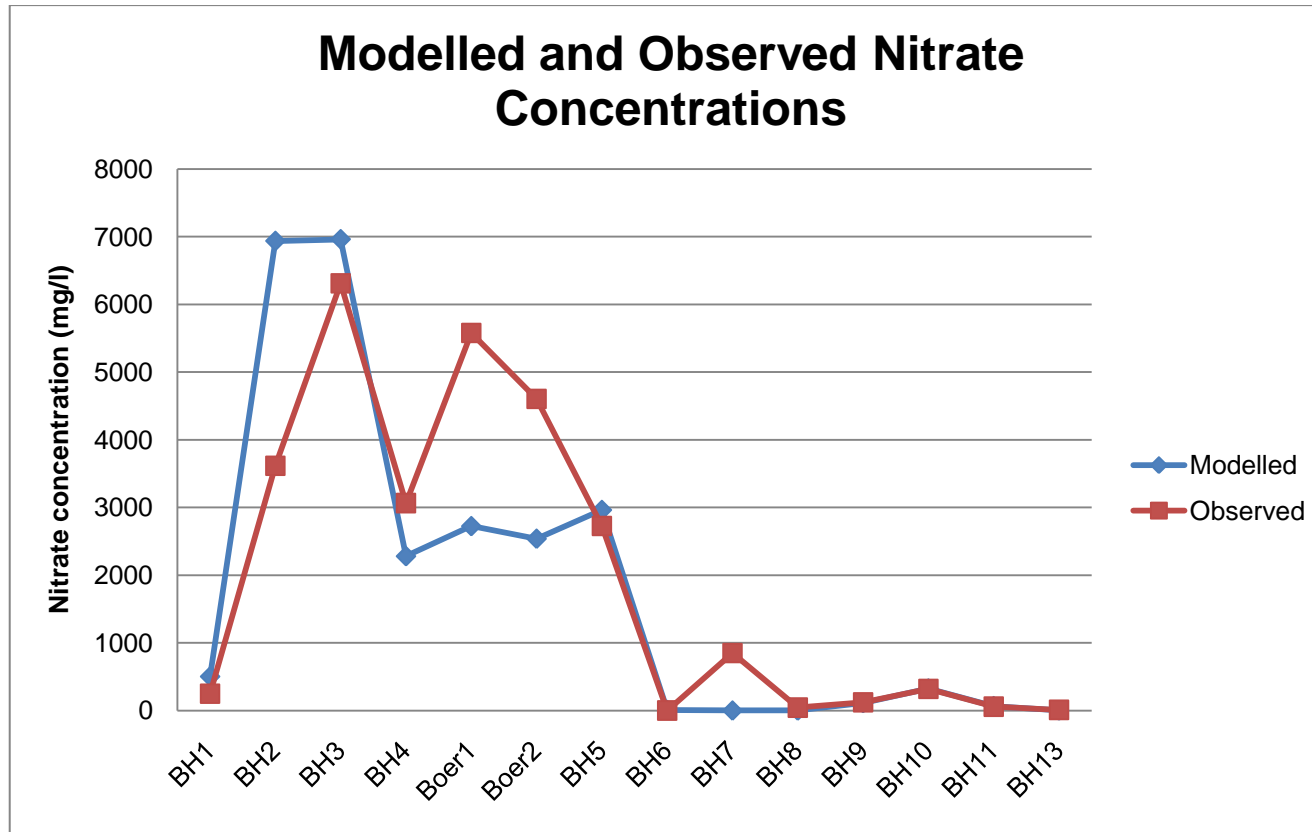
Figure 34: Modelled and observed nitrate concentrations

10.6 FLOW AND CONTAMINANT TRANSPORT SENSITIVITY ANALYSIS

Sensitivity analysis can be defined as a process whereby the input parameters are changed over a reasonable range while the relative change in model response is observed (Mandle, 2002). The sensitivity of transmissivity (hydraulic conductivity), effective porosity and dispersivity was assessed in the following runs. The breakthrough curve of BH5 of the refined model and different sensitivity analyses can be seen in Figure 35.

10.6.1 Transmissivity

The transmissivity was varied by increasing and decreasing the parameter, the change in plume geometry can be seen in Figure 36. As the layer thickness is known (30m) the hydraulic conductivity is consequently also varied. The transmissivity was changed to 0.5 m^2/d and 10 m^2/d. The 10 m^2/d transmissivity did not differ significantly from the refined model, the 0.5 m^2/d transmissivity resulted in the most elevated modelled nitrate levels. The model is relatively sensitive to changes in transmissivity, especially with regards to differences in the orders of magnitude.

10.6.2 Effective porosity

The current refined model was simulated with a effective porosity of 6%. While a 1% effective porosity resulted in the maximum concentration above 4000 mg/l reached only after the first 10 years (3650 days). The 10% effective porosity underestimated the nitrate concentrations in BH5 when compared to the refined model. The model is sensitive with regards to effective porosity. In Figure 37 the change in effective porosity can be seen.

10.6.3 Dispersivity

A 30m dispersivity value was used in the refined model. By decreasing the dispersivity to 5m the nitrate levels were slightly overestimated, a maximum concentration (~4500 mg/l) was reached after 50 years. The increased dispersivity of 70m resulted in an under estimation with regards to the refined model, however this under estimation is dominant between 20 and 50 years. The model is sensitive for changes in dispersivity, but to a lesser extent than for effective porosity as seen in Figure 38.

10.6.4 Discussion

After a period of 10 years since the commissioning of the plant (~1990) nitrate levels in the area near BH5 are likely to have ranged from 600 – 4000 mg/l. However the current (2009) modelled concentration range is this borehole may approach 2000 -4000 mg/l. The model is sensitive to change in effective porosity and dispersivity, to a lesser extent in transmissivity.
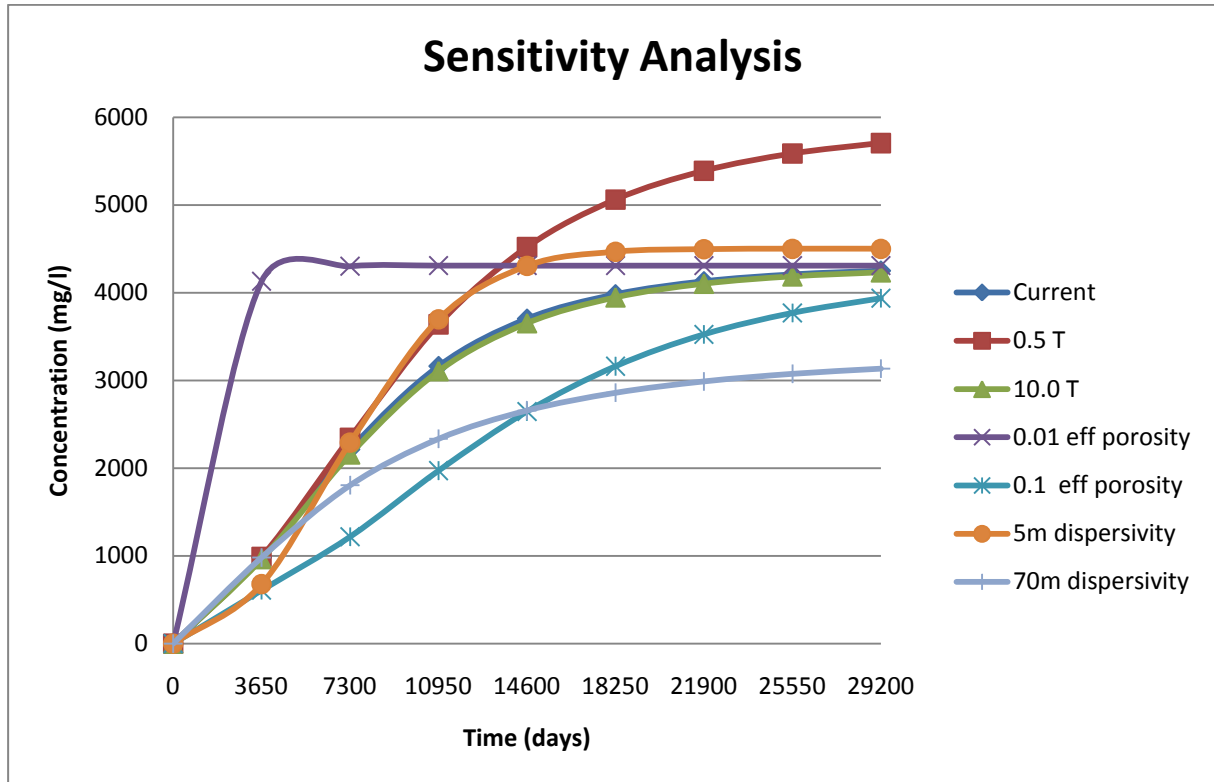
Figure 35: Break through curve of refined model and sensitivity analyses at BH5
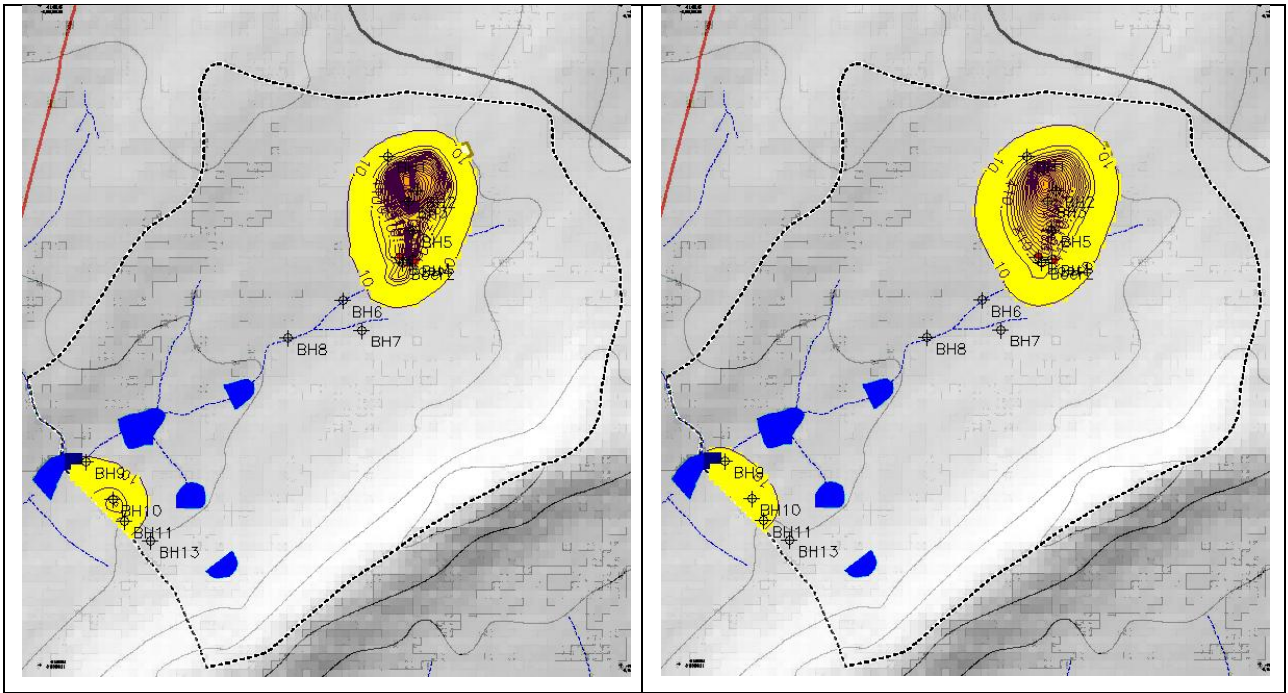
Figure 36: Nitrate plume for change in transmissivity of 0.5 m^2/d (left) and 10 m^2/d (right)
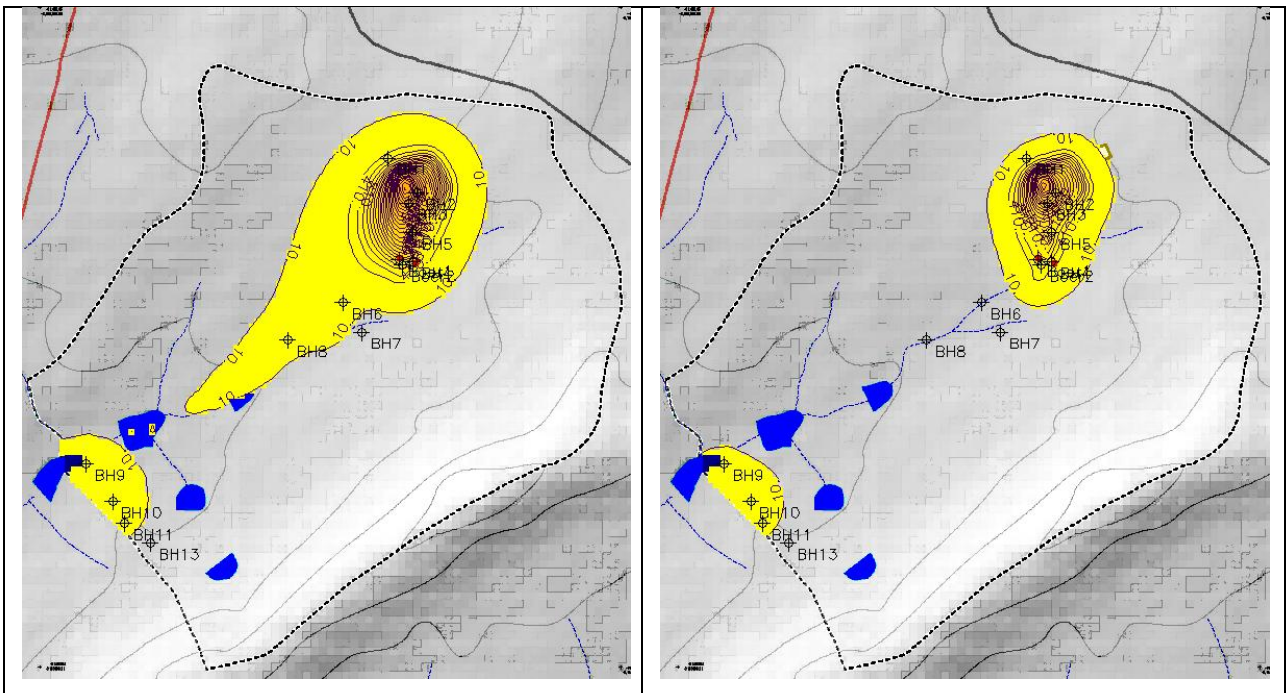
Figure 37: Nitrate plume for change in effective porosity of 0.01 (1%) (left) and 0.1 (10%) (right)
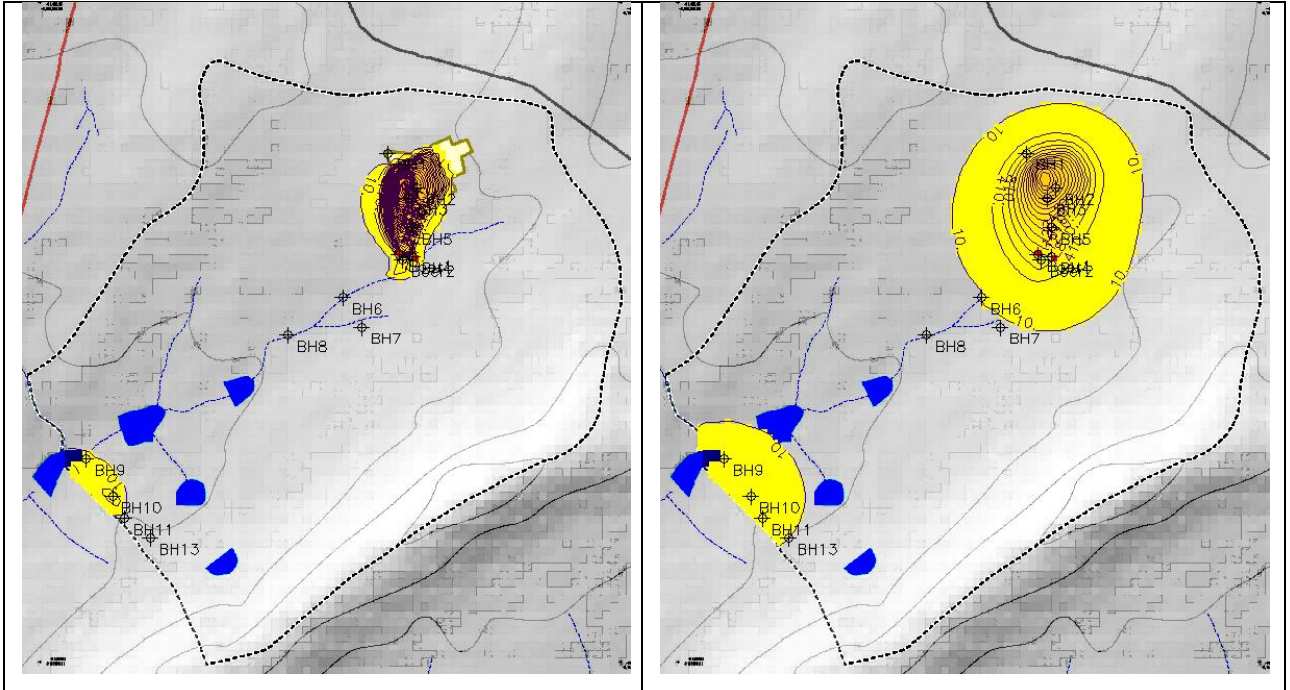
Figure 38: Nitrate plume for change in dispersivity of 5 m (left) and 70m (right)

10.7 PREDICTIVE SCENARIOS

Predictive modelling of the plume as it was modelled in Figure 30 will be discussed in this section. It is assumed that the model depicted in this figure represents the current status of the plume. This modelled plume will be used as initial conditions for predictive modelling. Groundwater abstraction from boreholes BH4 and Boer1 have ceased recently and therefore no water will be abstracted from these boreholes during the predictive modelling. The plume will be modelled for 40 and 80 years.

10.7.1 No mitigation

This scenario represents the situation during operation of the plant. In this scenario, all sources were deemed to be constant sources. Given the degree of uncertainty in model input parameters and the corresponding uncertainty in predictive model simulations, model input values were selected to result in a "worst-case" scenario. In modelling the current scenario, it has been accepted that the contamination has been entering the subsurface for at least the last 30 years (estimated age of the plant). This would mean that the groundwater levels and contaminant concentrations below the site has most likely attained steady state conditions, and that movement of the pollution plume has taken place. The nitrate seepage concentration was again taken as 32000mg/l.

If no mitigations are implemented the migration of the contaminant plume in 40 and 80 years is depicted in Figure 39 to Figure 41. As can be seen from the figures, the plume is expected to spread in the direction of the natural surface water drainage. The following observations can be made:

- The primary plume is likely to reach BH6 as well as BH7 and BH8. Concentrations of NO_3 are elevated across the plume.
- The NO_3 level in Boer1, Boer2 and BH4 range between 4000 and 5000 mg/l.
- After 80 years the plume has extended below Dam2, the NO_3 levels in the plume boreholes has remained relatively constant and has remained similar to the 40 year predicted levels.
- The plume front approached Dam 1 after 80 years, it is further expected the contaminated surface water seepage may surface in low lying areas (shallow groundwater tables).

- It must be noted that no form of retardation of the plume has been modelled as a result this scenario is likely to act as the worst case scenario.
- It can be said that the plume is not likely to reach Dam3 given the assumptions.
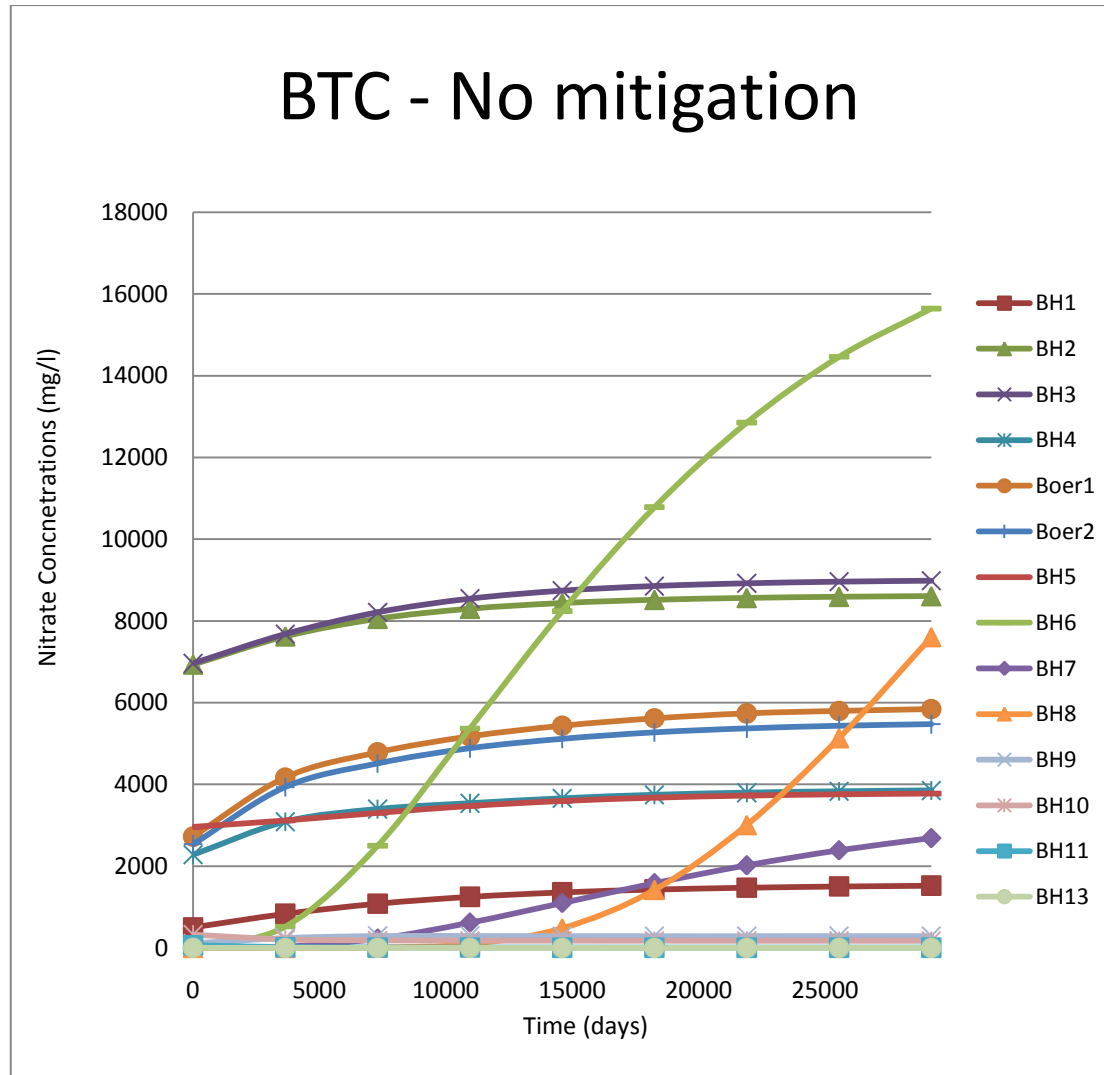
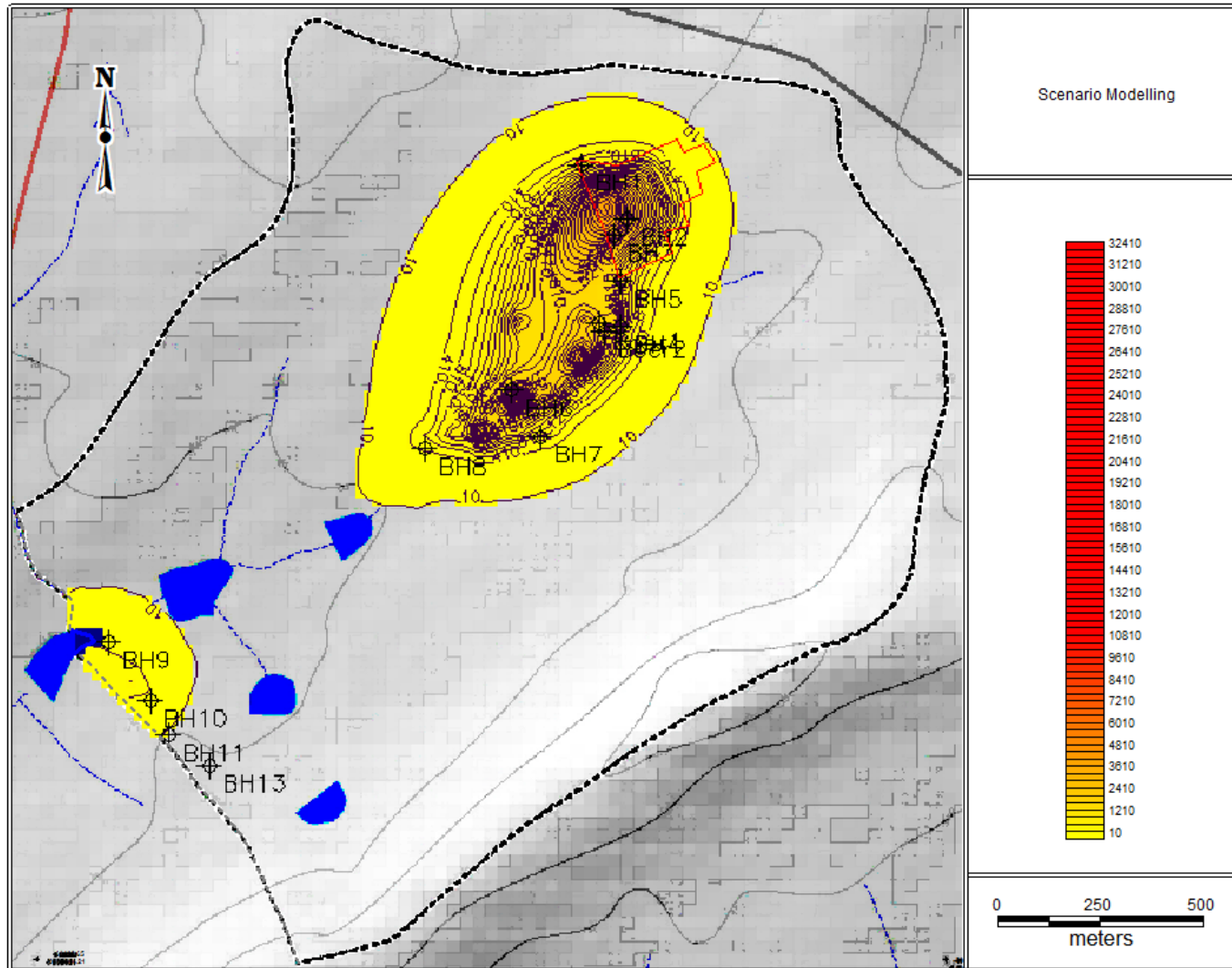Figure 39: Break through curve – no mitigation measures

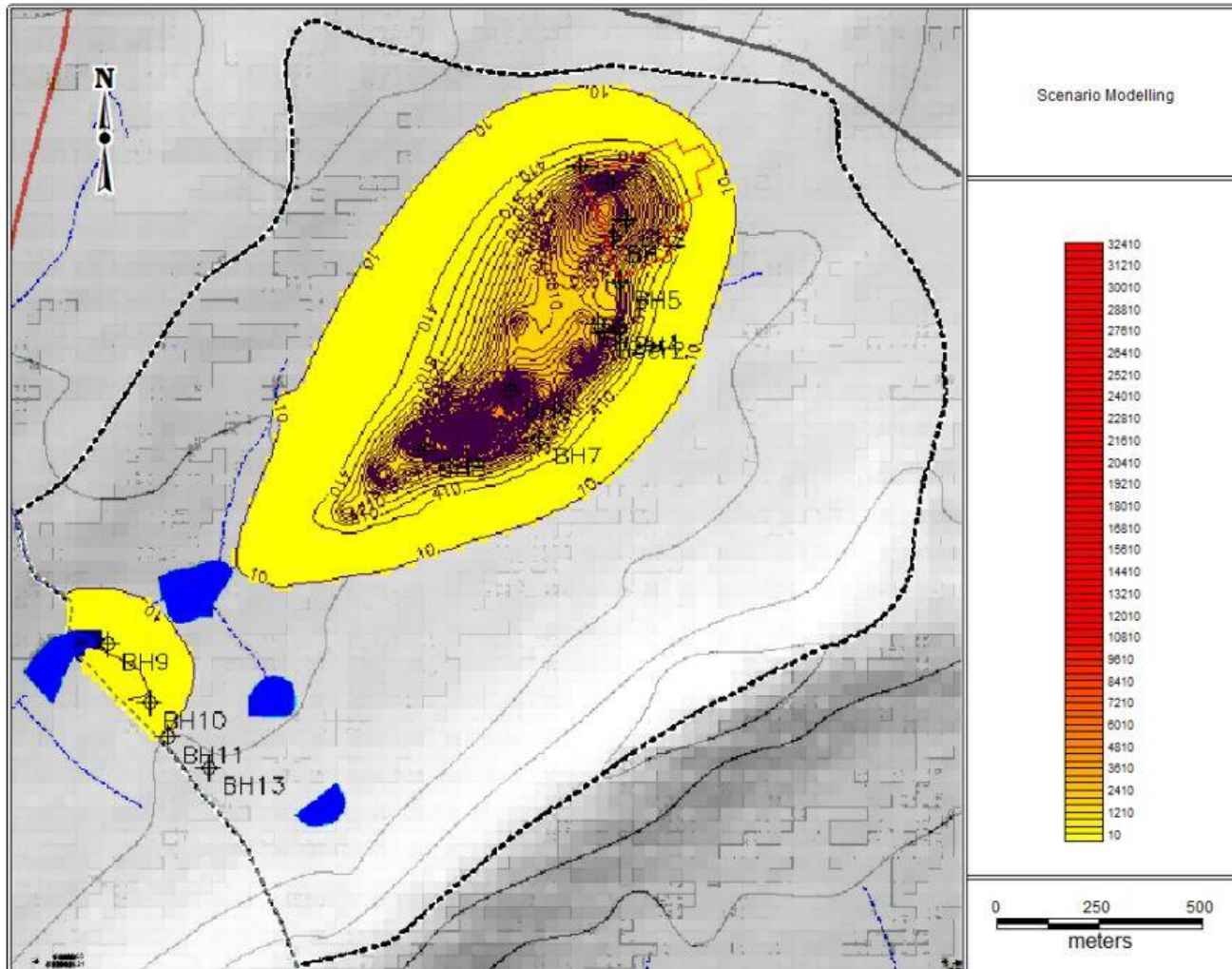Figure 40: Plume migration after 40 years (2049)

Figure 41: Plume migration after 80 years (2089)

10.7.2 Sources removed

The preferred mitigation measure is to remove the sources of contamination. It can only be speculated to what extent mitigation measures can reduce the contaminants from entering the subsurface. The soil horizon may still act as a secondary source of pollution for an unknown period. However, this scenario simulates the migration of nitrate if the primary sources have been removed and does not take any secondary sources into account i.e. prevent contamination from entering the subsurface as from 2009. The plume still migrates downstream but the concentrations decrease over time. The following observations can be made:

- After 40 years of the source removal, a decrease in on-site contaminant levels can be seen in Figure 43. Since the removal of the source shows the plume to be shrinking together with a decrease in nitrate concentrations. Due to advection the plume has migrated downstream, but not to the extent of the plume with the constant source, lower concentrations can be seen in the plume. The plume front is found at similar position as that in section 10.7.1 before Dam2.

- The centre of the plume is likely to be in proximity to BH8 after 80 years, the plume has almost entirely migrated off site, with on site nitrate levels approaching acceptable levels (<88 mg/l SANS drinking water standard). The nitrate concentrations in the plume have decreased as depicted in Figure 44.

- The breakthrough curve (Figure 42) of the concentrations in the boreholes show that the on-site boreholes and the plume boreholes decrease in contaminants levels when the sources are removed. However as the plume is advected, the downstream impact boreholes (BH7 and BH6) show an initial increase as the plume migrates across these boreholes after which contaminant levels start to decrease again. BH8 has shown an increase as the plume centre of mass approaches the borehole.

- It is however unlikely that the plume will migrate so far, as the retardation process would start to dominate advective forces. This scenario should be seen as the worst case plume movement if the source is removed.
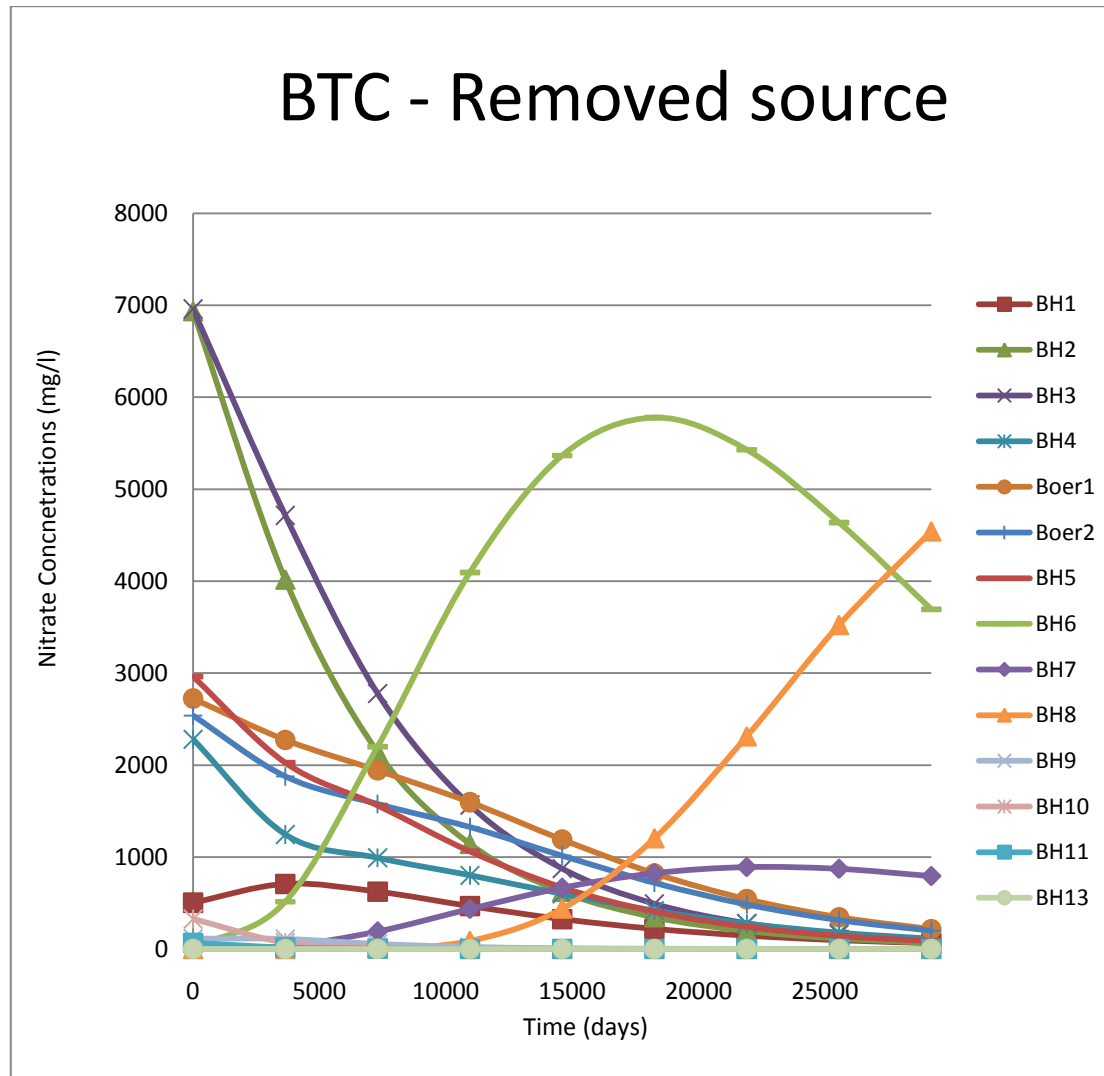
Figure 42: Break through curve – source removed
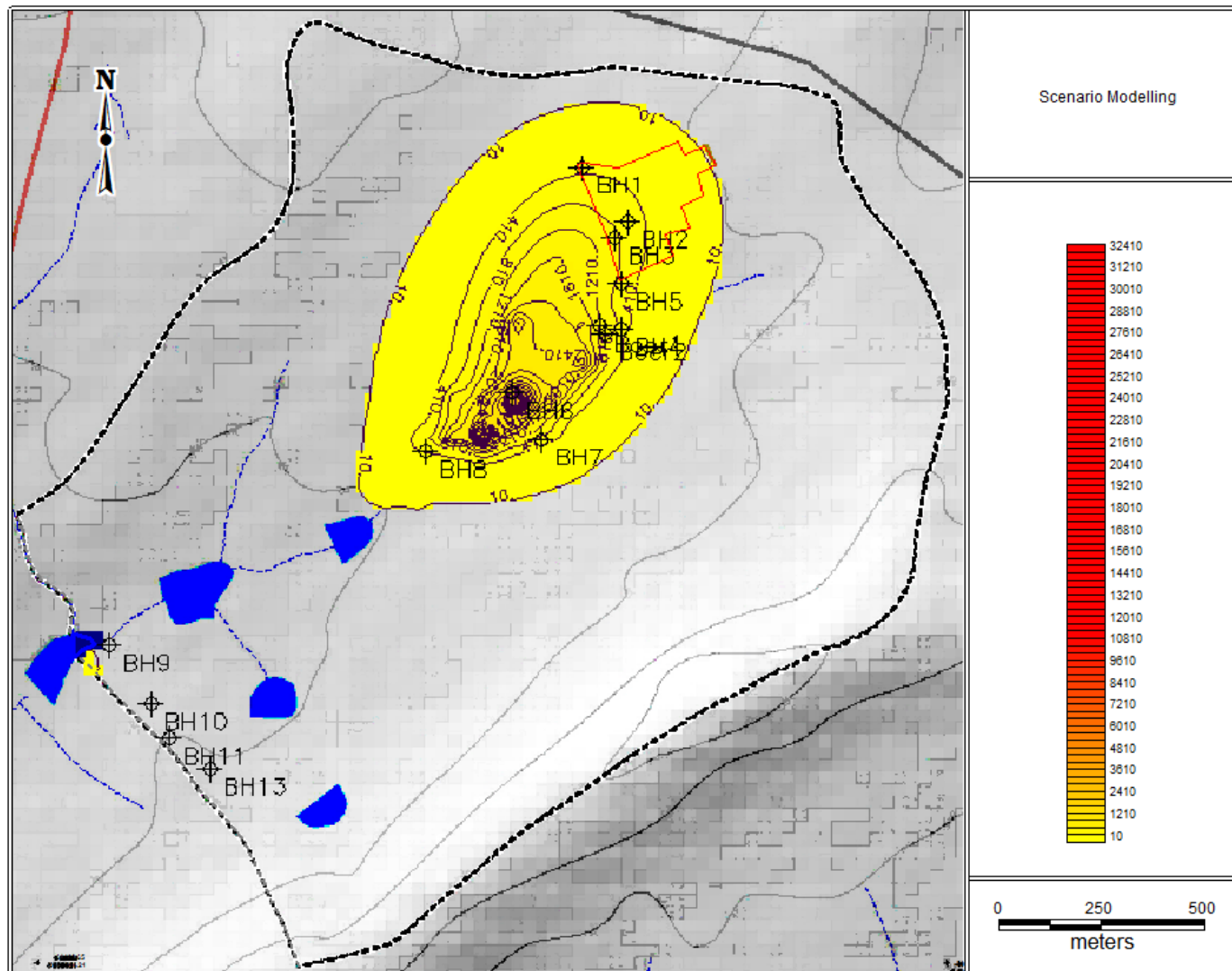
Figure 43: Plume migration after 40 years (source removed) (2049)
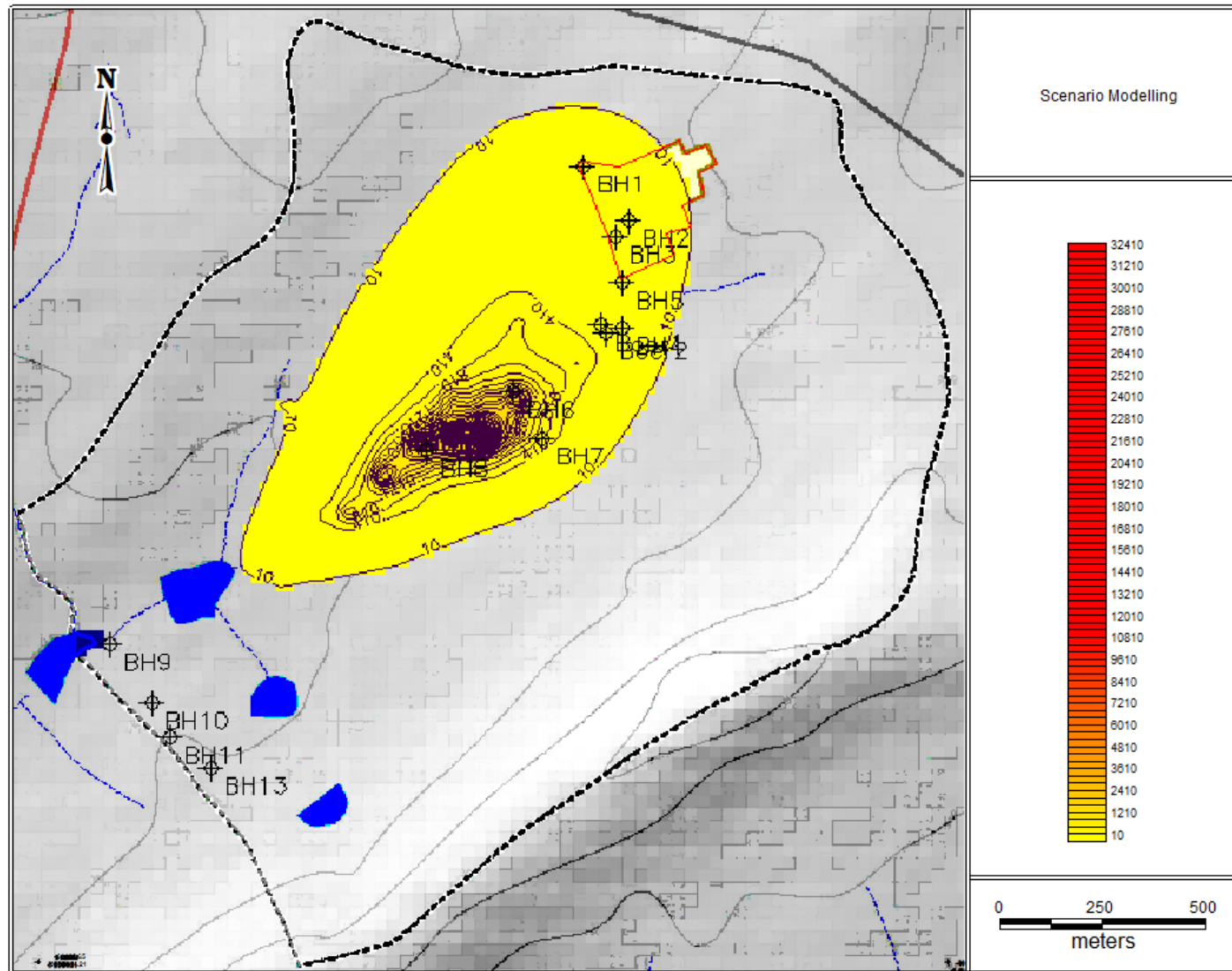
Figure 44: Plume migration after 80 years (source removed) (2089)

10.7.3 Mitigation by trench/drain (3m deep)

This scenario represents the construction of a L-shaped trench. A trench was installed downstream of the site, a drain was modelled on the south western boundary of the site. A 3m deep trench was firstly simulated.

With reference to the break through curve in Figure 45 it can be seen that nitrate concentrations are still elevated in all the currently contaminated boreholes, the 3m trench does not appear to be significantly effective in remediating the plume as the nitrate show a slight increase over time. The impact boreholes BH6 and BH8 show a large increase as the plume migrates. As can be seen in Figure 46 and Figure 47, the extent of the 40 year and 80 year plumes does not differ substantially from the un-mitigated plume with respect to its foot print. The nitrate concentrations in the plume is however lower than the un-mitigated scenario, however still elevated. Given the observations made during the intrusive investigations, it can be assumed that 3m is the maximum depth to which a trench can be excavated (without blasting or rock breaking) in the area of concern.
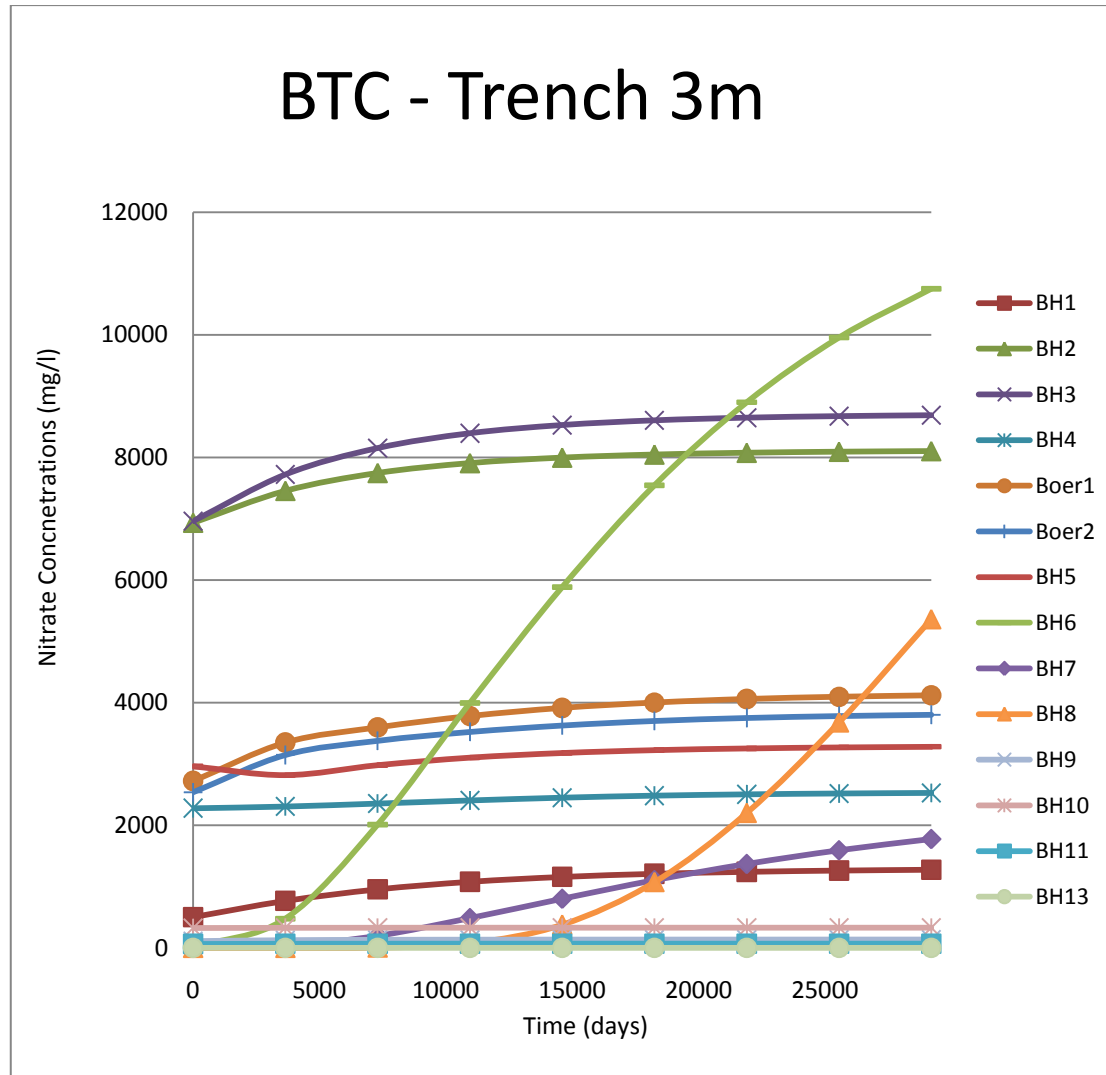
Figure 45: Break through curve – 3m deep trench
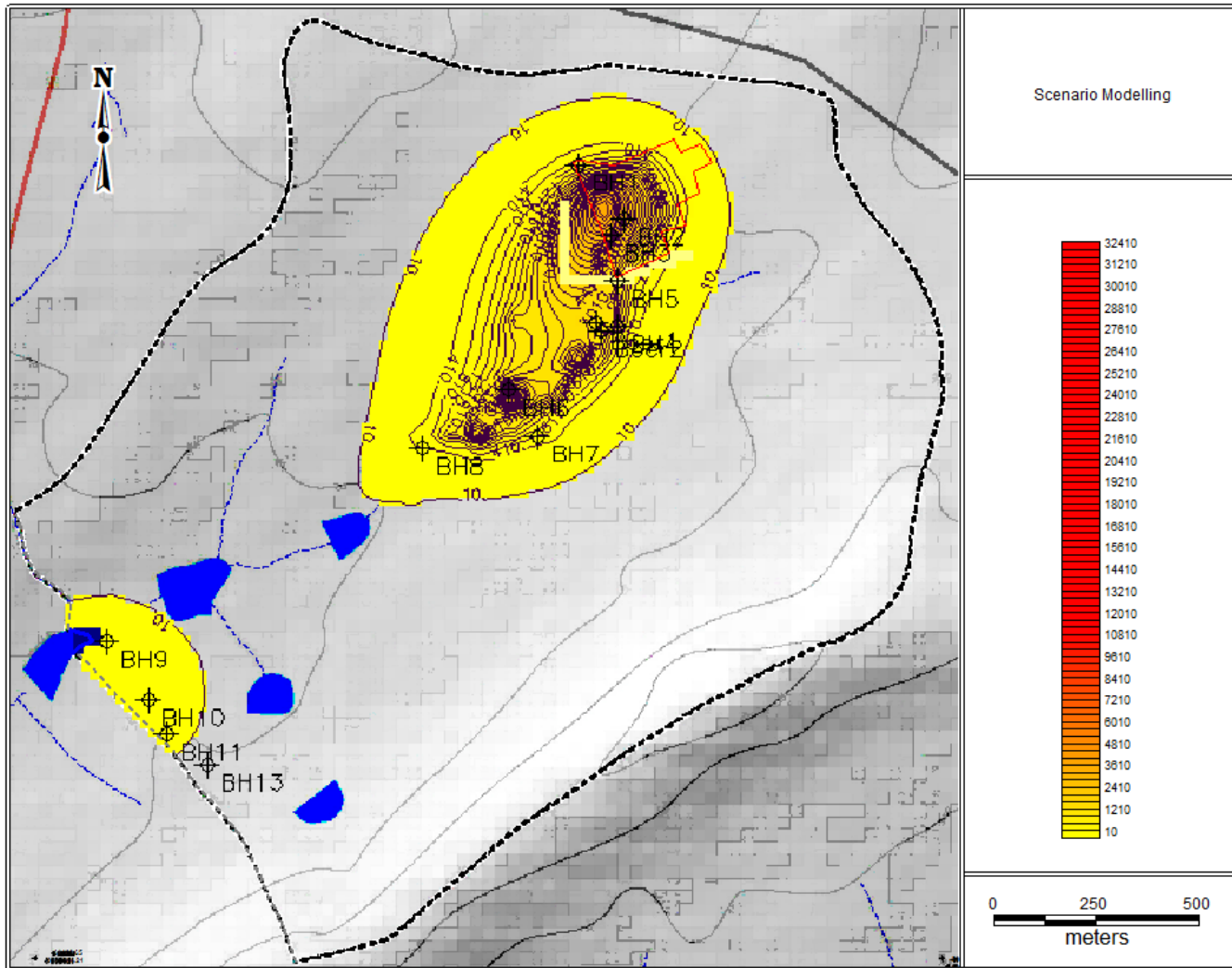
Figure 46: Trench 3m deep (plume simulation 40 years) (2049)
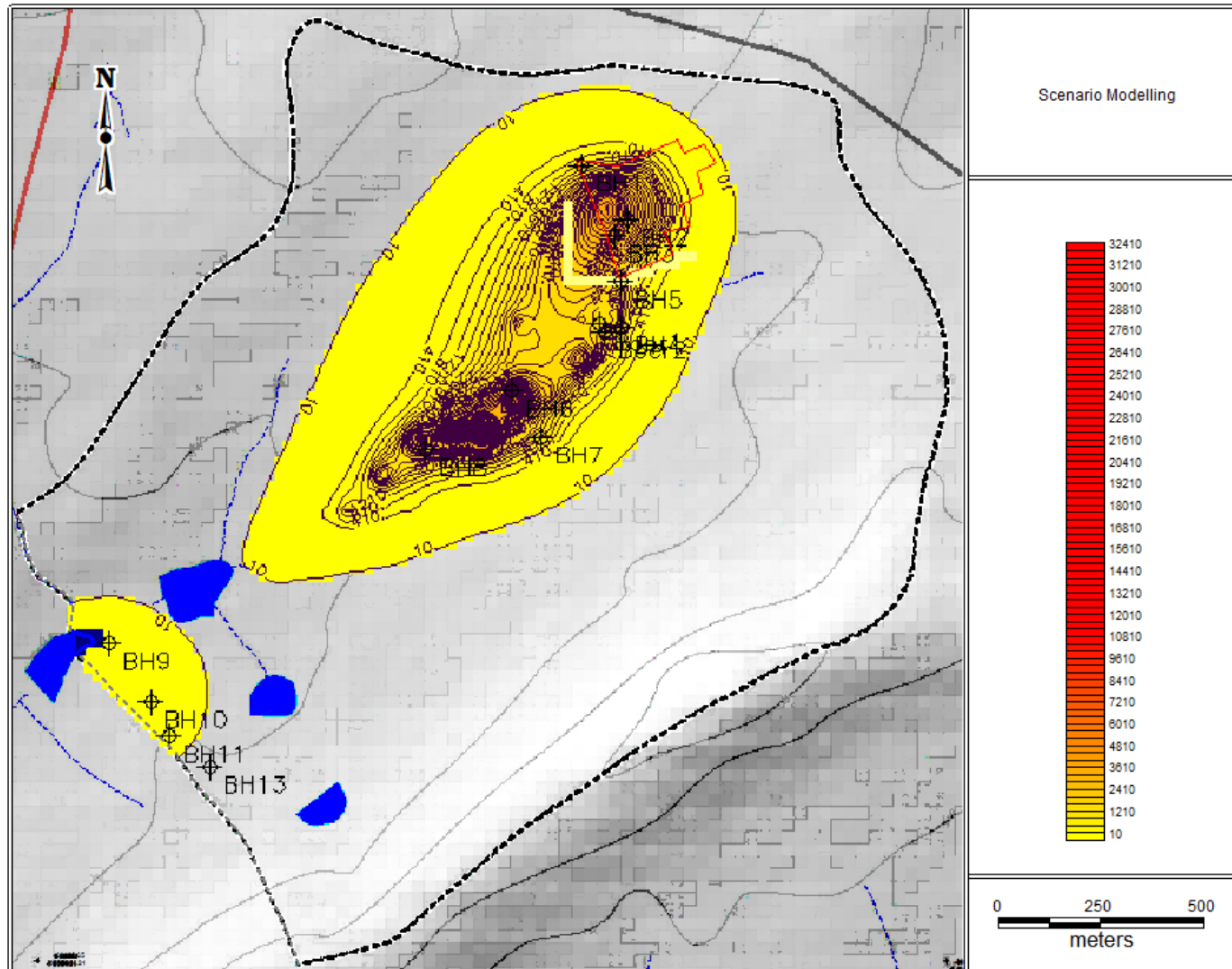
Figure 47: Trench 3m deep (plume simulation 80 years) (2089)

10.7.4 Mitigation by trench (6m deep)

Although excavation of a trench 6m deep is unlikely given the subsurface conditions, it was deemed necessary to investigate the mitigation potential of a deep trench/drain. With reference to Figure 48, it can be seen that no major increase in nitrate concentrations was observed when compared to the status quo scenario. However an increase in nitrate levels is discernable in BH6 and BH8 as the plume migrates. In Figure 49, the 40 year plume with the 6m deep trench is likely to have a lower plume mass than the un-mitigated scenario (as can be expected). In Figure 50, the 80 year plume is not as well developed as the un-mitigated plume, with lower plume concentrations and smaller extent (in the x direction).

In view of the above scenarios, It can be said that mitigation of the plume by means of a cut-off trench does have an effect on the plume concentrations, but unlikely to prevent the plume from migrating downstream. This mitigation measure is therefore deemed in-efficient given the potential expenditure of the construction of a trench.
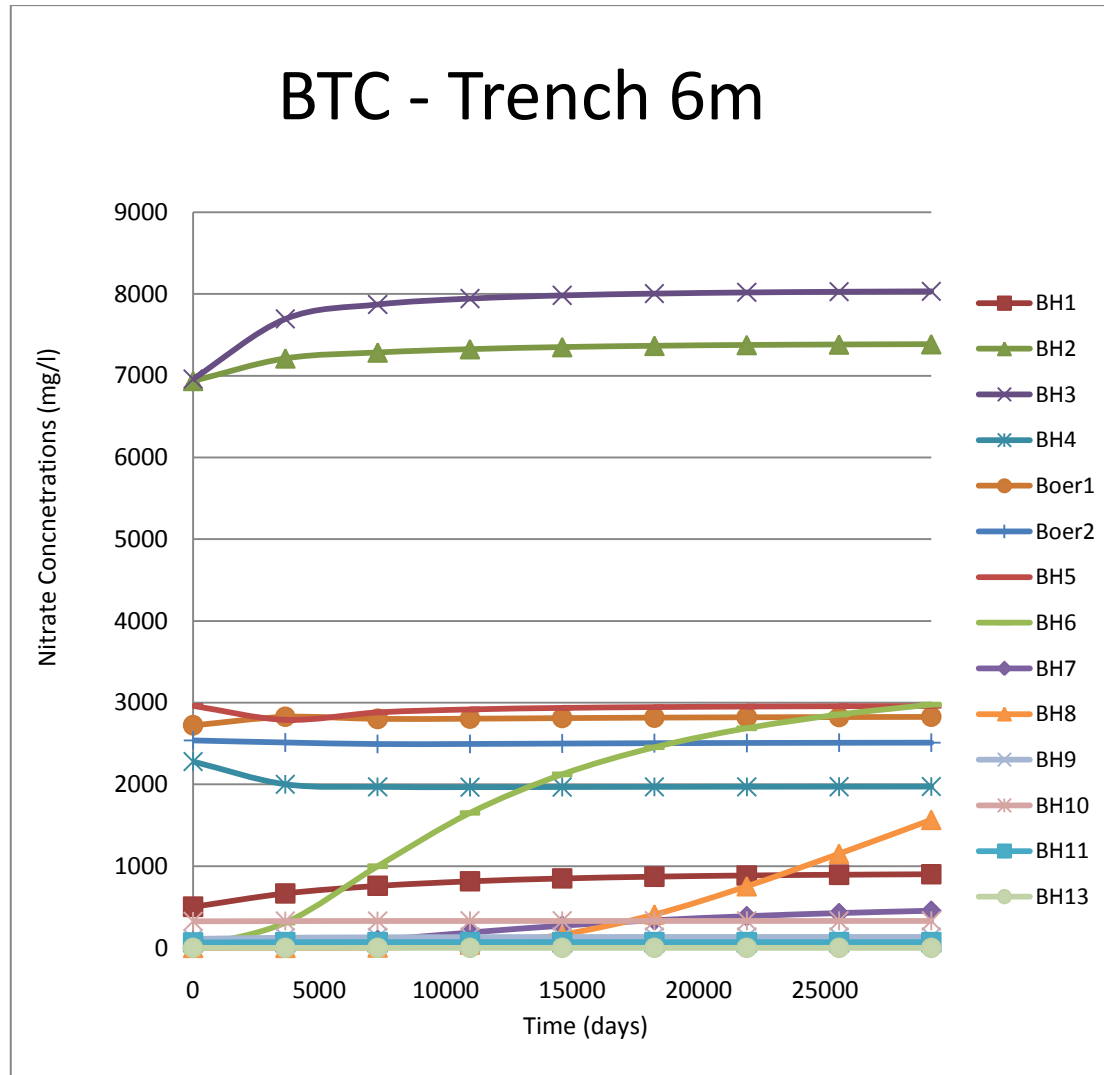
Figure 48: Break through curve – 6m deep trench
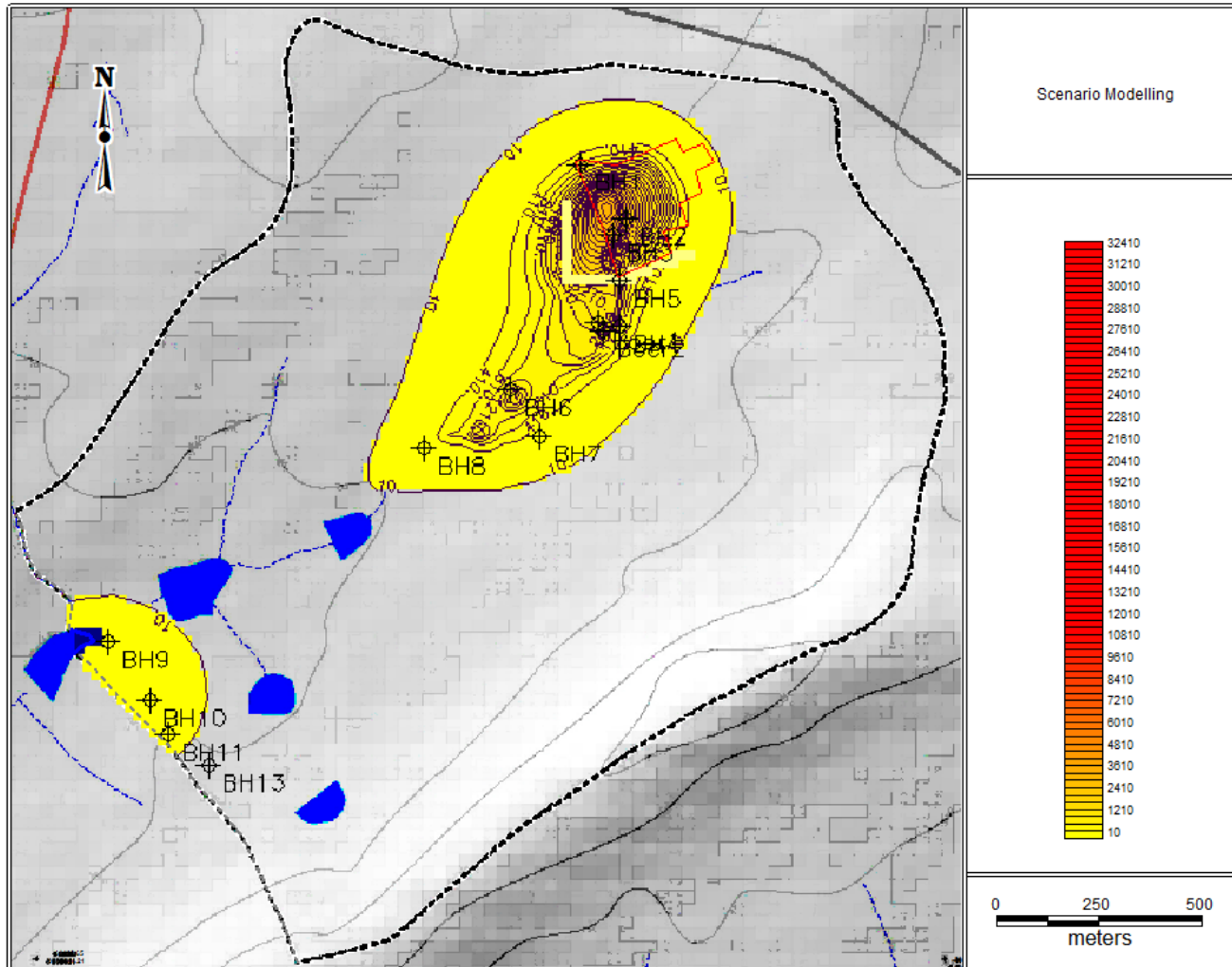
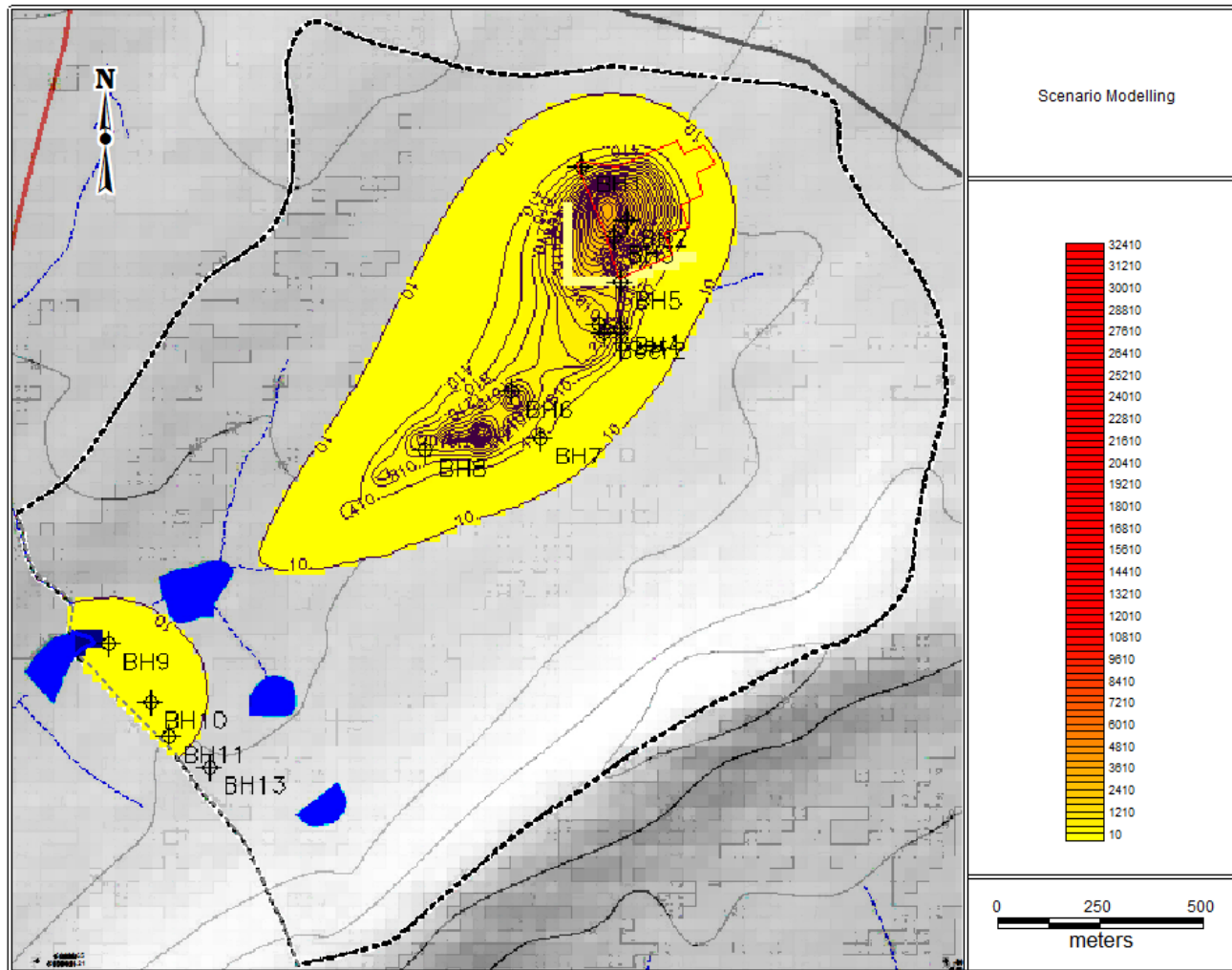Figure 49: Trench 6m deep (plume simulation 40 years) (2049)

Figure 50: Trench 6m deep (plume simulation 80 years) (2089)

10.7.5 Mitigation by groundwater abstraction

This scenario simulated the effect that groundwater abstraction will have on the migration of the nitrate plume. The primary sources continued to contaminate the groundwater in this scenario (i.e. no efforts were made to minimise the primary sources of contaminants).

Five on-site boreholes (BH1, BH2, BH3, BH5 and a new on-site borehole) were selected as boreholes to be pumped. It is accepted that the boreholes are low yielding and therefore low abstraction rates will be required to prevent the boreholes from being pumped dry. A pump rate of 0.1 litres per second (l/s) or ~8.64 m^3/d was used. The five boreholes were pumped for a 24 hour period per day resulting in a volume of 43200 l water abstracted per day. The breakthrough curves depicted in Figure 51 show that contaminant concentrations decreased substantially, furthermore the impact boreholes BH6 and BH8, do not show significant increasing nitrate levels. The onsite boreholes remain highly contaminated although their contaminant loads decreased significantly. The 40 year plume and 80 year plume (Figure 53 and Figure 54) have a lower plume mass and extent when compared to the un-mitigated plume and the trench simulation scenarios.

In Figure 52, the breakthrough curve of the 0.3 l/s pump rate can be seen. A pump rate of 0.3 l/s was used for a 12 hour period (~13 m^3/d), resulting in an abstracted volume of 78000 l per day. The effect of the slightly elevated abstraction rate can be seen as the nitrate concentrations are found to be lower than the 0.1 l/s abstraction rate. Similarly to the 0.1 l/s scenario, the contaminants do not show an increasing trend on site, the concentrations of contaminants are generally lower on site. The plume will migrate downstream as can be seen by the increase in contamination of the downstream boreholes, however the rate of increase is lower as well. With reference to Figure 55, it can be seen that BH7 and BH8 are not significantly affected as observed in the other simulations. In Figure 56, the 80 year plume is seen to be significantly less developed than the other scenarios, with the nitrate plume front inferred to be slightly beyond BH8.

In addition to the model observations, the following comments can be made:

- As can be expected the pumping of the boreholes inhibits the plume migration to an extent (plume containment). The concentrations downstream (off-site) have decreased as a result of this mitigation measure.

- The plume has generally shrunk downstream, the concentrations in the downstream plume have decreased significantly. As expected the nitrate concentrations in the groundwater below the site remains elevated due to the continued source of nitrates.
- The effectiveness of the higher abstraction rate (0.3 l/s) can be seen. The plume has decreased to a greater extent than if a 0.1l/s pump rate is used .
- Therefore the viability of this scenario is likely to depend on a feasibility study of the pumping and whether the plant can consume the contaminated water abstracted.
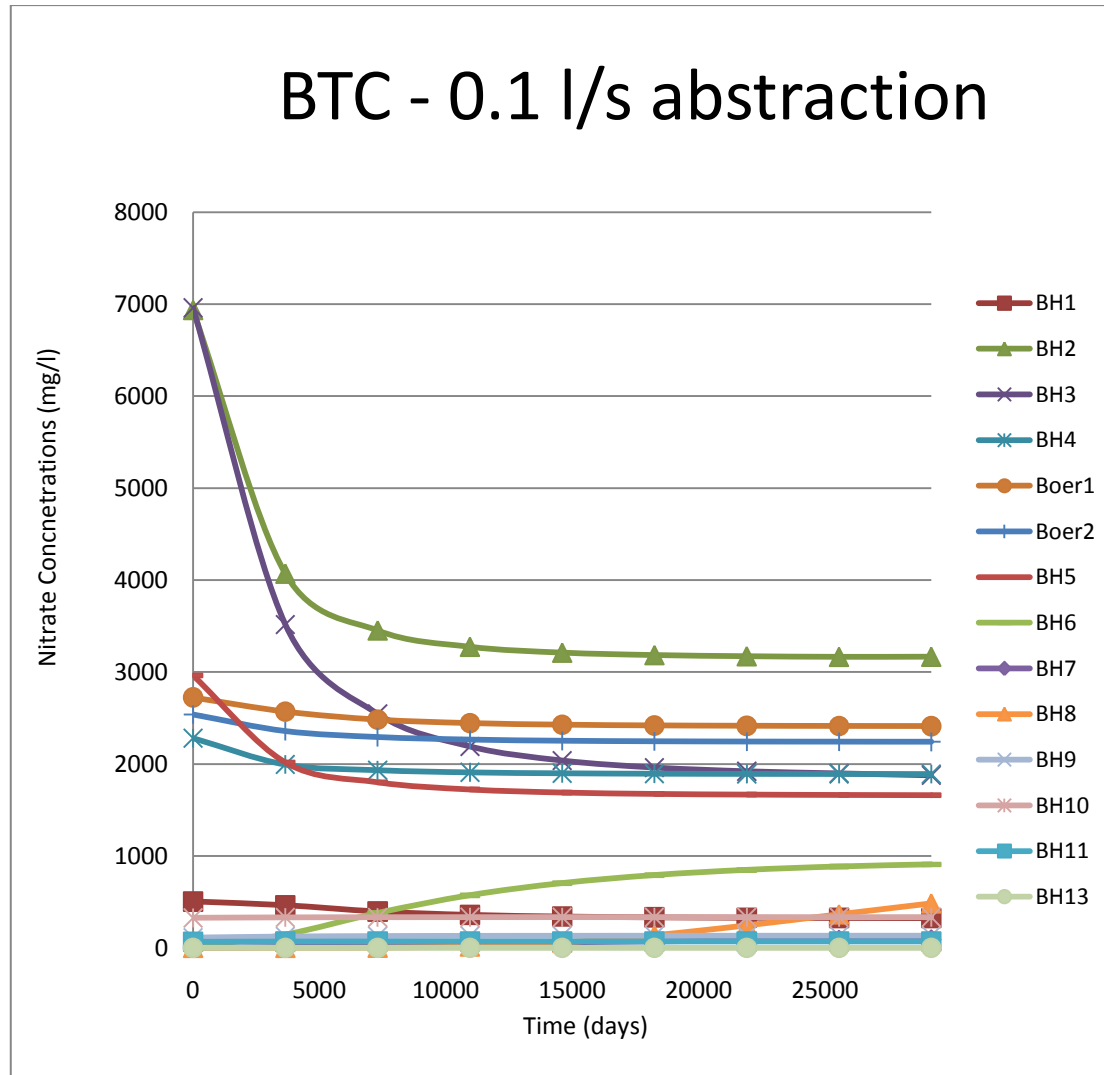
Figure 51: Break through curve – pumping at 0.1 l/s
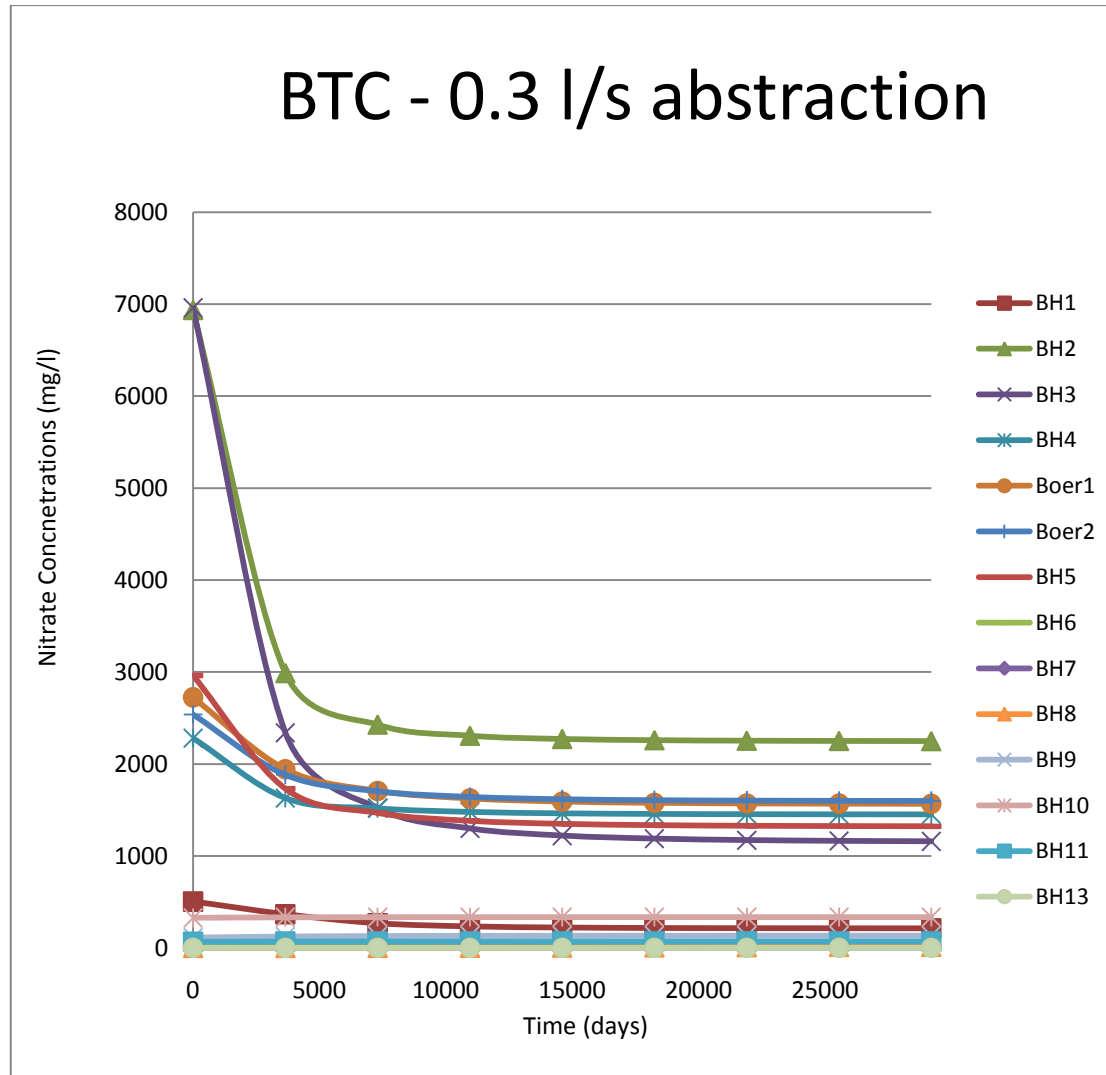
Figure 52: Break through curve – pumping at 0.3 l/s
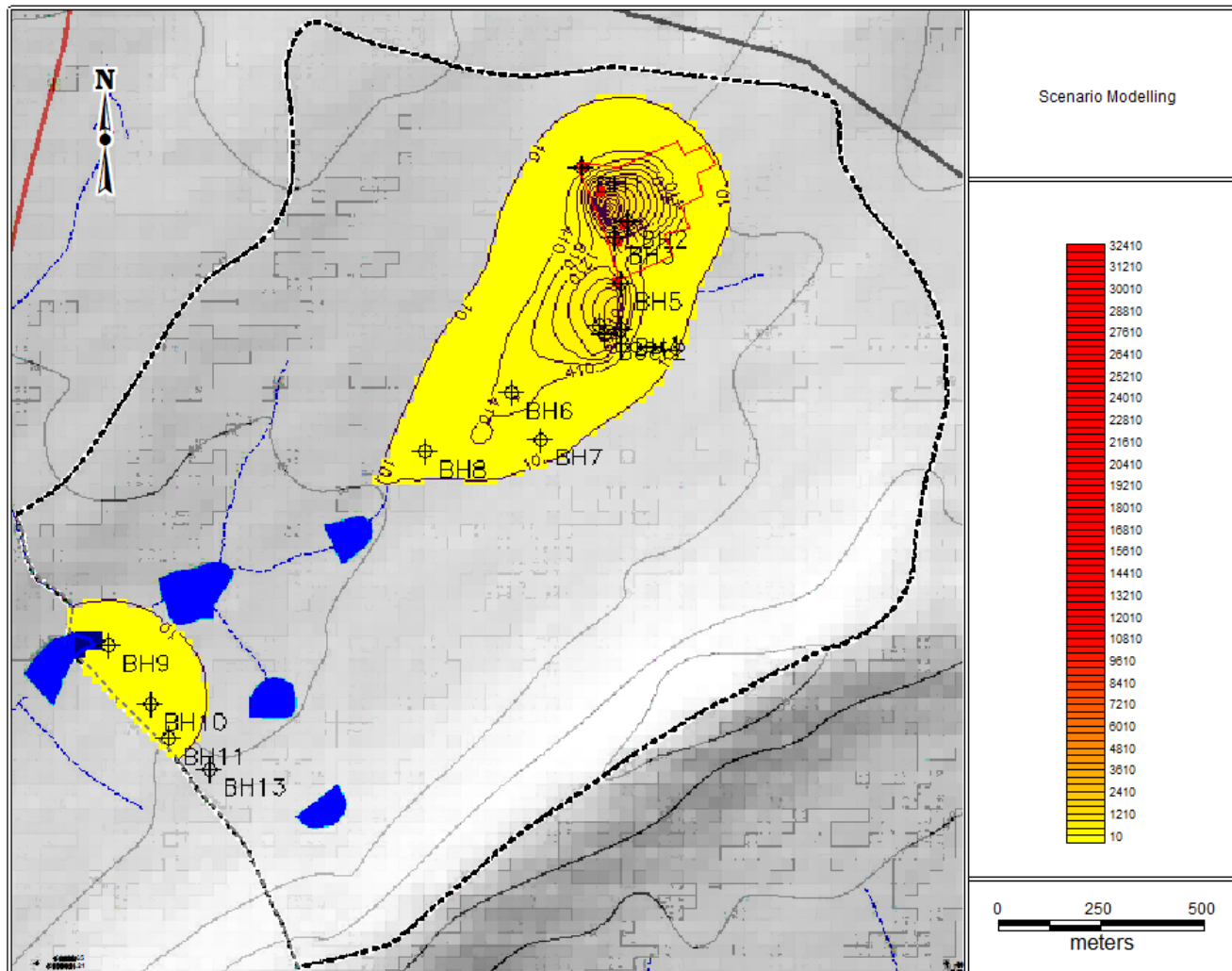
Figure 53: Plume migration after 40 years (with pump rate of 0.1l/s) (2049)
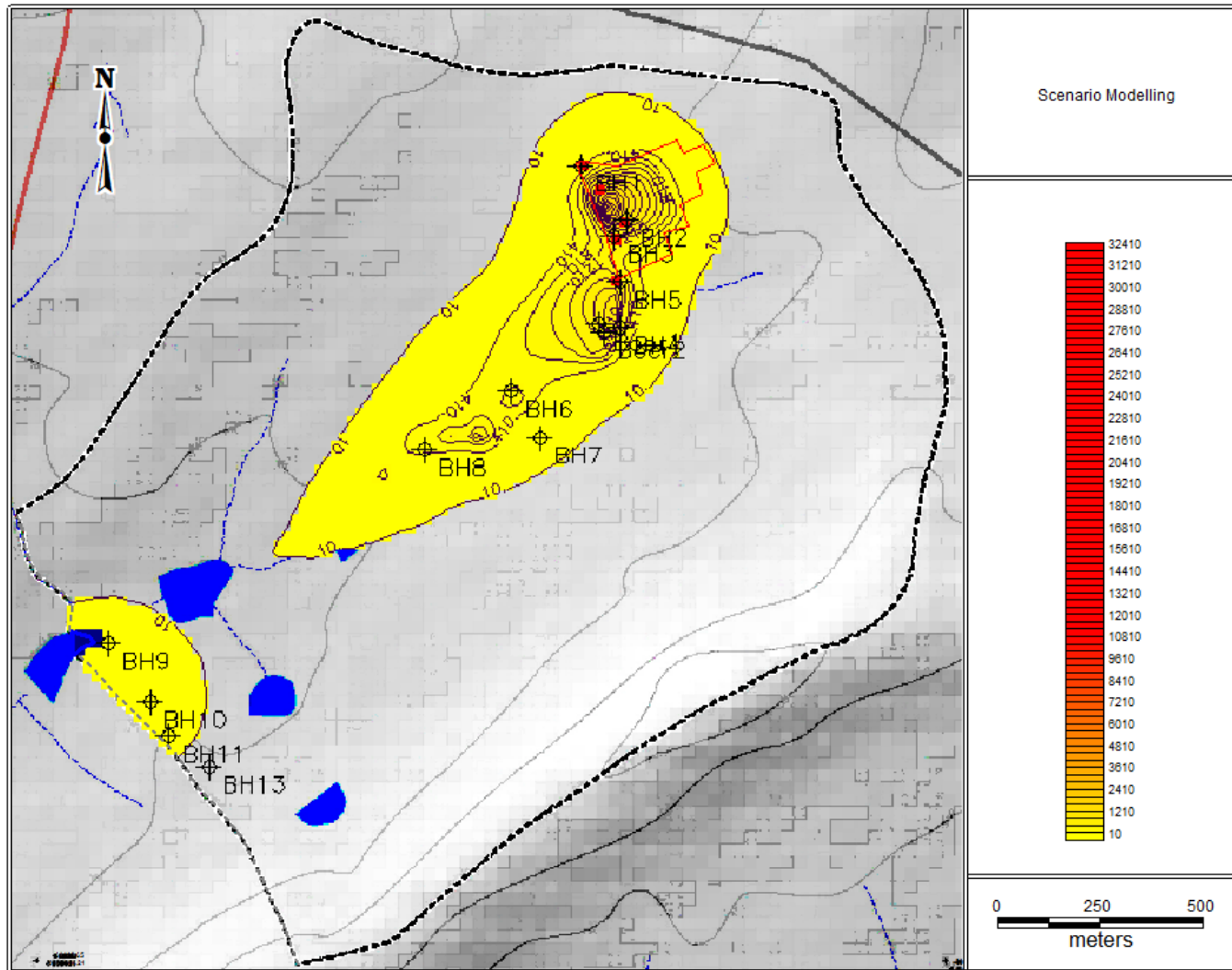
Figure 54: Plume migration after80 years (with pump rate of 0.1l/s) (2089)
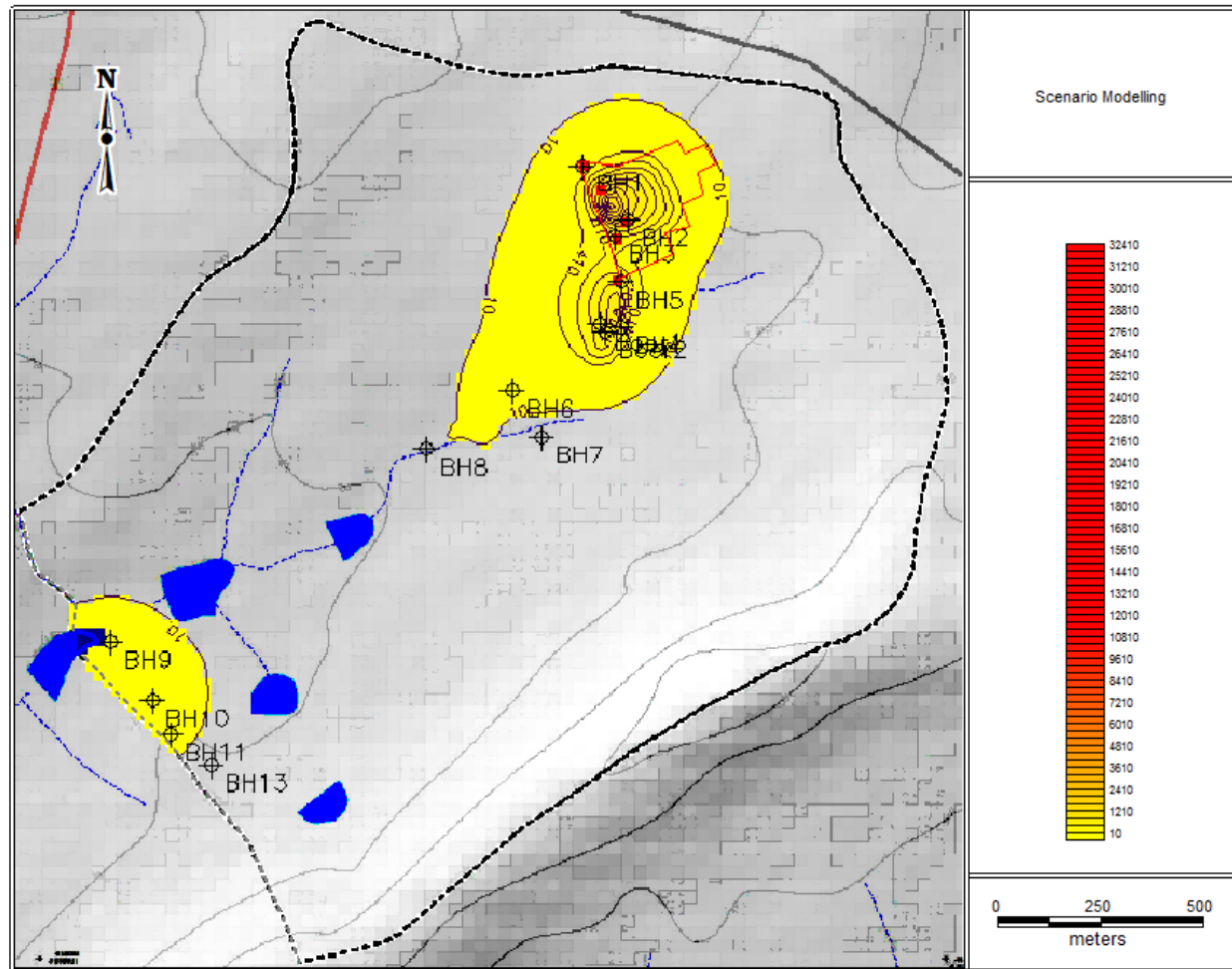
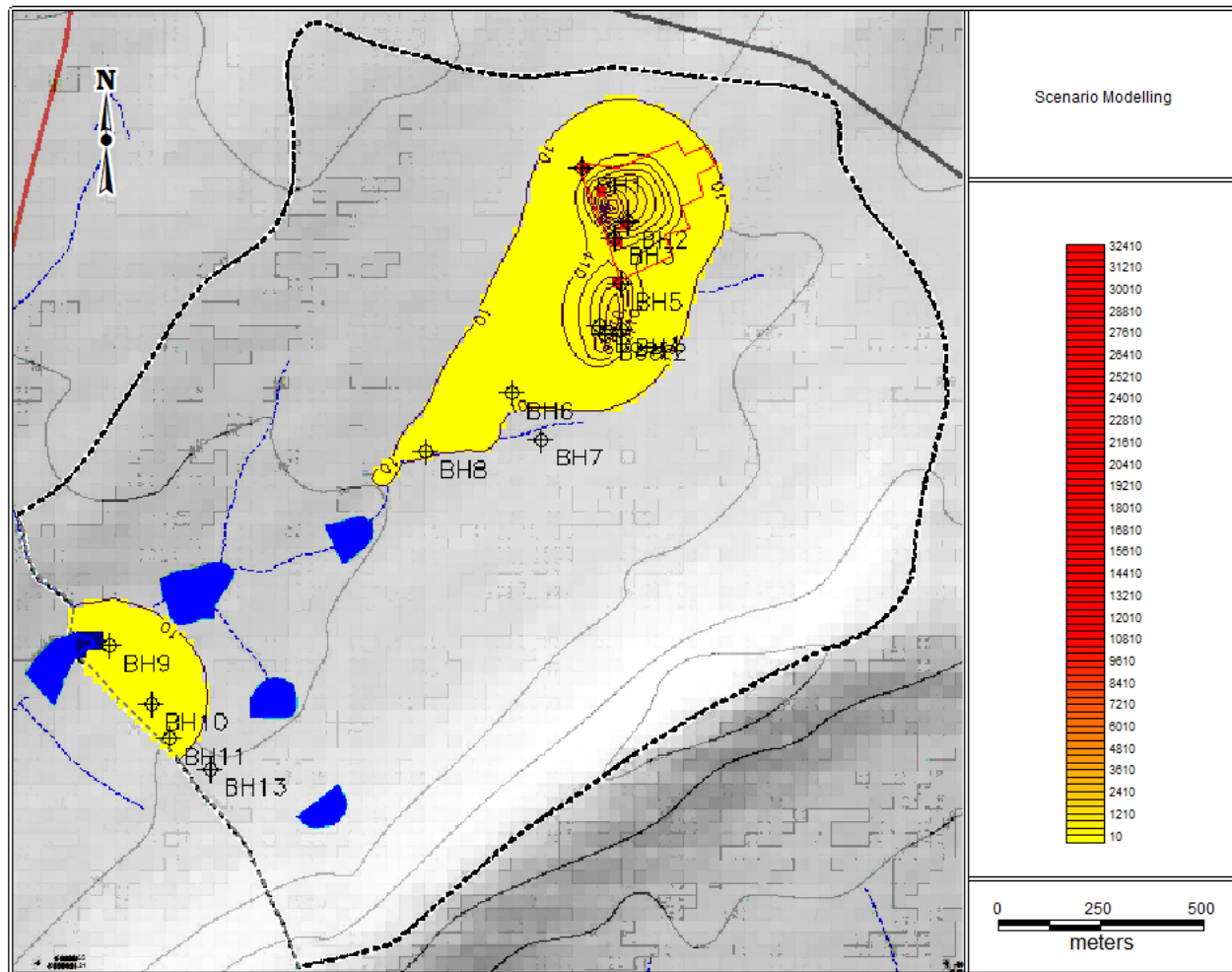Figure 55: Plume migration after 40 years (with pump rate of 0.3l/s) (2049)

Figure 56: Plume migration after 80 years (with pump rate of 0.3l/s) (2089)

10.8 LIMITATIONS OF THE MODELLING EXERCISE

The modelling was done within the limitations of the amount of monitoring data available. It was assumed that a two-dimensional aquifer system was found with horizontal flow dominating. Nitrate was assumed to act as a conservative un-reactive tracer. Although all efforts have been made to base the model on sound assumptions and has been calibrated to observed data, the results obtained from this exercise should be considered in accordance with the assumptions made. Especially the assumption that a fractured aquifer will behave as a homogeneous porous medium, this may lead to errors and uncertainty. However, on a large enough scale (bigger than the REV, Representative Elemental Volume) this assumption may bed validated to a degree. Due to the complexity of the subsurface, exact concentrations cannot be modelled. Therefore the contaminant levels derived from the model may be lower or higher than the actual concentrations.

11 CONCLUSIONS

Subject to the information currently available as discussed in the preceding sections the following conclusions were made:

The raw materials and processed products which are handled and stored on the fertilizer production facility have the potential to act as soil, groundwater and surface water contaminants. From observations made and numerical modelling it can be deduced that the main area which sources the contaminants is the product loadings areas.

Furthermore, run-off generated on site that cannot be contained in the loading area, is drained directly off site without any form of treatment or entrapment. Dust from the production process, spillages from equipment and any water which the sump cannot accommodate may be transported by the run-off. This aspect is likely to be a major contributing factor to contaminating the groundwater resources especially during the wet season when higher levels of precipitation occurs.

It can be deduced from the geophysical survey, aquifer test and borehole drilling, that the area of concern (downstream of the site between the plant and BH8) has a relative low groundwater abstraction potential. Whereby no discernable vertical or sub-vertical geological features are likely to influence groundwater flow. The groundwater contaminant plume found between the site and BH6 most likely emanates from contaminants which leach into the

subsurface at the plant area, as well as downstream of the site (between the site and the artesian boreholes Boer1, Boer2 and BH4).

Groundwater monitoring conducted on site illustrates fluctuating contaminant concentrations, although these fluctuations can be explained by differences in the seepage chemistry, it is likely that contaminants were constantly sourced over the monitored period. A distinct difference could be observed between the geochemical signature of the potential contaminated seepage and that of the groundwater. This geochemical characterisation of the contaminant plume identified an interaction of the leachate and the soil with a high clay (montmorillonite) content, with various cation exchange and sorption processes occurring. Potassium is largely exchanged, while phosphates are likely to sorbed on the clay particles. Nitrate is likely to be retarded to a limited extent, especially when redox conditions are conducive to the conservation of the nitrate specie. It could furthermore be observed that no major retarding processes occur between the site and the artesian boreholes, as a result no major changes in the fate of the contaminants could be observed. Geochemical modelling may substantiate the hypothesis.

A number of boreholes and surface water bodies were identified as potential receptors. All the boreholes sampled downstream except BH6, BH11 and BH13 appear to be negatively affected by fertilizer-related contamination especially nitrates. These surface water bodies may be contaminated either by surface water (storm water run-off) from the site or by the groundwater through the seepage interface near the farmers boreholes (Boer1, Boer2 and BH4) which then flows along natural drainage and eventually reaching the surface bodies. These dams (Dam1 and Dam2) may act as secondary sources of groundwater contamination.

The contaminants pose a health risk to potential users and livestock which may ingest the water. Currently all the sampled boreholes except BH6 pose a risk to human health. Currently it does not appear if any contaminants are negatively affecting the property downstream of the game camp. The three downstream surface water bodies (Dam1, Dam2 and Dam3) can be regarded as being relatively unaffected by contaminants emanating from the site.

Although the soil/weathered horizon has a high clay content, the layer was observed to be thin on site, furthermore the layer is compromised on-site as certain structures have been founded on the competent mudstone. As a result artificial recharge due to contaminated

seepage is found below the plant area. The mudstone and sandstone are likely to act as a fractured aquifer system.

Numerical modelling was used to validate and develop the site conceptual model. Iterative modelling improved the initial correlation of modelled and observed nitrate concentrations, the correlation improved from 29% to 64%. The model was validated by assuming the following:

- Horizontal and bedding plan fractures are likely to be present and are inferred to play a role in contaminant transport (elevated NO_3 levels in Boer1, Boer2 and BH4) not modelled.
- An increased artificial recharge (seepage and leachate infiltration) is present at the plant area mainly around the loading bay. The increased recharge in the localised areas did not have a significant effect on the groundwater flow calibration, a 98% correlation was still found between the modelled and calibrated heads.
- The groundwater abstraction from Boer1 and BH4 has an influence on the plume movement. No major volumes of groundwater was abstracted from the boreholes Boer1, Boer and BH4 in at least the past five years. These boreholes were however perceived to be pumped prior to 2004.
- Surface water contamination contributed to the current plume geometry and therefore partly responsible for the current plume extent.
- A secondary groundwater contaminant found in proximity to BH9 and BH10 was present and substantiated by the modelled NO_3 levels in those boreholes.

Although an exact solution was not reached and uncertainties still exist, the current conceptual model allows the numerical model to approach reality. The predictive modelling scenarios that were simulated, found abstraction of groundwater (~65 m^3/d) from site to be the most effective mitigation measure when compared to a cut-off trench. The plume front was modelled to be between BH6 and BH8 after 80 years.

Although the removal or mitigation of the sources would be highly recommended, it would be unlikely during the operation phase. The nitrate plume front will be found below Dam2 if no mitigation measures are implemented, given it being a worst case scenario.

The groundwater contamination is likely to pose a low risk to groundwater users, as no current groundwater users are found in proximity to the site and the contaminant plume. This

statement is only valid if no groundwater abstraction wells are drilled in the footprint of the 80 year (unmitigated) plume.

However, given the potential for the groundwater to interact with surface water (near the artesian boreholes) through seeping to surface and draining towards the surface water bodies, the risk which the contamination pose to surface water is likely to be high, when seepage from this area occurs. By abstracting groundwater from site the plume migration is retarded together with a lowering of the groundwater table near the artesian boreholes. Preventing the groundwater table from reaching the surface and seeping.

There is a potential risk to contaminate down stream surface water bodies during a flood event especially down gradient of Dam1.

12 REFERENCES

Baran, E. 2003. *An Explanation of the 1:500 000 General Hydrogeological Map.* Pretoria : Department of Water Affairs and Forestry, 2003.

Chiang, W H and Kinzelbach, W. 2001. *Processing Modflow for Windows version 5.3.* 2001.

DWAE. (Sited August 2009) Hydrology. *Hydrological Services.* available from http://www.dwaf.gov/hydrology.

DWAF a. 1996. South African water Quality Guidelines, domestic use. Pretoria : s.n., 1996. Vol. Volume 1.

DWAF b. 1996. South African water Quality Guidelines, Livestock watering. Pretoria : s.n., 1996. Vol. Volume 1.

Farr, T G. 2007. The Shuttle Radar Topography Mission Rev. Geophys., 45, RG2004,. (Internet) available from http://www2.jpl.nasa.gov/srtm/.

Fetter, C W. 2001. *Applied Hydrogeology 4th Ed.* Englewood Cliffs, NJ : Prentice Hall, 2001.

Harbaugh, A W and McDonald, M G. 1996. *User's documentation for MODFLOW-96, an update to the U.S. Geological Survey modular finite-difference ground-water flow model.* s.l. : U.S. Geological Survey, 1996. Open-File Report 96-485, 56 p..

Kruseman, G. P. and de Ridder, N. A. 1990. *Analysis and evaluation of pumping test data.* Wagningen : International Institute for Land Reclamation and Improvement. The Netherlands, 1990. 2nd ed ILRI publication ; 47.

Mandle, R J. 2002. *Groundwater Modeling Guidance.* s.l. : Groundwater Modeling Program Michigan Department of Environmental Quality, 2002.

Rodriguez, E., et al. 2005. *An assessment of the SRTM topographic products Technical Report JPL D-31639.* Pasadena, California. : s.n., 2005.

SANS. 2006. *Drinking water standard Ed. 6.1.* [Standard] Pretoria : Standards South Africa, 2006. ISBN 0-626-18876-8.

Soil Classification Working Group. 1991. *Soil Classification- A taxonomic system for South Africa, memoirs on the Agricultural Natural Resources of South Africa No. 15.* Pretoria : Soil and Irrigation Institute, Department of Agricultural Development, 1991.

van Tonder, G., Kunstmann, H. en Xu, Y. 2000. FC-Method. Bloemfontein : Institute for Groundwater Studies, 2000. Vol. Version 2.

van Tonder, G.; Xu, Y. 2000. RECHARGE program to Estimate Groundwater Recharge. Bloemfontein : Institute for Groundwater Studies, 2000.

Visser, D.J.L., et al. 1989. *Explanation of the 1:1000000 geological map,fourth edition, 1984: the geology of the Republics of South Africa, Transkei, Bophuthatswana,Venda and Ciskei and the Kingdoms of Lesotho and Swaziland.* Pretoria : The Government Printer, 1989.

Warren and Root. 1963. Warren-Root's straightline methods. [book auth.] G.P. Kruseman and N.A. de Ridder. *Analysis and evaluation of pumping test data.* s.l. : International Institute for Land Reclamation and Improvement, The Netherlands, 1963.

Waterloo. 2005. Aquifer Test Pro.

Zheng, C and Wang, P. 1999. *MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulationof Advection, Dispersion, and Chemical Reactions of Contaminants in Gro.* s.l. : U.S. Army Corps of Engineers ; monitored by U.S. Army Engineer Research and Development Center., 1999. no.SERDP-99-1.

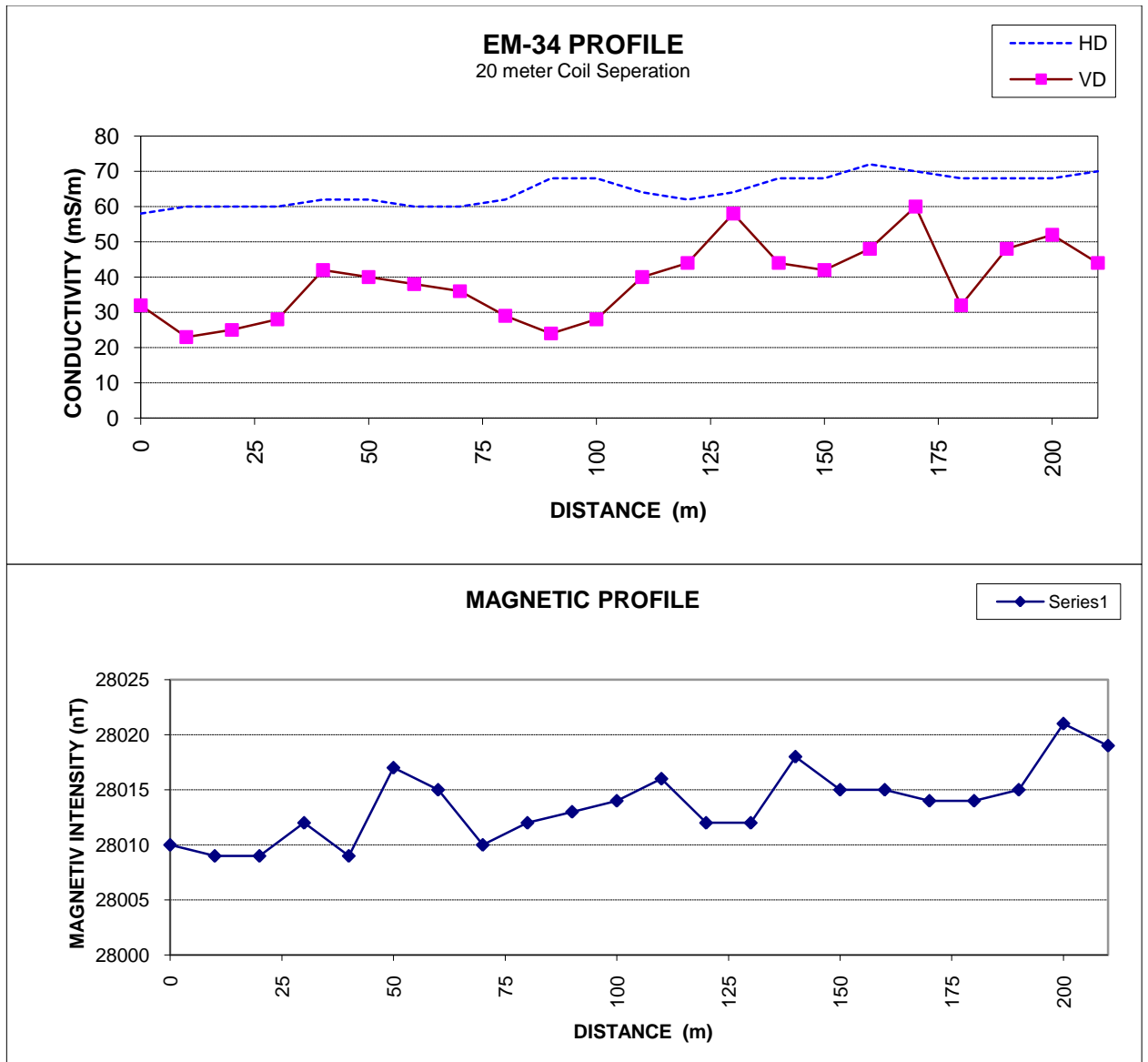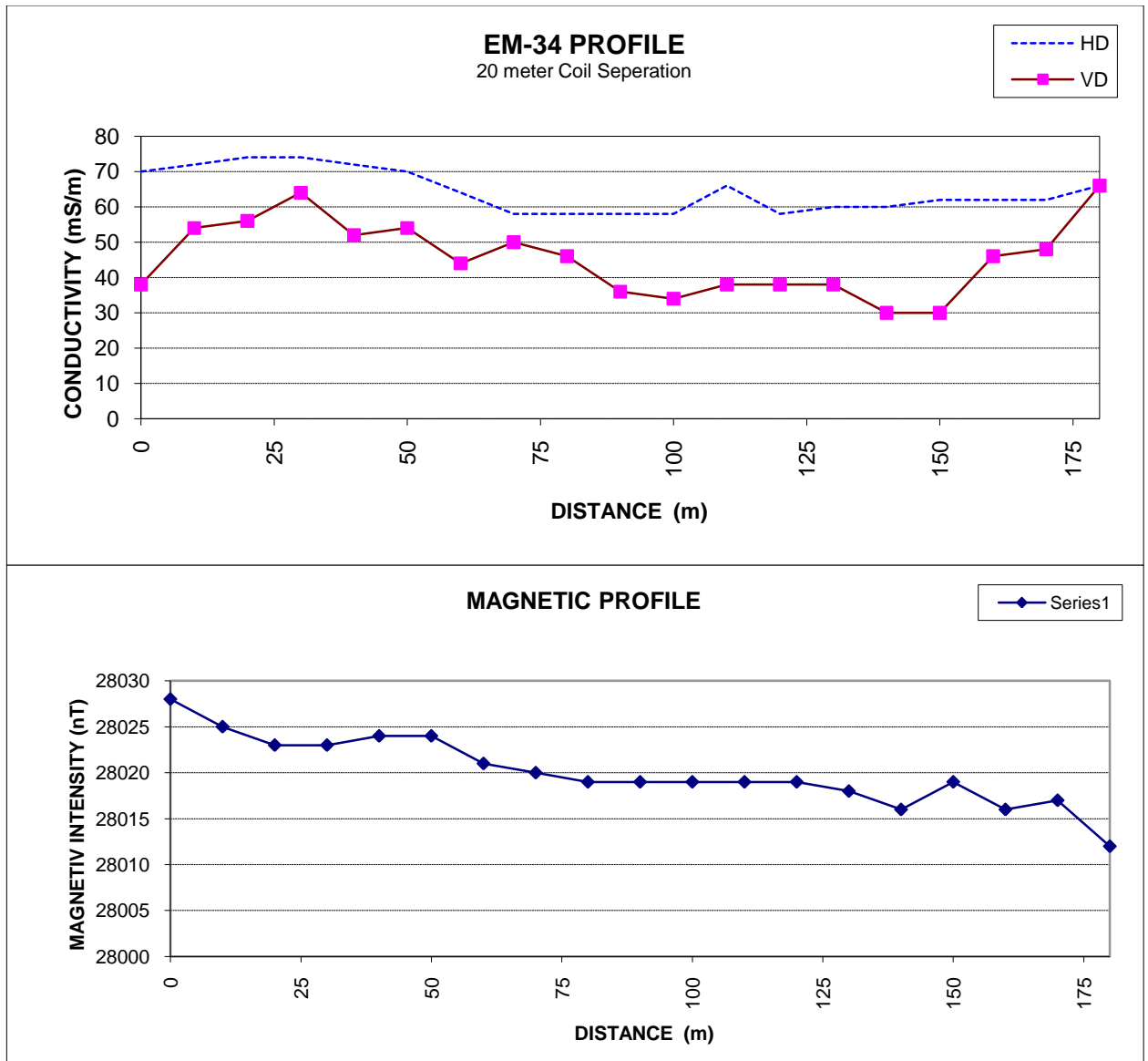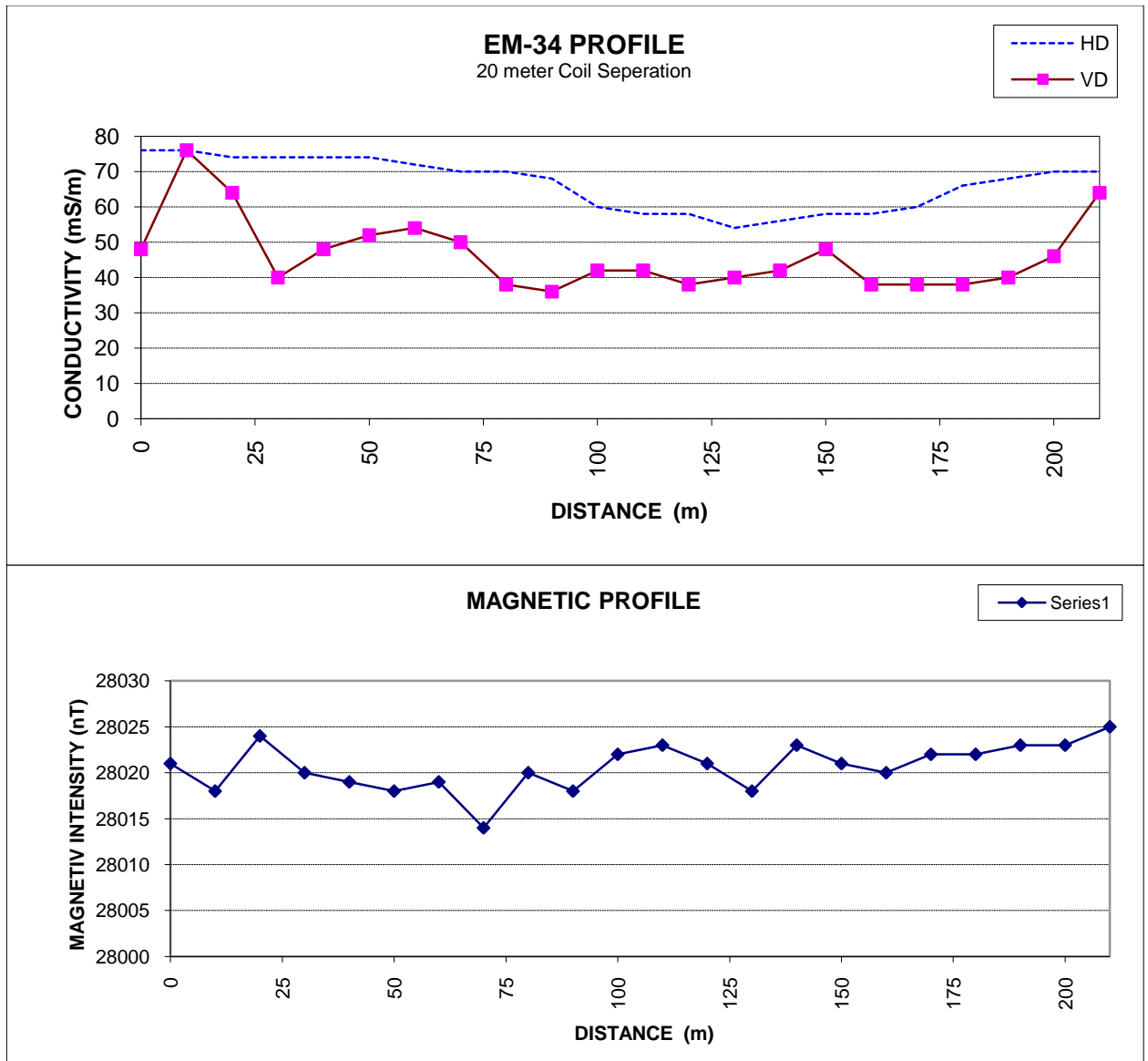# APPENDIX A

RESULTS OF THE GEOPHYSICAL SURVEY

Reactive transport modelling of fertilizer waste in a dual porosity aquifer
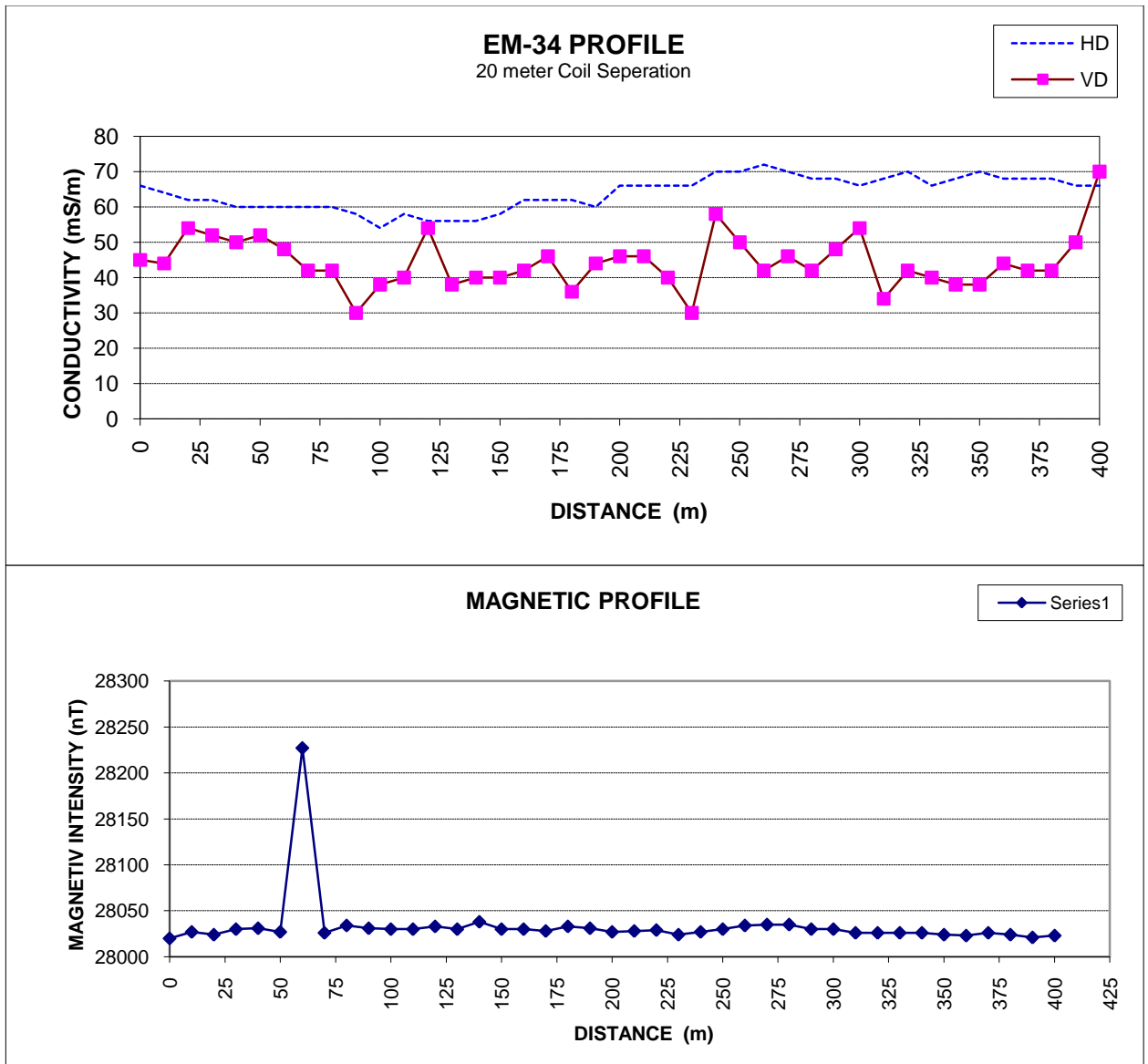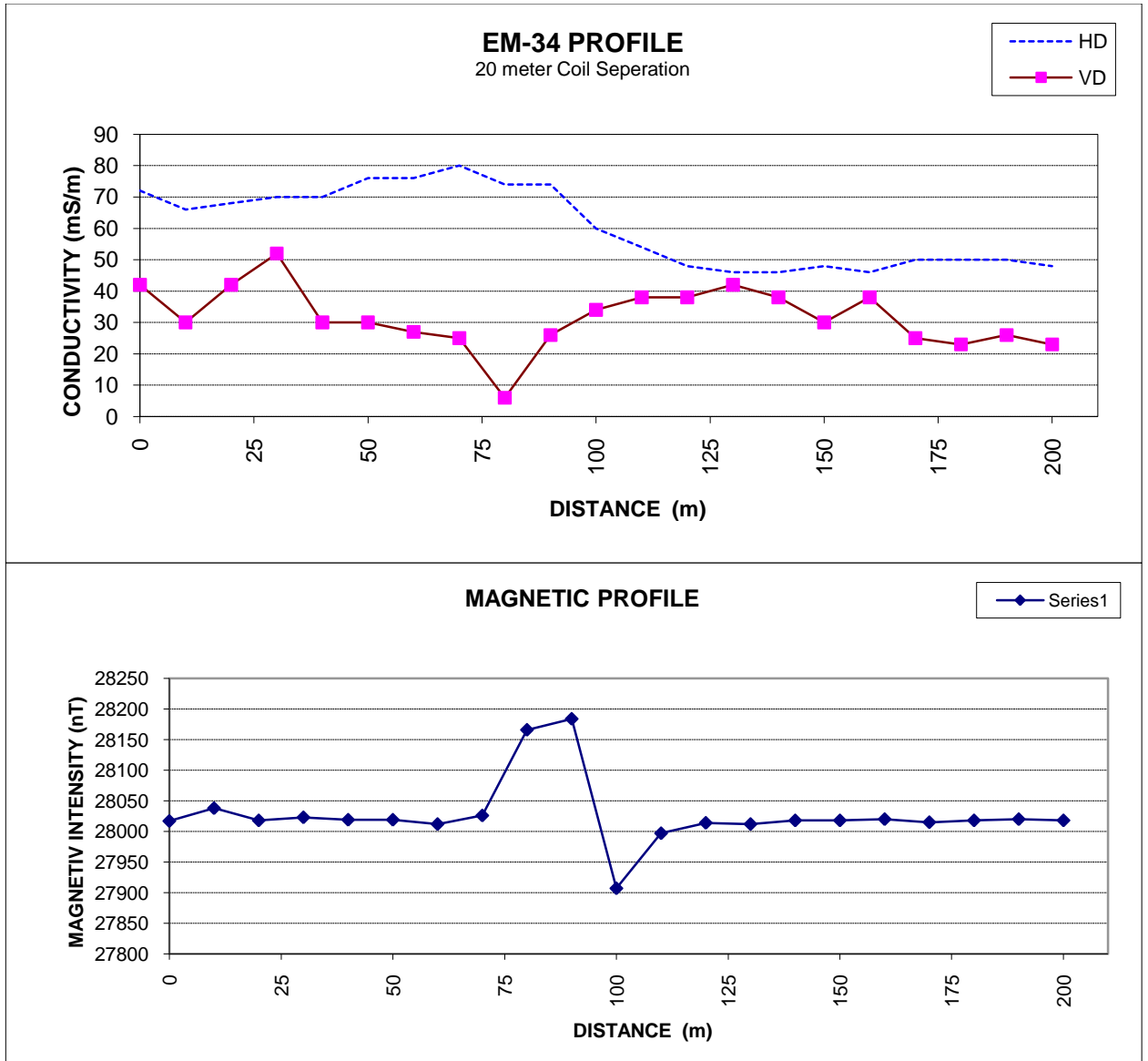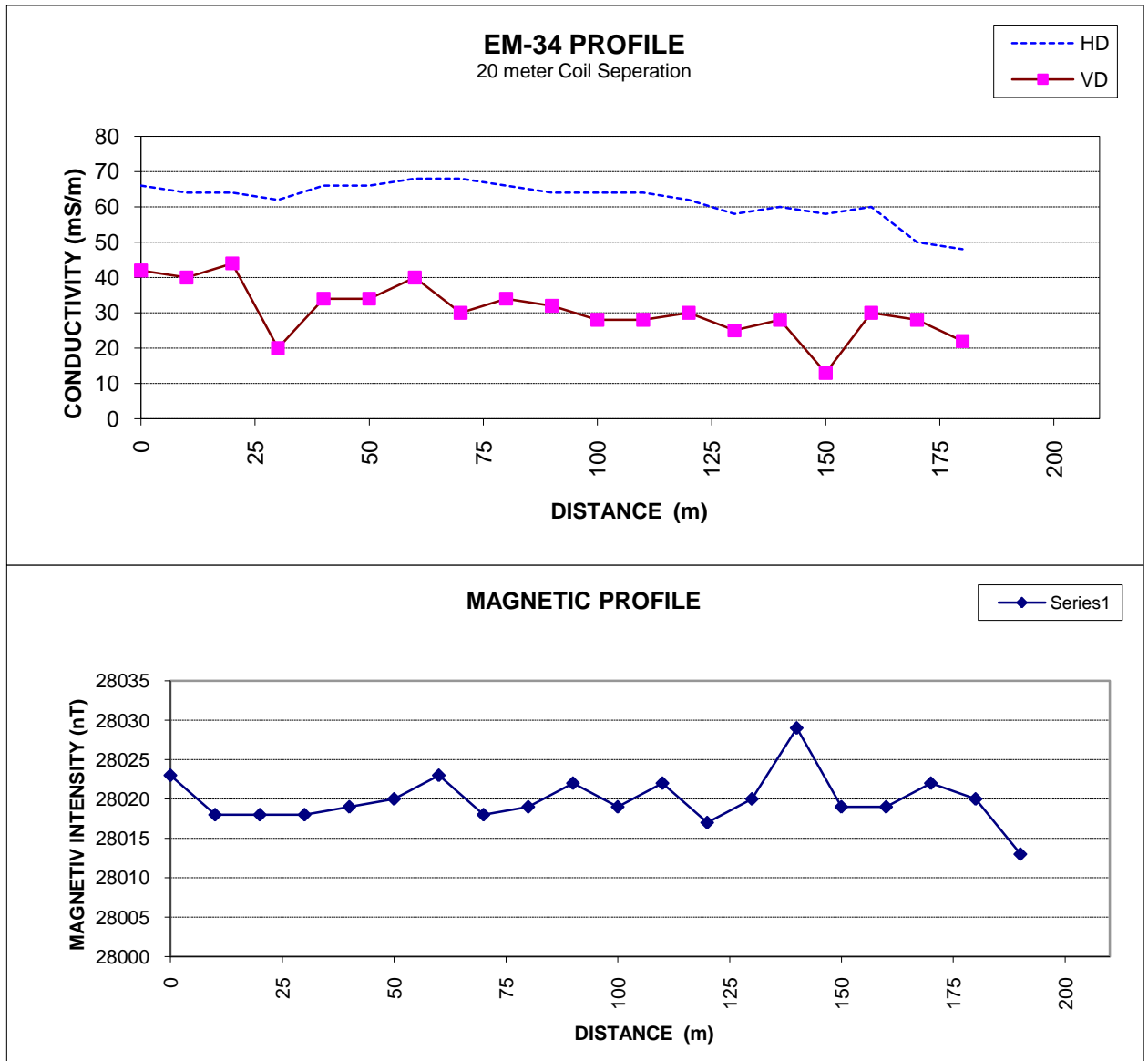
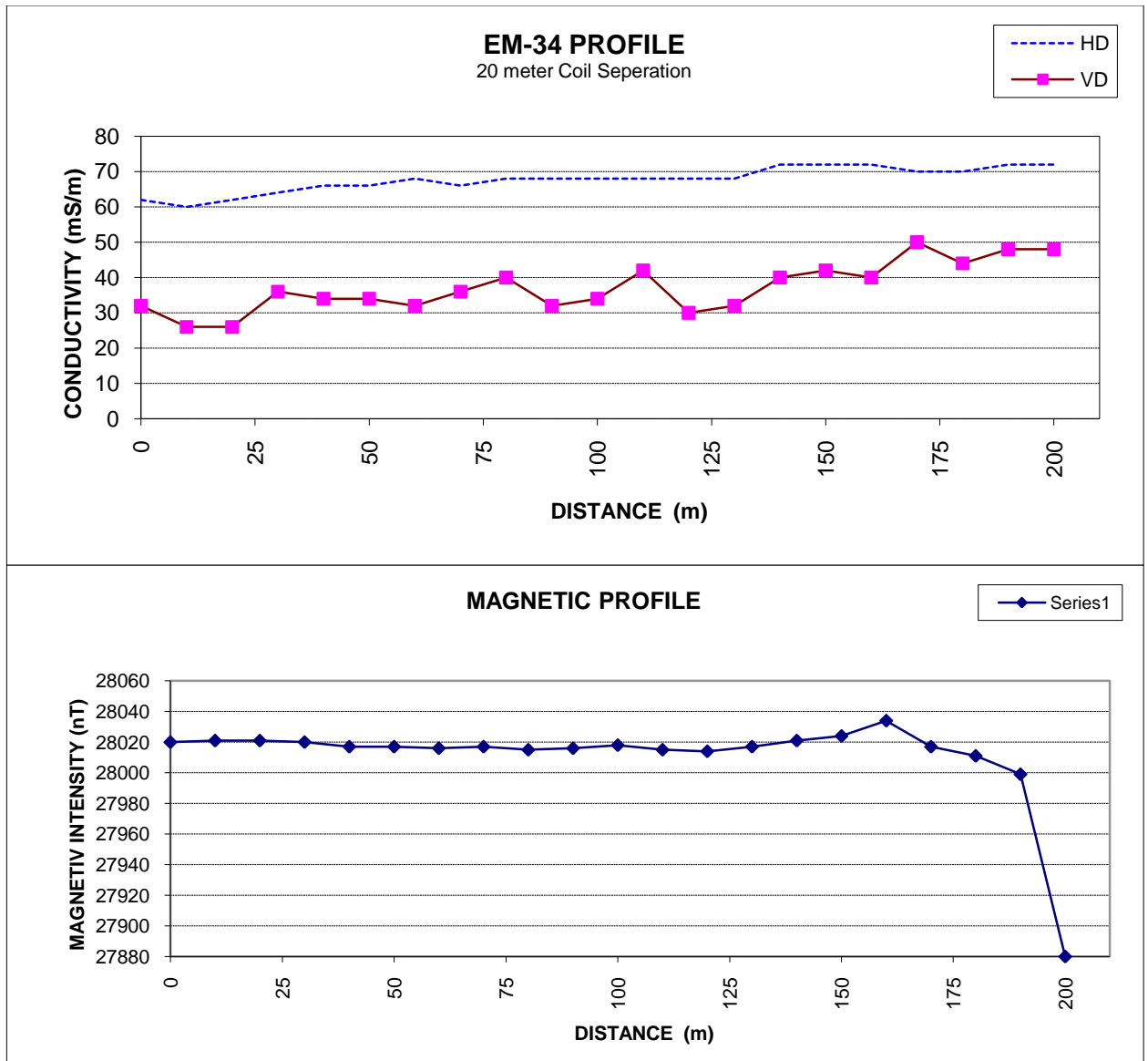# Traverse 1
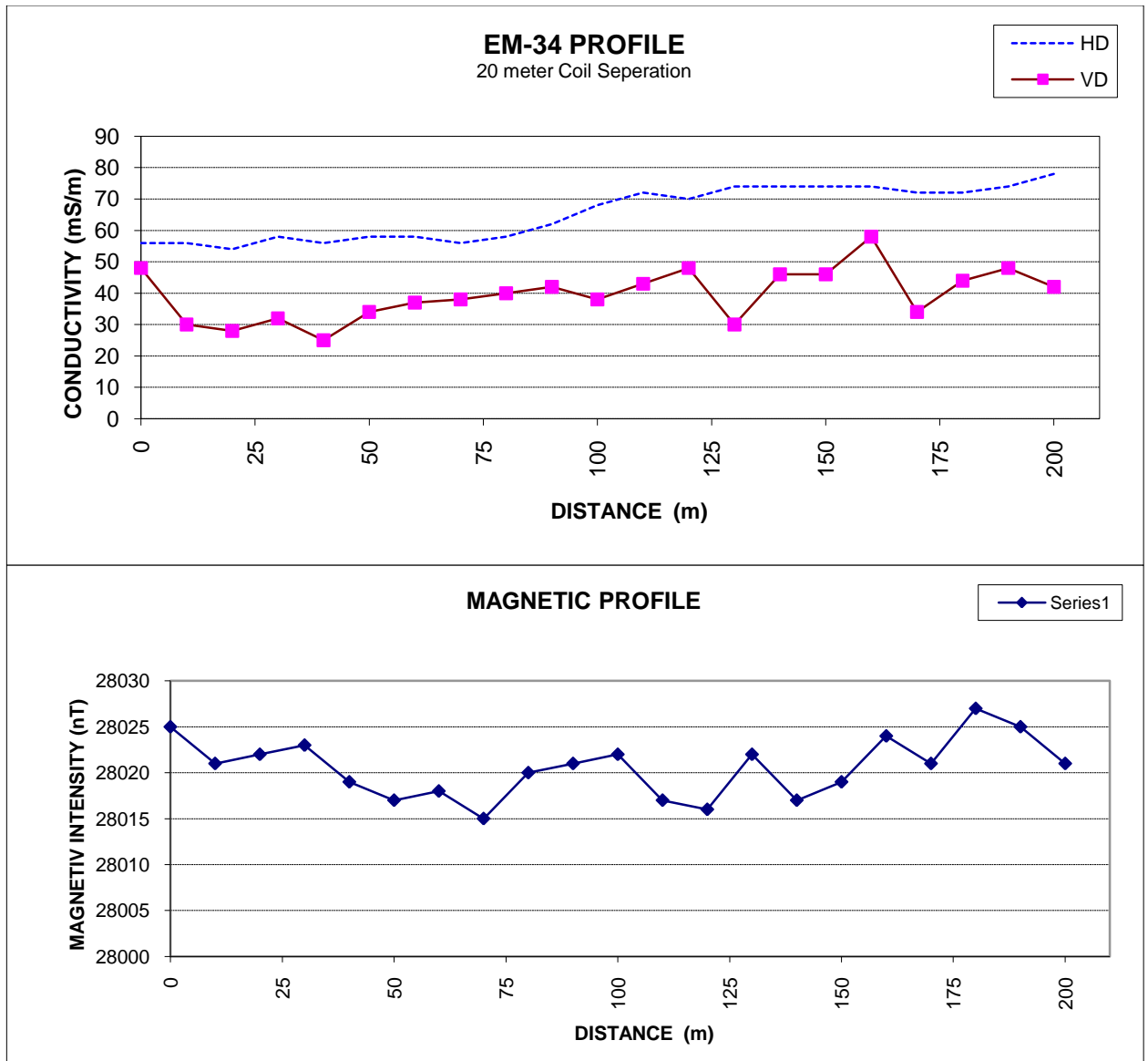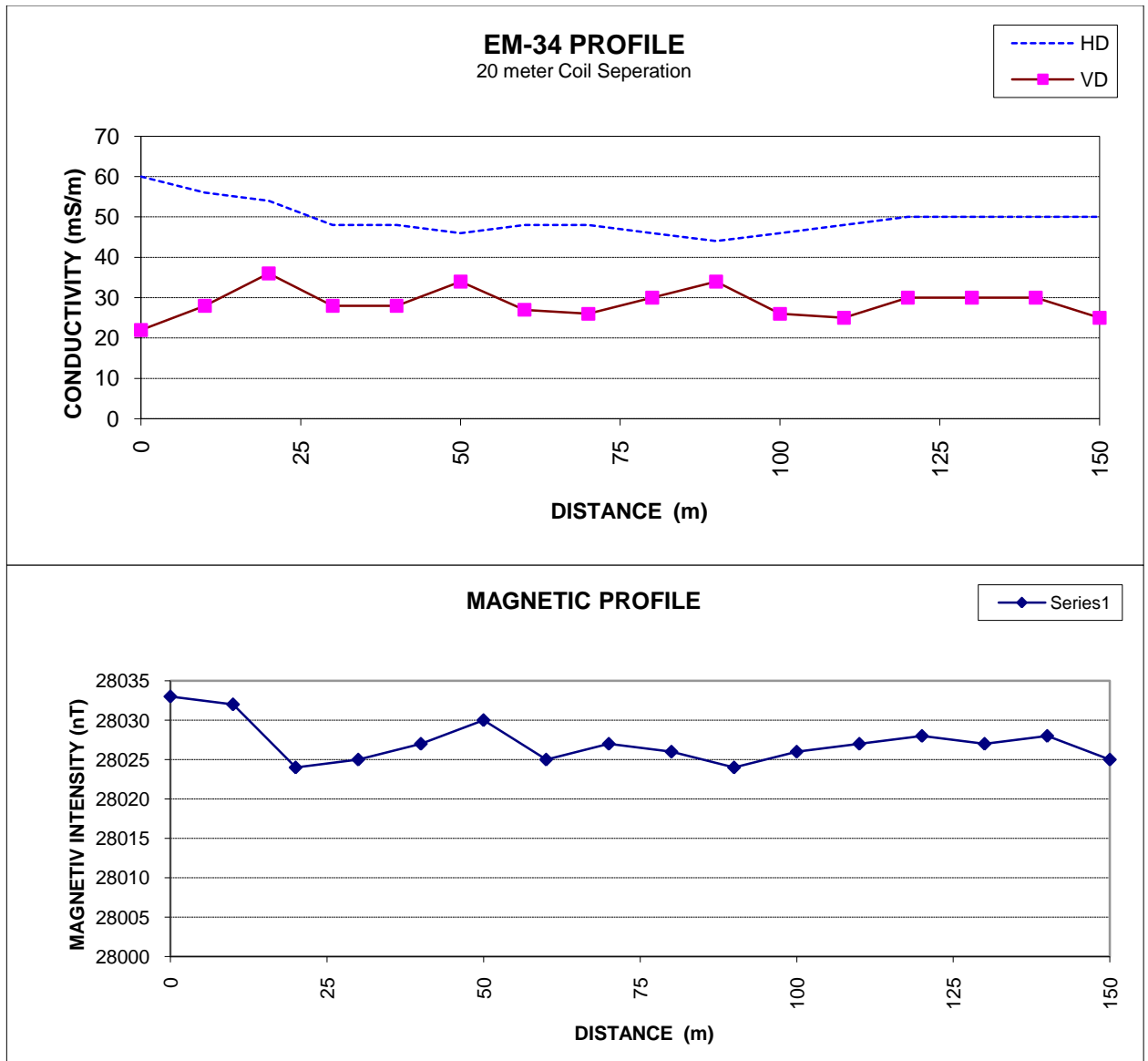
Traverse 2

Traverse 3

Traverse 4

Traverse 5

Traverse 6

Traverse 7

Traverse 8

Traverse 9

Traverse 10

Traverse 11

EM-34 PROFILE
20 meter Coil Seperation

- - - HD
■ VD

CONDUCTIVITY (mS/m) vs DISTANCE (m)

MAGNETIC PROFILE

◆ Series1

MAGNETIV INTENSITY (nT) vs DISTANCE (m)

Traverse 12

EM-34 PROFILE
20 meter Coil Seperation

MAGNETIC PROFILE
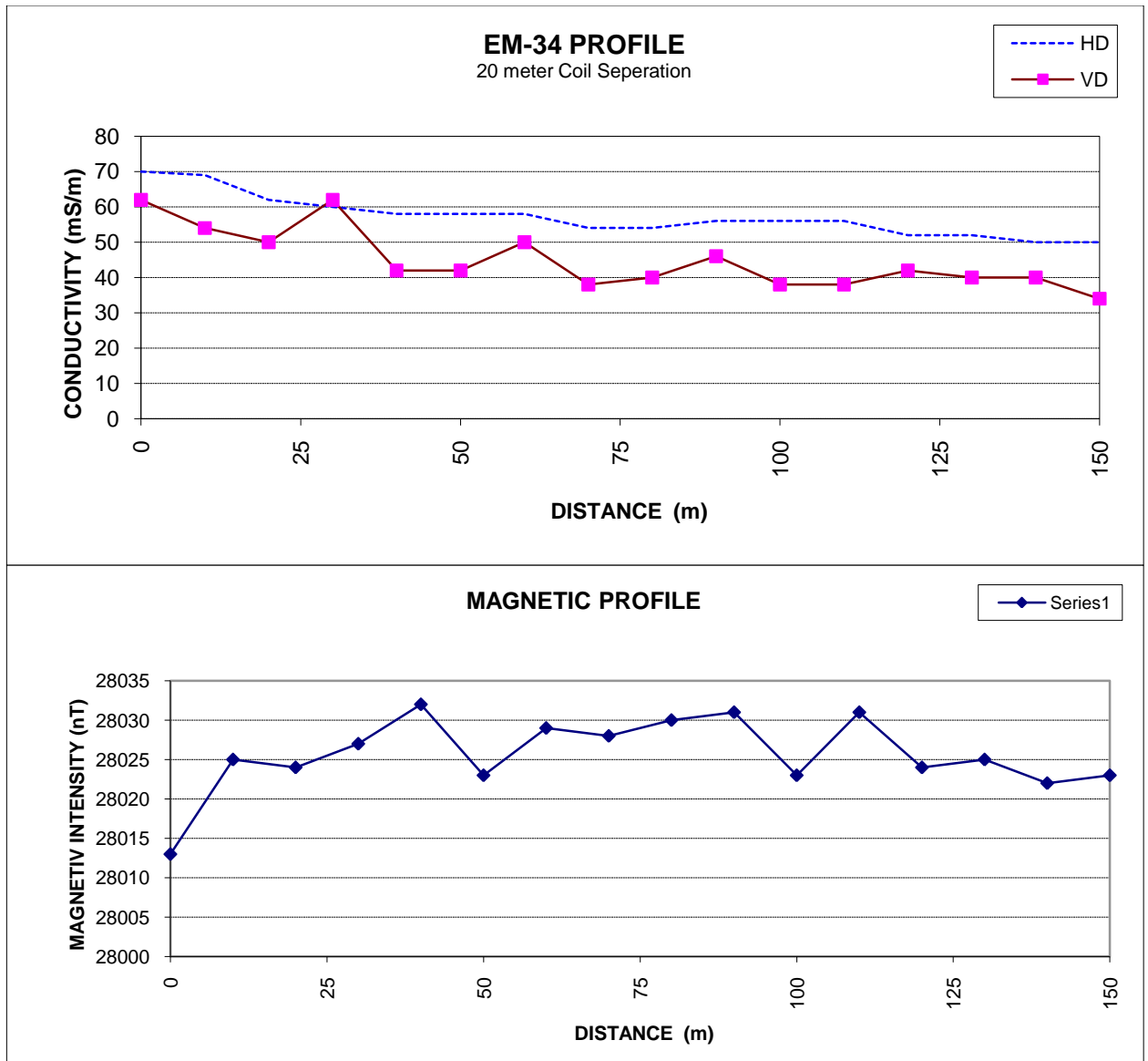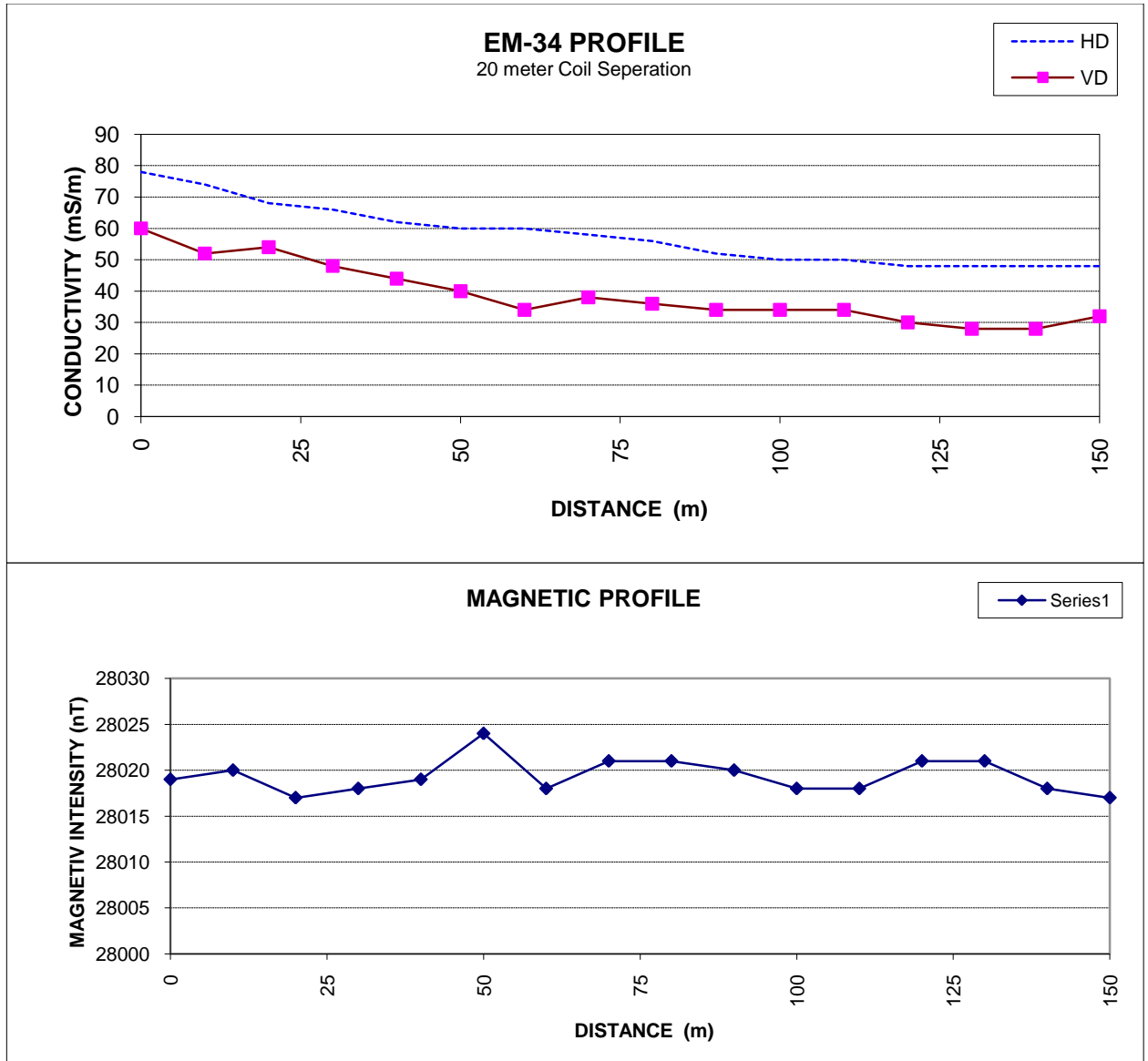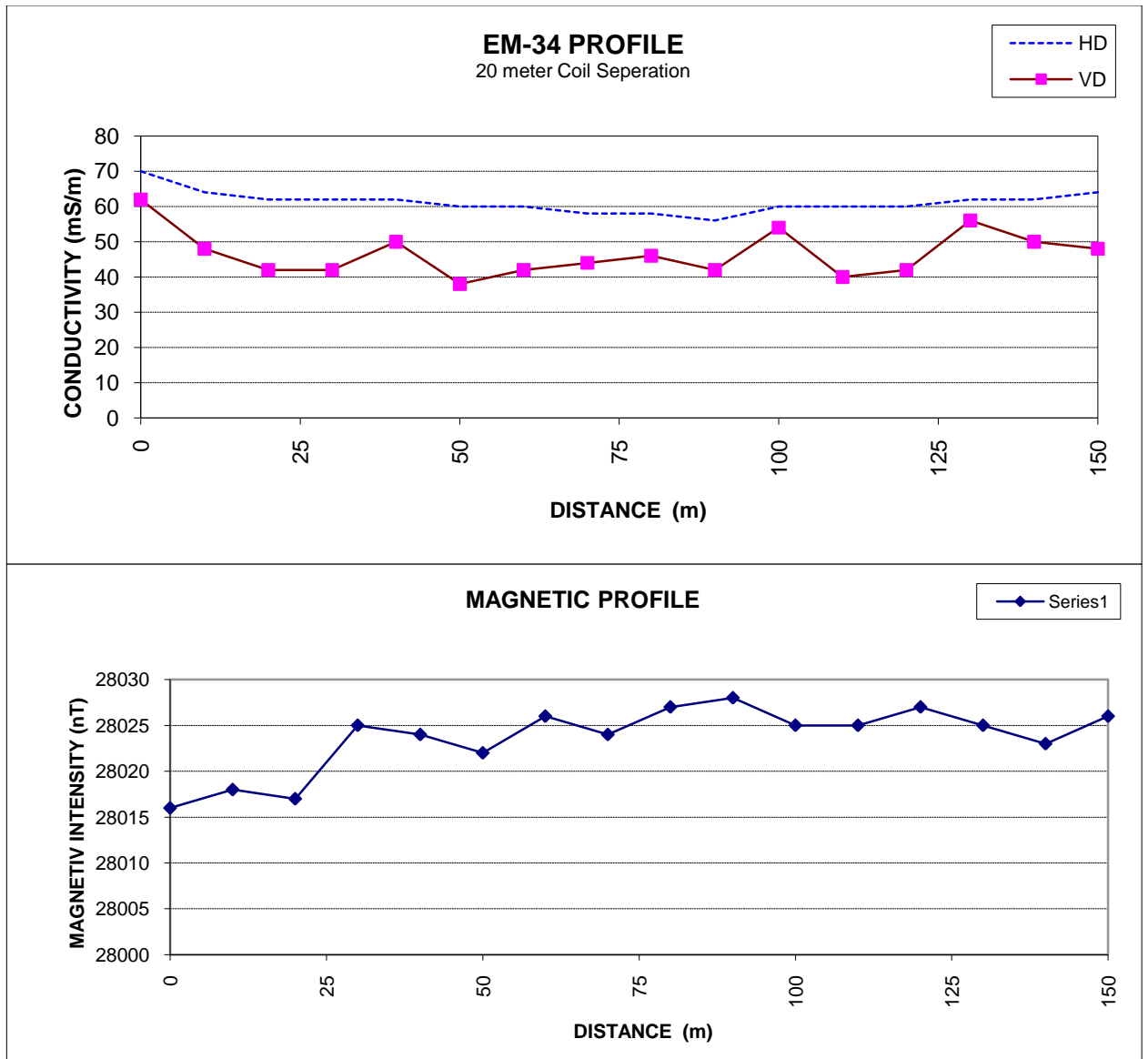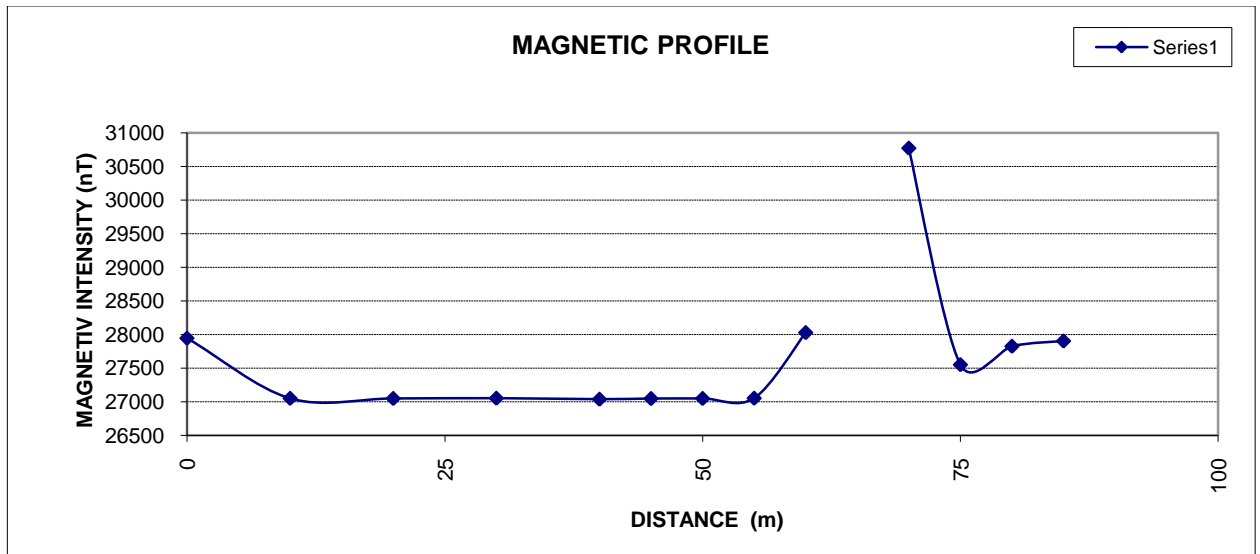
Traverse 13

Abstract

The fertilizer production facility had a negative impact on the soil, groundwater and surface water environment due to the handling / storage and production activities at the site. Observations and numerical modelling found the fertilizer product loadings areas as the main source area of contaminants viz. Ca, Mg, NO_3, Cl, SO_4, EC and TDS. Uncontrolled run-off emanating from the site is a major contributing factor to contaminating the groundwater and surface water resources.

A distinct difference could be observed between the geochemical signature of the potential contaminated seepage and that of the groundwater. This geochemical characterisation of the contaminant plume identified an interaction of the leachate and the soil with a high clay (montmorillonite) content, with various cation exchange and sorption processes occurring. Potassium is largely exchanged (for sodium), while phosphates are likely to sorbed on the clay particles. Nitrate is likely to be retarded to a limited extent, especially when redox conditions are conducive to the conservation of the nitrate specie. The elevated contaminant concentrations pose a health risk to potential users and livestock which may ingest the water, especially nitrate concentrations.

Numerical modelling was used to validate and develop the site conceptual model. Iterative modelling improved the initial correlation R^2 of modelled and observed nitrate concentrations, the correlation improved from 0.29 to 0.64. The model was validated by assuming that horizontal and bedding plan fractures are likely to play a role in contaminant transport (which was not modelled). Artificial recharge (seepage and leachate infiltration) was present at the plant area. Groundwater abstraction from farmers boreholes downstream had an influence on the development of the nitrate plume. Surface water contamination contributed to the current plume geometry and therefore partly responsible for the current plume extent. A secondary groundwater contaminant source was found in the south western part of the study area. Predictive modelling found abstraction of groundwater from site to be the most effective containment measure when compared to a cut-off trench. The groundwater contamination is likely to pose a low current and future risk to groundwater users, as no current groundwater users are found in proximity to the site and the contaminant plume. However a potential surface contaminant risk does occur to down stream surface water bodies during a flood event.

Uitreksel

Die kunsmis vervaardigings fasiliteit het 'n negatiewe impak op die grond, grondwater en oppervlakwater omgewing as gevolg van die hantering / stoor-en produksie-aktiwiteite op die terrein. Waarnemings en numeriese modellering het gevind dat die kunsmis laai gebiede die hoof bron van kontaminante nl. Ca, Mg, NO_3, Cl, SO_4, EC en TDS is. Onbeheerde opervlak water vloei afkomstig van die terrein is 'n groot bydraende faktor tot die besoedeling van die grondwater en oppervlakwater hulpbronne.

'n Duidelike verskil tussen die geochemiese eienskappe van die potensiële besoedelde loog water en die van grondwater kan waargeneem word. Hierdie geochemiese karakterisering van die besoedelings pluim dui aan dat daar 'n interaksie tussen die loog water en die grond met 'n hoë klei (montmorilloniet) inhoud geïdentifiseer is. Verskeie katioon-uitruiling en sorpsie prosesse vind plaas. Kalium word grootliks gewissel (met natrium), terwyl fosfate geneig is om op die klei deeltjies te adsorbeer. Nitraat word waarskynlik tot 'n beperkte mate vertraag, veral wanneer redox kondisies bevorderlik is vir die bewaring van die nitraat spesie. Die verhoogde kontaminant konsentrasies skep 'n risiko vir die gesondheid vir potensiële gebruikers en vee wat die water inneem (veral nitraat konsentrasies).

Numeriese modellering is gebruik om die terrein konseptuele model te kontroleer en te ontwikkeling. Iteratiewe modellering verbeter die aanvanklike korrelasie R^2 van die gemodelleerde en waargeneemde nitraat konsentrasies. Die aanvanklike korrelasie van 0,29 het verbeter na 0,64. Die model is gevalideer deur die veronderstelling dat horisontale en naatvlak frakture geneig is om 'n rol speel in die besoedelings vervoer (wat nie gemodelleer is nie). Kunsmatige aanvulling (loging en infiltrasie) was teenwoordig in die aanleg area. Die onttrekking van grondwater stroom-af van die terrein uit die boere se boorgate het 'n invloed gehad op die ontwikkeling van die nitraat pluim. Oppervlakwaterbesoedeling het grootliks bygedra tot die huidige grondwater besoedelings pluim en dus deels verantwoordelik vir die huidige pluim ontwikkeling. 'n Sekondêre grondwater besoedelings bron is gevind in die suid westelike deel van die studie area. Voorspellende modellering het gevind dat onttrekking van grondwater op terrein die mees effektiewe vorm van pluim inperking is, in vergelyking met 'n afsny sloot. Die grondwater besoedeling het waarskynlik 'n lae huidige en toekomstige risiko in terme van impak op grondwater-gebruikers; aangesien daar geen huidige grondwater gebruikers gevind word in die nabyheid van die terrein en die besoedelings pluim. Daar is egter 'n potensiële oppervlakte besoedelings risiko na benede strome en oppervlakwater liggame tydens 'n vloed gebeurtenis.

keywords:

Fertilizer related contaminants, nitrate, contaminant transport, numerical modelling, seepage, groundwater, surface water, contaminant risk, predictive modelling