# Impact of Fertilizer Effluent Disposed in Dolerite Quarries on the Groundwater Quality

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**Abstract**

Coal-based fertilizer effluent with high concentrations of nitrate (>12 500 mg/L), ammonium (>11 900 mg/L) and sulphate (>2 500 mg/L) from a coal-based fertilizer plant was stored in two unlined dolerite quarries. This resulted in the degradation of the groundwater quality in a nearby borehole to a state that is not suitable for human or animal consumption. Elevated nitrate concentrations in groundwater are a concern because, when ingested by infants, it could potentially interfere with the blood-oxygen levels and cause methemoglobinemia (blue baby syndrome). A Geohydrological investigation was therefore initiated to quantify the impact of the fertilizer effluent on the groundwater regime.

A hydrocencus was conducted to determine if other boreholes in the vicinity of the quarries had elevated nitrate, ammonium or sulphate concentrations. A geophysical survey was also conducted to understand the geological regime by identifying geological structures that may influence the movement and act as preferential pathways for groundwater. The geophysical survey included a detailed magnetic survey that consisted of 30 profiles at line spacing of 200 m, and with average lengths of approximately three kilometres. Where areas of interest were identified from the interpretation of the magnetic data, two-dimensional (2D) electrical resistivity tomography (ERT) surveys was conducted to obtain a model of the subsurface resistivity distribution.

The magnetic survey revealed a well-defined linear magnetic anomaly corresponding to the position of a mapped dolerite dyke less than 200 m from the Fertilizer Quarry. A broad linear zone of increased magnetic field strength with a south-east/north-west strike was also identified. The hydrocencus identified boreholes situated along these structures that are highly contaminated with nitrate. It is therefore plausible that these lineaments acts as preferential pathways for groundwater flow and contaminant transport from the quarries.

The quarries have been rehabilitated since the investigation was initiated. Thus, if there is no natural attenuation of nitrate in the groundwater regime over time, the results of the geophysical investigations will then be used to identify five sites for the drilling of boreholes to investigate the geological and geohydrological conditions in the vicinities of the quarries. All the geological and geohydrological information gathered will be used during the feasibility phase of the study to determine the most feasible option to remediate or manage the contamination of the groundwater regime.

Key words: Fertilizer effluent, preferential pathways, hydrocencus, geophysical surveys, natural attenuation

## Introduction

Coal-based fertilizer effluent with high concentrations of nitrate (>12 500 mg/L), ammonium (>11 900 mg/L) and sulphate (>2 500 mg/L) from a coal-based fertilizer plant (production of fertilizer based on coal gasification) was stored in two unlined dolerite quarries (labelled Fertilizer Quarry & Farmhouse Quarry). This resulted in the degradation of the groundwater quality of the underlying aquifer to a state that is not suitable for human or animal consumption. Elevated nitrate concentrations in groundwater are a concern because, when ingested by infants, it could potentially interfere with the blood-oxygen levels and cause methemoglobinemia (blue baby syndrome). A Geohydrological investigation was therefore initiated to quantify the impact of the fertilizer effluent on the groundwater regime.

**Objectives**

The objective of the investigation is to (1) understand the geological regime by identifying geological structures that may influence the movement/flow of groundwater, (2) understand the geohydrological regime (aquifer parameters), (3) determine the extent by which the underlying aquifer have been effected by contaminants and (4) determine the most feasible option for remediation if there is no natural attenuation.

**Materials and Methods**

A hydrocencus was conducted to determine the extent by which the underlying aquifer have been affected. This involved the identification, sampling and chemical analyses of boreholes in a ten kilometres radius from the two dolerite quarries that was filled with fertilizer effluent.

Two geophysical techniques were employed during the investigation, namely the ground magnetic method electrical resistivity tomography (ERT). The ground magnetic survey consisted of 30 profiles at line spacing of 200 m, and with average lengths of approximately three kilometres (fig. 1). The ERT survey consisted of three profiles across the mapped dolerite dyke situated near the dolerite quarry labeled as Fertilizer Quarry. The ERT survey made use of the Lund Imaging System developed by ABEM Instruments. Four cables with 21 take-outs each and a standard electrode spacing of 5 m were employed to allow a maximum depth of investigation of approximately 70 m.

A quarterly groundwater monitoring programme was also initiated to monitor the quality of the boreholes that have been affected by the dolerite quarries filled with fertilizer effluent over time. This is to monitor if there is any natural attenuation of the contaminants in the underlying aquifer.

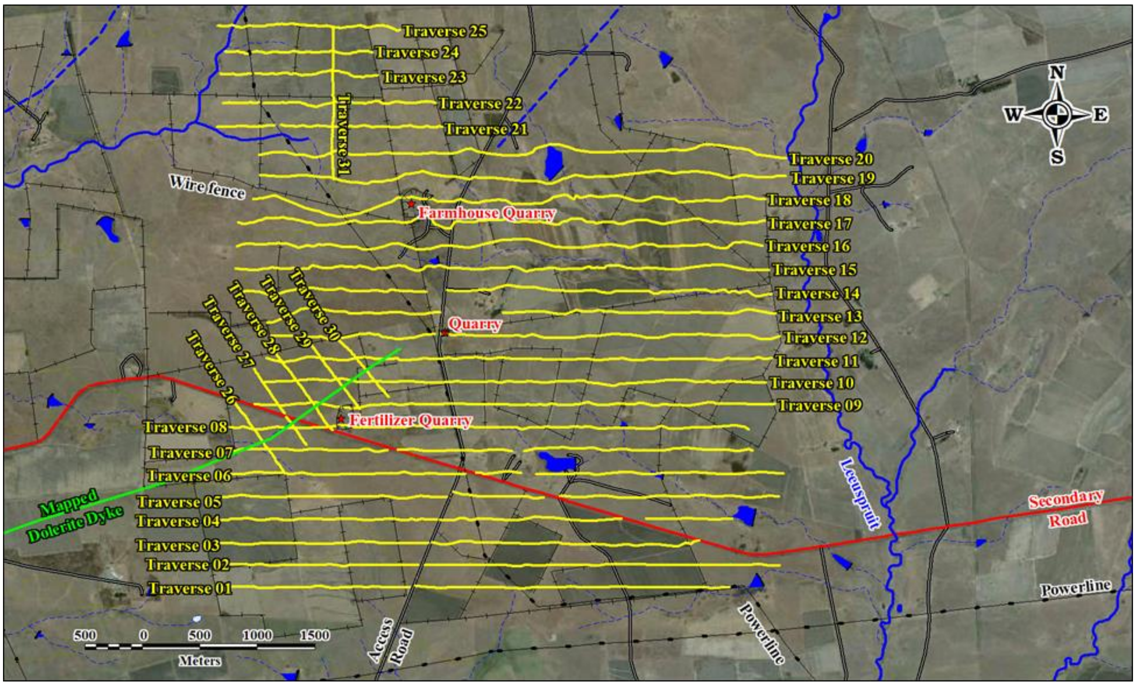


***Figure 1*** *Position and orientations of the traverses on which ground magnetic data were recorded.*

**Nitrogen in the Environment**

Nitrogen is present in the environment in a wide variety of chemical forms including organic nitrogen, ammonium ($NH_4^+$), nitrite ($NO_2^-$), nitrate ($NO_3^-$), nitrous oxide ($N_2O$), nitric oxide (NO) or inorganic nitrogen gas ($N_2$). Organic nitrogen may be in the form of a living organism, humus or in the intermediate products of organic matter decomposition. The processes of the nitrogen cycle transform nitrogen from one form to another.

This transformation can be carried out through both biological and physical processes. Important processes in the nitrogen cycle include fixation, ammonification, nitrification, and denitrification. The majority of Earth's atmosphere (78%) is nitrogen, making it the largest pool of nitrogen (Carrol & Salt 2004). However, atmospheric nitrogen has limited availability for biological use, leading to a scarcity of usable nitrogen in many types of ecosystems. The nitrogen cycle is of particular interest to ecologists because nitrogen availability can affect the rate of key ecosystem processes, including primary production and decomposition. Human activities such as fossil fuel combustion, use of artificial nitrogen fertilizers, and release of nitrogen in wastewater have dramatically altered the global nitrogen cycle (Galloway *et al.* 2004). The diagram below (fig. 2) shows processes of the nitrogen fit together to form the nitrogen cycle.

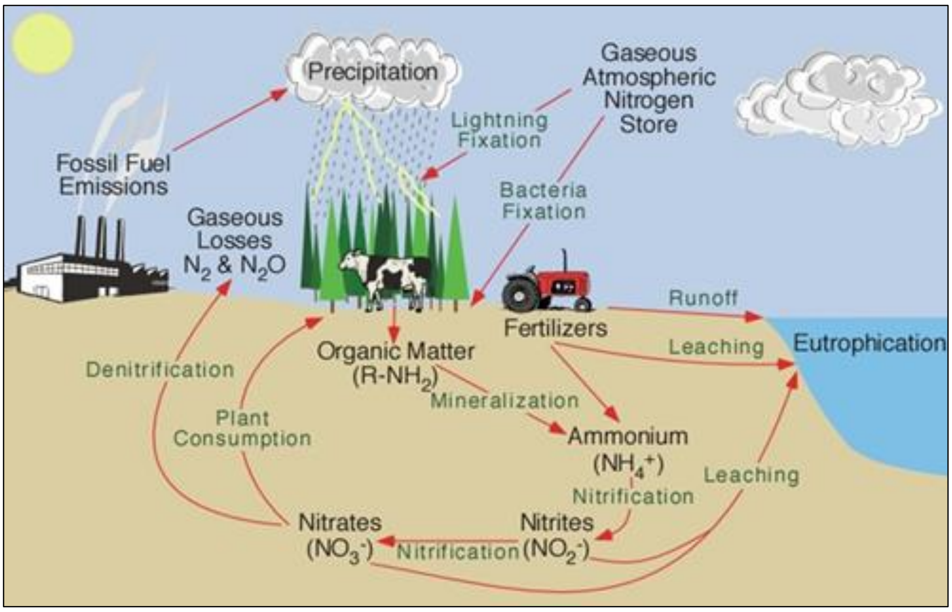


***Figure 2*** *The nitrogen cycle. (Source: PhysicalGeography.net)*

## Geological Setting

The 1:250,000 geological map presented (fig. 3) is the intellectual property of the Council for Geoscience and is used by permission. Copyright and all rights are reserved by the said Council.

The study area is mostly underlain by a massive dolerite sill intrusion. Sedimentary rocks belonging to the Vryheid Formation of the Ecca Group (Karoo Supergroup) are exposed in the central and eastern parts of the study area. These exposures occur at positions where the dolerite sill has been eroded away to reveal the underlying Karoo formations. The sedimentary rocks predominantly consist of sandstones and shales. Coal beds occur within the Vryheid Formation, but no coal exposures at surface are observed within the study area.

A dolerite dyke with an approximate south-west/north-east strike has been mapped in the south-western parts of the study area. In addition, a number of prominent magnetic lineaments with south-west/north-east strikes have been mapped in the vicinity of the study area. These lineaments are thought to be due to large dolerite dykes that do not appear as outcrops.

## Regional Magnetic Setting

The airborne magnetics map presented in this section is the intellectual property of the Council for Geoscience and is used by permission. Copyright and all rights are reserved by the said Council. From the airborne magnetics map (fig. 4) it is seen that prominent linear magnetic anomalies with south-west/north-east strikes occur to the west, north-west and north of the study area. These anomalies correspond to the magnetic lineaments shown in the geology map covering the study area (refer to fig. 3).

The mapped dyke does not yield a strong magnetic response in the airborne data. This observation suggests that the dyke is a much smaller feature than the dykes responsible for the large linear magnetic anomalies. A possible magnetic lineament with a south-east/north-west strike may be identified within the study area (black dashed line in fig. 4).

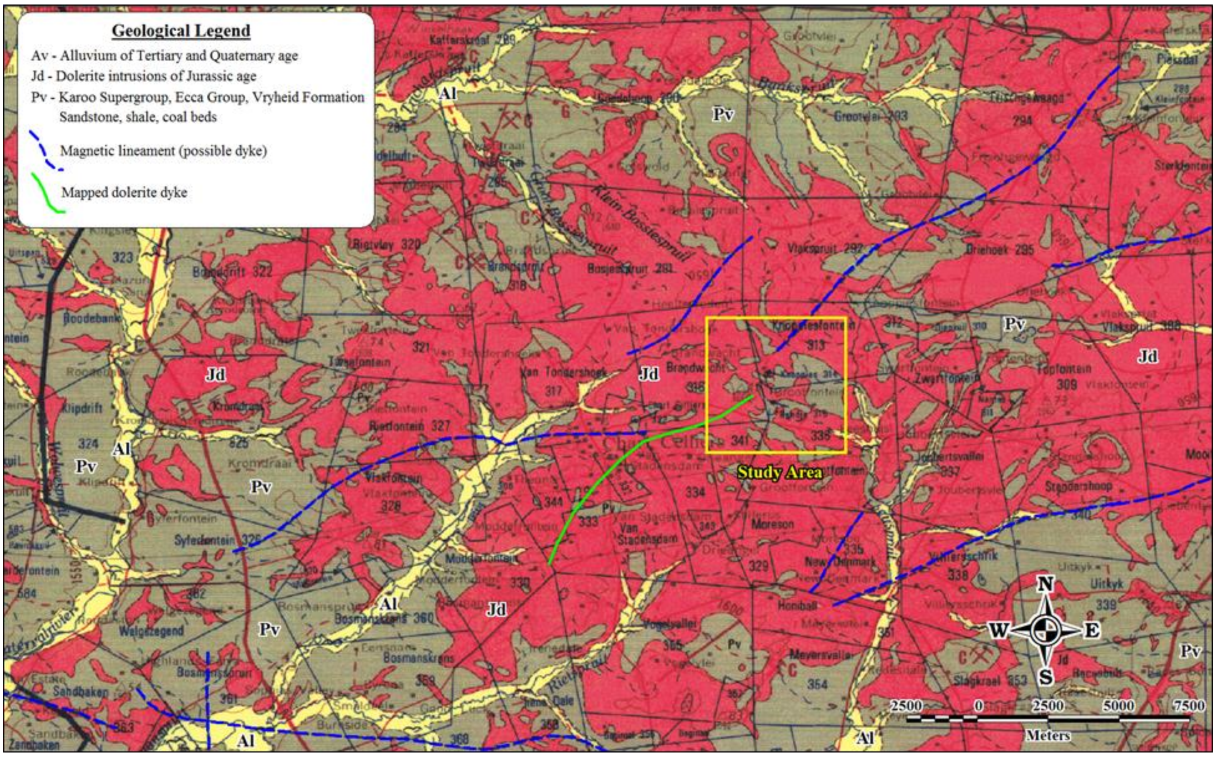


***Figure 3** Geological setting of the study area*

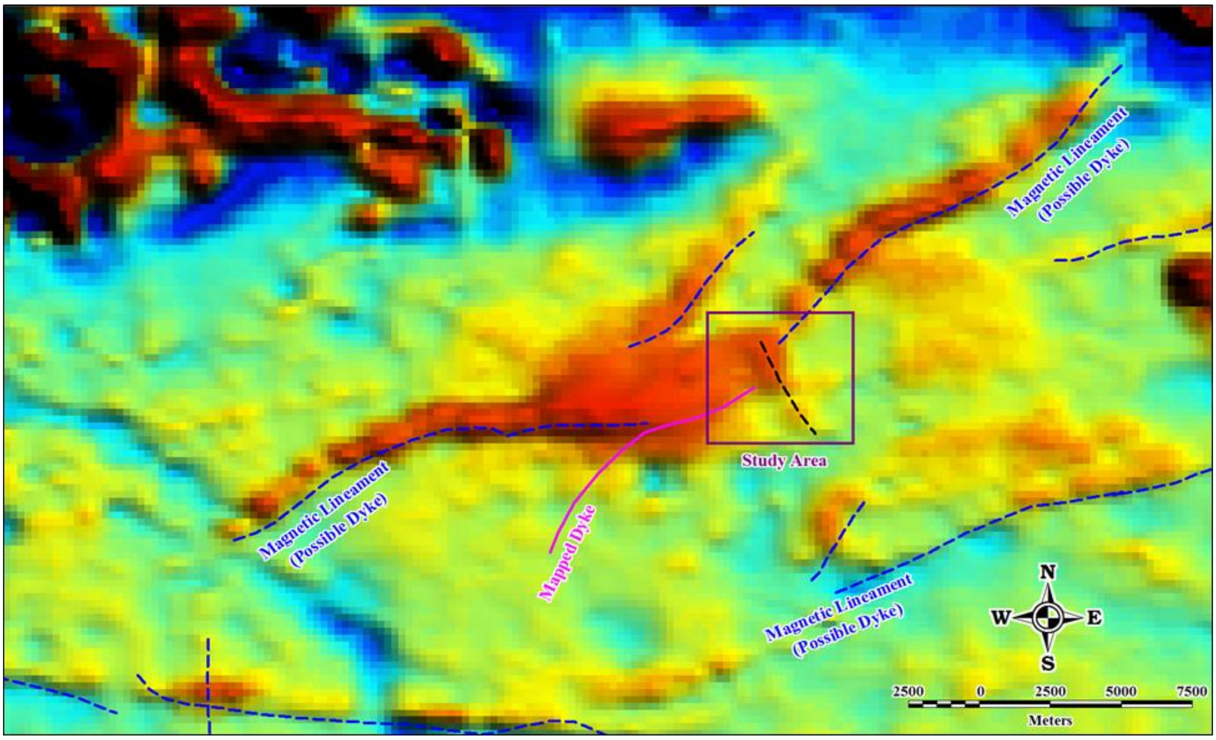


***Figure 4** Airborne magnetics map covering the study area.*

## Results and Discussion

A contour map of the total magnetic field is presented in (fig. 5). From the contour map, a number of observations may be made:

- A well-defined linear magnetic anomaly corresponds to the position of the mapped dolerite dyke. This dyke occurs at a distance of less than 200 m from the Fertilizer Quarry.

- A change in the magnetic field intensity is observed along a linear boundary with a south-east/north-west strike running between the Fertilizer Quarry and the Quarry. This apparent contact runs parallel to the linear magnetic anomaly identified from the airborne magnetics map (refer to fig. 4, indicated by the right-hand dashed white line in fig. 8). The broad linear zone of increased magnetic field strength demarcated by these lines may be a large linear dolerite intrusive, but may also be due to a local upwelling of the underlying dolerite sill. The Farmhouse Quarry occurs within this broad zone.
- A zone of low magnetic field intensity occurs to the east of the eastern contact of the broad zone of high magnetic field intensity (see fig. 5). This zone is in all probability due to the fact that the shallow sill has been eroded away at this position (refer to fig. 4), exposing the underlying, non-magnetic Karoo sedimentary rocks. This zone also corresponds to a change in the colour of the vegetation; within the zone, the vegetation appears to be greener.

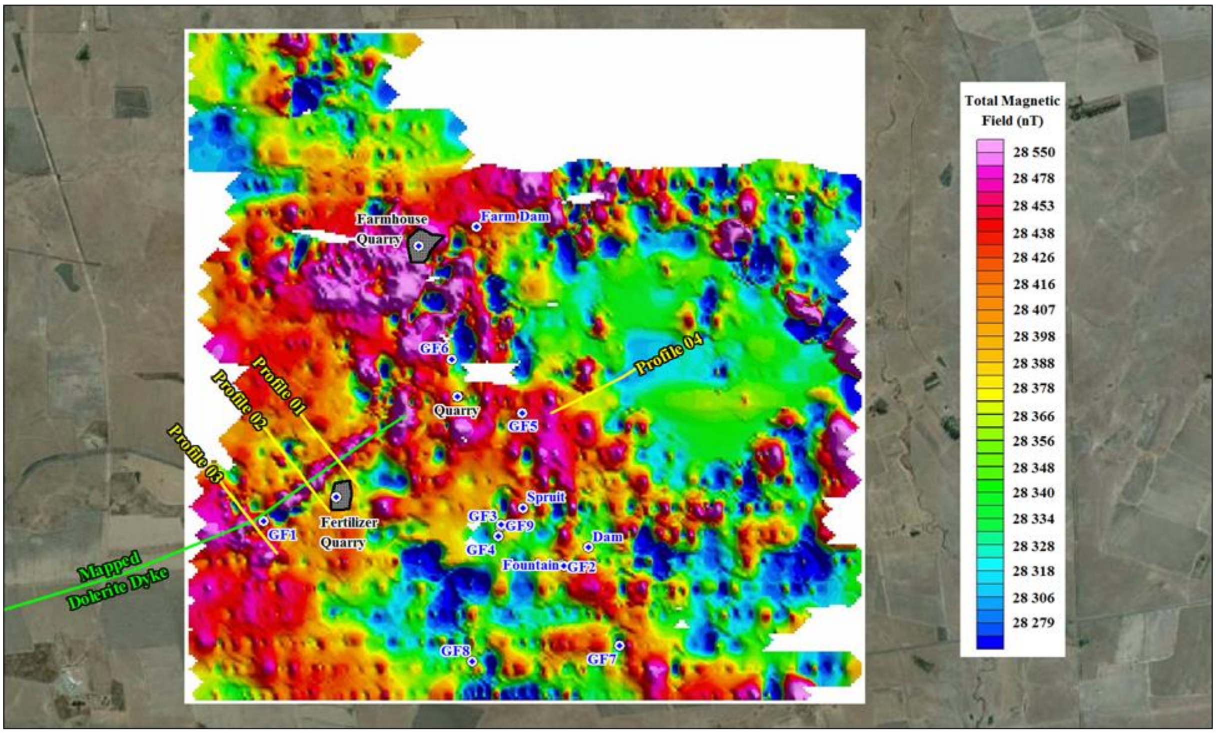


*Figure 5* *Contour map of the total magnetic field recorded during the ground magnetic survey and positions and orientations of the four ERT profiles.*

The results of the ERT surveys along Profiles 01, 02 and 03 are shown in fig. 6. The positions where the mapped dyke was traversed are indicated in these profiles. A number of observations may be made:

- On Profile 01, the position of the mapped dyke corresponds to a local zone of high resistivity at shallow depths. Immediately to the east of this zone, a zone of low resistivity is observed. This zone may indicate the presence of earth materials with a higher degree of water saturation. It is possible that this zone acts as a preferential pathway for groundwater migration.
- Profile 02 displays a similar resistivity distribution as Profile 01. A pronounced change in the resistivities of the near-surface materials is observed to the east of the mapped dyke, possibly indicating higher degrees of water saturation.
- The character of Profile 03 is somewhat different to Profiles 01 and 02. The position of the mapped dyke does not correspond to a local zone of high resistivity. In addition, the materials to the west of the mapped dyke now have lower resistivities as compared to the material to the east. The reason for the different response on Profile 03 is probably related to the fact that it is located in an area with higher magnetic field intensities as compared to Profiles 01 and 02 (refer to fig. 5). Local magnetic anomalies observed on the eastern part of Profile 03 correspond with the zones of high resistivity and are likely due to the presence of shallow dolerite.

Resistivity data were recorded on Profile 04 to detect and map the boundary between the dolerite sill and the Karoo rocks exposed by erosion of the sill (refer to fig. 5). The inverse resistivity model along Profile 04 is presented in fig. 7. The most prominent feature of the resistivity model is the dramatic change in the resistivities of the deeper earth materials near position 515 m. The model suggests an abrupt ending of the dolerite sill at this position. The low resistivity material to the east of this position probably consists of Karoo sedimentary rocks, possibly with a high degree of water saturation.

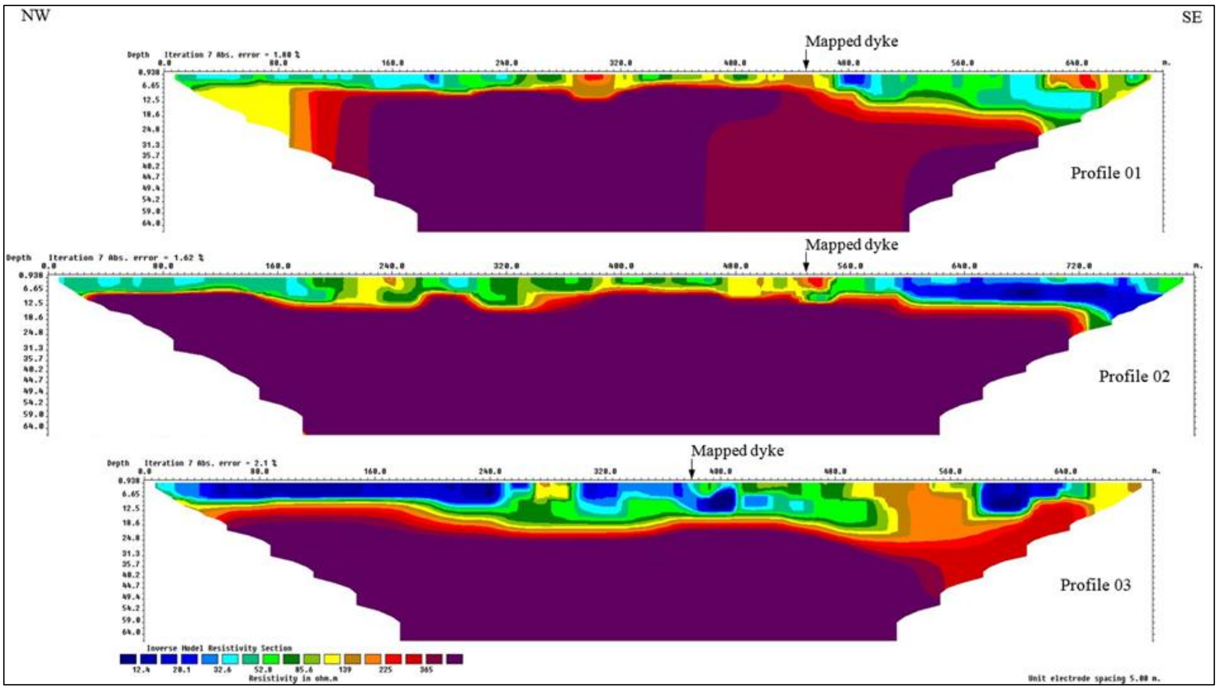


***Figure 6** Inverted resistivity models along Profiles 01, 02 and 03 (north-west to south-east)*

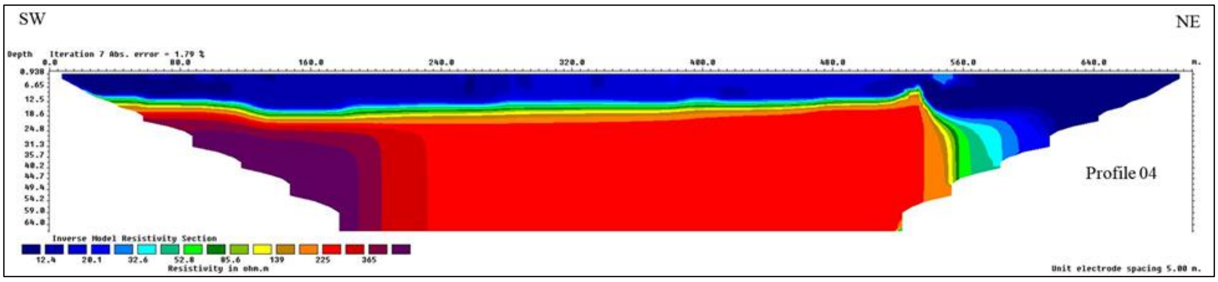


***Figure** 7 Inverted resistivity model along Profile 04 (south-west to north-east)*

Analyses of samples collected from the Fertilizer Quarry and the Farmhouse Quarry showed that the quarries contained water that was heavily contaminated with nitrate, ammonium and sulphate. The chemical composition of the water samples had a typical fertilizer effluent signature.

In fig. 8, the nitrate concentrations of the groundwater and surface water at the various sites sampled are shown using a colour-coding scheme. Five groundwater sites showed nitrate concentrations above the allowable limits. Borehole GF1 is located adjacent to the mapped dyke that runs past the Fertilizer Quarry. The high nitrate concentration (1725 mg/L) recorded at this groundwater site suggests that the fertilizer effluent may have migrated along preferential pathways associated with the dyke.

Boreholes GF3 and GF9 are heavily contaminated with nitrate, exhibiting concentrations of 581 and 447 mg/L, respectively. These two groundwater sites occur within the broad magnetic lineament that extends beyond the Farmhouse Quarry in the north. It is plausible that this lineament is due to a dolerite structure that may also be associated with preferential pathways for groundwater flow and contaminant transport. The elevated nitrate concentration (16 mg/L) at borehole GF6 may also be due to the mobilisation of contaminants from the Farmhouse Quarry along the broad magnetic structure.

High nitrate concentrations were also recorded at borehole GF2 (102 mg/L) and at the spring (316 mg/L; labelled Fountain). Although these elevated concentrations may be due to the mobilisation of fertilizer effluent from the Farmhouse Quarry.

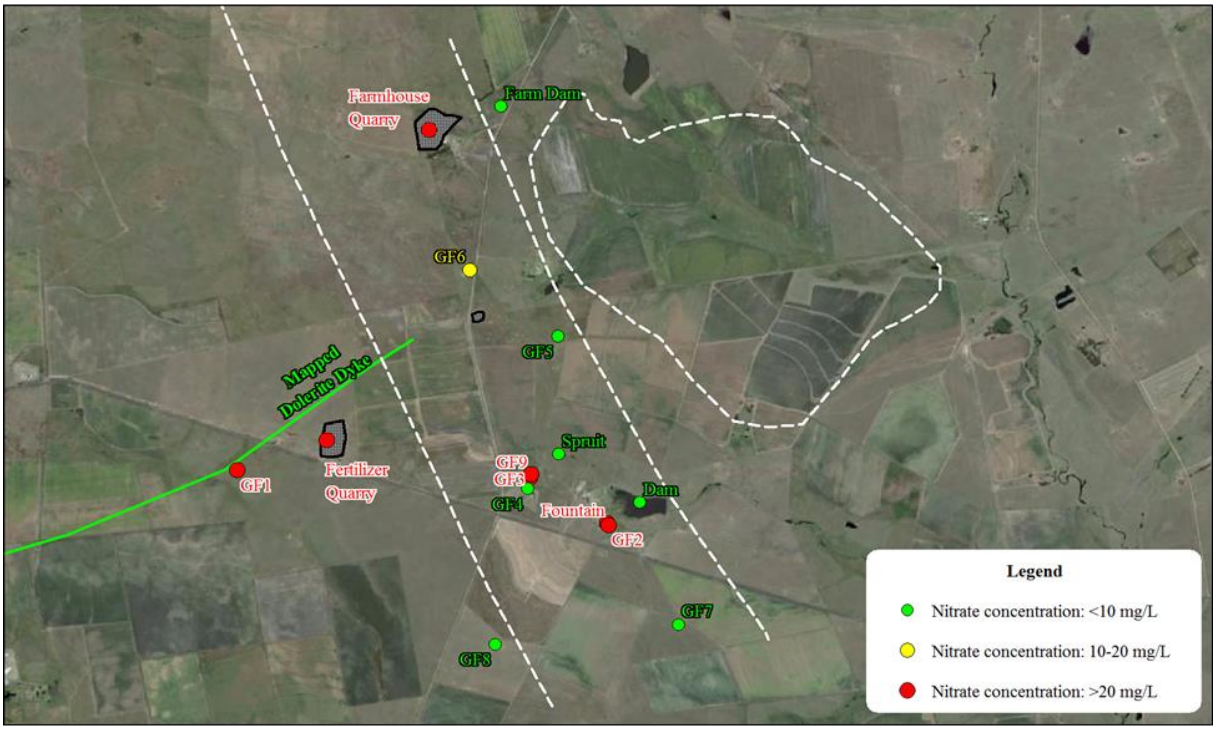


***Figure 8*** *Nitrate concentrations observed at groundwater and surface water sites.*

The quarries have been rehabilitated since the investigation was initiated, thus the pollution source have been removed. The time graphs of the electrical conductivity and nitrate concentrations of boreholes sampled is displayed in fig. 9. From this it is clear that most contaminated boreholes (GF1, GF3 & GF9) have improved significantly since November 2015, indicating that the rainfall received since then might have a dilution effect on the groundwater quality, as the sources of pollution is now removed.

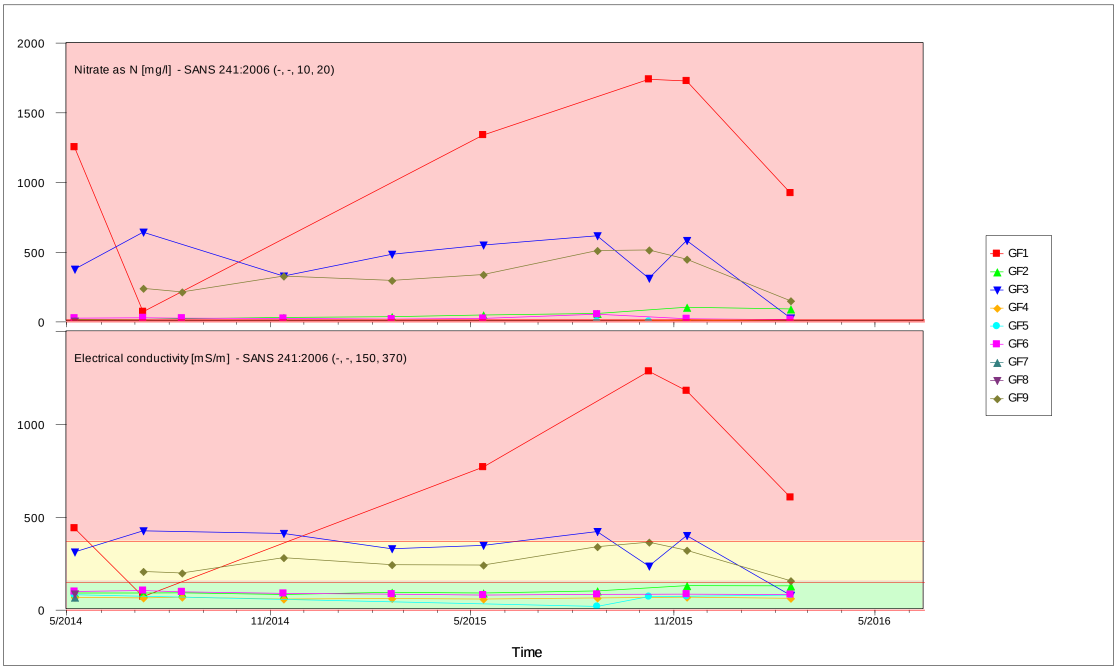


***Figure 9*** *Time graphs of the electrical conductivity and nitrate concentrations of the boreholes since 2014.*

## Conclusions and Recommendations

The magnetic survey revealed a well-defined linear magnetic anomaly corresponding to the position of a mapped dolerite dyke less than 200 m from the Fertilizer Quarry. A broad linear zone of increased magnetic field strength with a south-east/north-west strike was also identified. The hydrocencus identified boreholes situated along these structures that are highly contaminated with nitrate. It is therefore plausible that these lineaments acts as preferential pathways for groundwater flow and contaminant transport from the quarries.

The water quality in the most contaminated boreholes (GF1, GF3 & GF9) have improved significantly over the last three months, thus indicating that the rainfall in this three month period might have flushed the underlying aquifer (and the source of contamination has been removed). These trend will be monitored during the course of 2016.

The quarries have been rehabilitated since the investigation was initiated. Thus, if there is no natural attenuation of nitrate in the groundwater regime over time, the results of the geophysical investigations will then be used to identify five sites for the drilling of boreholes to investicate the geological and geohydrological conditions in the vicinities of the quarries. All the geological and geohydrological information gathered will be used during the feasibility phase of the study to determine the most feasable option to remediate or manage the contamination of the groundwater regime.

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