# Optimization of water quality monitoring in a typical quaternary catchment in Mpumalanga, South Africa

by

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# Declaration

I, Jacobus Nicolaas Brits, declare that the dissertation, which I hereby submit for the degree [Master of Science (Water Resources Management)] at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature:  Date: 12 January 2015

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## Abstract

Water is a scarce and precious natural resource in South Africa. The Department of Water and Sanitation (DWS) has been appointed as the custodians of the water in South Africa with Catchment Management Agencies (CMA's) assisting in this cause. A management measure used for the protection of the water resources in South Africa is water quality monitoring, a process that can be very complex and difficult within a quaternary catchment. This study was undertaken to investigate optimization of water quality monitoring within a typical quaternary catchment in the Mpumalanga Province of South Africa. The study area is the C12D quaternary catchment and consists of several $1^{st}$ to $4^{th}$ order tributaries with the geology consisting of ultramatic / mafic intrusive rocks arenaceous rocks consisting of sandstone. The optimization of placing surface and groundwater monitoring points were investigated in the study area through identifying pollution sources and establishing a correlation between groundwater flow and surface water flow directions. A desktop study and a site visit to the study area identified five main pollution sources, namely gold mining, coal mining, agriculture, town of Secunda and a sewage treatment plant. To establish a correlation between groundwater levels and surface topography, a Bayesian correlation test was performed. The test showed a significant positive correlation between the groundwater levels and surface elevation within the study area, $r^2 = 0.9437$, $p < 0.001$. As a result, the surface water flow direction was used to determine the direction of groundwater flow in the study area. Identifying specific water quality variables to be monitored for each pollution source was also investigated as a means for optimizing water quality monitoring. Historic water quality data were assessed for significant variation between upstream and downstream monitoring points. A literature review was used to supplement historic water quality data where absent or lacking. The results showed significant variations in Total Dissolved Solids (TDS), Sodium (Na), Electrical Conductivity (EC), Calcium (Ca), Chloride (Cl), Sulphates ($SO_4$), Fluoride (F) and Magnesium (Mg) concentrations for the gold mining activities, Ca, Nitrates ($NO_3$), Na, Cl, F, EC, TDS and $NH_4$ concentrations for the sewage treatment plant, Cl concentrations for the town of Secunda, no variation for the agricultural activities and $SO_4$, Ammonium ($NH_4$) and $NO_3$ concentrations for the coal mining activities.

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# List of acronyms

| | | |
|---|---|---|
| Ca | – | Calcium |
| Cl | – | Chloride |
| CMA | – | Catchment Management Agency |
| DOC | – | Dissolved organic carbon |
| DTWQR | – | Domestic target water quality range |
| DWAF | – | Department of Water Affairs and Forestry |
| DWS | – | Department of Water and Sanitation |
| EC | – | Electrical conductivity |
| F | – | Fluoride |
| GDA | – | Groundwater database archive |
| mamsl | – | meters above mean sea level |
| Mg | – | Magnesium |
| Na | – | Sodium |
| $NH_4$ | – | Ammonium |
| $NO_3$ | – | Nitrates |
| $SO_4$ | – | Sulphates |
| TDS | – | Total dissolved solids |
| WHO | – | World health organisation |

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# Chapter 1: Introduction

## *1.1 Background*

Water is the most important natural resource on earth today. Although the earth has approximately 1.386 billion cubic metres of water, only 2.5% of that amount is in the form of fresh water. Of this 2.5%, 68.7% is made up of icebergs and snow, 29.9% is groundwater and 0.26% is surface water (Roux and Nel, 2013). It is estimated by the World Health Organisation (WHO) that approximately 1.1 billion people of the earth's population have no access to water (WHO, 2013; Armah, 2014). The lack of water and poor sanitation is one of the biggest contributors to deaths in the world, especially amongst children. Almost 2 million people die every year because of diarrhoeal diseases, most of them children less than 5 years old (WHO, 2013; Armah, 2014). These figures highlight the importance and significance of the earth's water resource, especially the potable water resource (Jones and Lee, 1984).

The earth's water reticulation system is a closed system. The system cannot gain or lose any water (Roux and Nel, 2013). In spite of this, water is becoming scarcer making it the most sought after natural resource in the world (Barnes and Vermeulen, 2012). If water cannot be lost through the water reticulation system, water is becoming less available for domestic or potable usage through mismanagement of our water resources. The increase in demand for fresh potable water due to an increasing world population is one of the main attributes for the significant decline in available water (Barnes and Vermeulen, 2012; Jones and Lee, 1984; Al-Hogaraty et al., 2008). More so, the pollution of the world's freshwater system is of major concern for potable water availability (Khan and Liang, 1989; Barnard et al., 2013).

Main water users and polluters in South Africa comprises mainly the agricultural sector, mining sector, industrial sector, informal settlements and municipal waste water treatment works (Tredoux et al., 2004; De Villiers and Mkwelo, 2009; Bester and Vermeulen, 2010). Different sectors have different water quality variables that are of concern for water quality monitoring. The agricultural sector and municipal waste water treatment works contributes mostly to high levels of $NH_4$, Dissolved Organic Carbon (DOC) and $NO_3$ in water resources (DWAF, 1996). The over use of pesticides in the agricultural sector not only leads to poor water quality, it also poses a major risk to aquatic ecosystems (Ansara-Ross et al., 2008). One of the main concerns in the coal and gold mining sectors is acid mine drainage (Nengovhela et al., 2007; Barnes and Vermeulen, 2012; Luis et al., 2009; Kang et al., 2001; Tiwary, 2001). Water and oxygen comes in contact with sulphide bearing minerals releasing iron hydroxide into the groundwater resource and into the rivers and streams, when water starts decanting

on the surface (Barnes and Vermeulen, 2012). Measuring dissolved SO4 in water is a good indicator of acid mine drainage in a water resource (De Villiers and Mkwelo, 2009). Although acid mine drainage is a big environmental issue around the globe it must be emphasised that coal mining provides coal for most of the electricity generated in the world (Tiwary, 2001; Cook and Fritz, 2002). Due to the importance of coal mining and the lack of implementation of renewable energy sources it can be said with certainty that coal mining will have an impact on water resources for many years to come and that focus should be on managing the impacts associated with coal mining.

South Africa is a water scarce country (Barnes and Vermeulen, 2012). In addition, South Africa is also one of the biggest mining and industrial countries in Africa, if not in the world. Mining and industrial activities contributes significantly to pollution of the fresh water system, impacting on an already limited resource. It is therefore fundamental to have a good governing body and even better legislation to help protect the water in South Africa. Section 24 of the constitution of South Africa states "*that every person has the right to an environment that is not harmful to their health and that will be protected for present and future generations*" (Constitution of the Republic of South Africa, Act 108 of 1996). A big responsibility is placed on government to protect the water resource as custodians for all South African citizens. The National Water Act was drafted in 1998 to help government manage the water resources. This Act was promulgated to provide for the fundamental reform of the law relating to water resources. The Act regulates the relationship between these new laws and reforms and repeals certain laws (Compendium of South African Environmental Legislation, 2006). Furthermore, a DWS has been established to enforce and regulate water use in South Africa.

In addition to drafting legislation and establishing a national water regulator, additional water management measures are available to help protect the water resources in South Africa. One of these measures includes the establishment of a CMA in a water management area. The establishment of CMA's to help regulate water use, protect the water resource and to involve local communities in decision making is contained in Chapter 7 of the National Water Act, 1998. The aim is to establish a CMA for each of the water management areas in South Africa. The idea of establishing a body that can focus on protecting the water resource of a specific area is a very good initiative. However, the establishment of these CMA's over the past 16 years have been very slow, with only a few established in South Africa.

In a press release from the DWS in March 2012, the Minister of Water and Environmental Affairs have approved the establishment of nine CMA's. The Minister decided to reduce the number of CMA's from nineteen CMA's to nine CMA's due to technical capacity requirements of CMA's and the challenge of regulating the performance of a large number of

CMA's. Although the Minister approved the establishment of 9 CMA's, they are still to provide significant success in their newly established roles.

Water monitoring is one pathway for the CMA's to help protect South Africa's water resources. The DWS published a best practise guideline for water monitoring systems, BPG G3: Water monitoring systems (DWAF, 2007). Water monitoring can detect sources of pollution, the depletion of a water resource (either being surface water or groundwater), it can set standards for certain catchments and it can assist in setting licensing conditions for water users. To regulate the discharge of effluent, the DWS published general and special effluent standards to which companies and individuals need to comply with if wastewater is to be released in the environment (Roux et al., 1993). The DWS also published water quality guidelines for domestic use, ecosystems, livestock and irrigation. All these monitoring measures can be used by the CMA's to establish a water monitoring programme and setting appropriate and achievable water quality limits for water management catchments.

Using the same standards and water quality guidelines, mentioned above, in different catchments in South Africa may, however, not be achievable. Different environments with different sources of pollution require that standards be set for specific conditions in a catchment. The natural environment of different areas in South Africa is also very diverse resulting in different background water qualities (groundwater and surface water) for different areas and catchments in South Africa (Barnard et al., 2013; Venter and van Vuren, 1997; Al-Hogaraty et al., 2008). The objectives of water quality monitoring and the limits of parameters specified must be evaluated against limits specific to the end-user and pollution source (Jones and Lee, 1984). More concerns for complying with standards and water quality guidelines are the high cost and the almost impossible task to monitor all water resources in South Africa. The onus therefore falls on companies and individuals to monitor water resources and report to the DWS. Although most water quality monitoring data is submitted to the DWS, capacity constraints at the regulator prevents processing and interpretation of the applicable data. Shifting the responsibility of water quality monitoring to the CMA's can help ease the capacity constraints at the DWS.

A water quality monitoring programme for a catchment with different types of water users and multiple chemical and physical attributes to be monitored can be very technical and complex. However, if water quality monitoring is optimized at quaternary catchment level, the CMA's can assist water users to allocate resources more efficiently towards water monitoring in the catchment. It will also give the CMA's a guideline on keeping people or industries liable for pollution, as water qualities for the quaternary catchment will be available.

Regular reporting to the DWS on non-compliances is essential to ensure enforcement. Roux et al. (1993) also highlights the importance of optimization of water quality monitoring as this will establish chemical, physical and biological baselines on regional and national levels. This will in turn help determining the rate of water quality change in an aquatic environment (Roux et al., 1993).

### *1.2 Research aims and objectives*

The research question is: how can water quality monitoring in a typical quaternary catchment be optimised so that the CMA can use the results for effective water quality monitoring? The aim of this study is therefore to investigate the optimization of water quality monitoring in the C12D quaternary catchment in the Mpumalanga Province of South Africa. In order to show optimization of water quality monitoring in the study area, the following objectives for this dissertation were undertaken:

1. To determine the main pollution sources in the study area and to establish a correlation between surface water and groundwater flow, which will ensure optimal placement of surface water and groundwater monitoring points;
2. To determine water quality variables to be monitored and frequency of monitoring through establishing water quality patterns from historic water quality data of the study area and complimenting the water quality data with available literature;
3. To discuss how the CMA can use the results from this study for optimal water monitoring in the study area.

### *1.3 Thesis outline*

In Chapter 2, a general overview of the study area in which quaternary catchment C12D is situated, the climate of the area, surface water characteristics and groundwater characteristics is provided. Within this chapter is also an illustration of the adjacent catchments as well as the tributaries within the study area. A link between the characteristics of the study area and the importance of managing water quality within the study area are also discussed in this chapter.

In Chapter 3, the main pollution sources of the study area are identified and a correlation between surface water and groundwater flow is investigated. The identification of pollution sources and surface water and groundwater flow directions are used to select upstream and downstream water monitoring points within the study area.

In Chapter 4, historic water quality data for the study area are assessed to determine changes in water quality variables over time. Historic water quality data is also used to

identify water quality variables to be monitored as well as determining the frequency of water quality monitoring in the study area. Where water quality data for the study area is lacking or absent, available literature was used to determine water quality variables to be monitored upstream and downstream of specific pollution areas. Literature was also used to supplement the water quality changes identified from historic water quality data.

In Chapter 5, a discussion on the results of the study and how it can be applied by the CMA for effective water monitoring within the study area are provided. Recommendations for further water quality monitoring optimisation are also discussed in this chapter. A conclusion of the main results of this study is also provided in this chapter.

# Chapter 2: Study area description

## *2.1 Study area*

Quaternary catchments are the major constituents in which water management in South Africa is divided. There are 1 946 quaternary catchments that have been demarcated by the DWS. A quaternary catchment is the most basic unit for water management in South Africa. For this dissertation, the C12D quaternary catchment as defined by the DWS, will be used to apply water monitoring principles and to show optimization of such principles.

The C12D quaternary catchment is located in the Govan Mbeki local municipality (SANBI, 2013). The study area is located in the south western part of the Mpumalanga Province of South Africa, and adjacent to the Gauteng Province of South Africa, approximately 150 km east of Johannesburg and approximately 300 km southwest of Nelspruit (Figure 1). Situated within the study area is the towns of Secunda, Kinross, Evander, Embalenhle, Leandra and Trichard.

## *2.2 Climate*

The C12D quaternary catchment falls within the upper reaches of the Vaal River primary catchment that is situated in the Upper Vaal Water Management Area. The catchment is the responsibility of the regional DWS in Gauteng. According to data from a weather station situated close to the study area (weather station number C1E004), the total average rainfall from 1962 to 1983 is 703.8 mm, with the highest rainfall between November and January. The rainfall is almost exclusively in the form of thunderstorms in the summer, and the winter months are normally dry. Evaporation data from the same weather station indicates that the average evaporation for the area is 1729.8 mm, for the period 1962 to 1983.

An area that is characterised by a distinct wet and dry season, as is the case with this study area, usually has two water quality features associated with the specific climatic conditions. After the dry season and at the beginning of the wet season, elevated levels of pollutants can be expected in surface water and groundwater resources. This is especially the case at agricultural practises where fertilisers and pesticides were used during the dry season on crops and that is washed into the water resources during the first heavy rainfall event (Khanif et al., 1984). Poorer surface water qualities can also be expected during the dry season in the study area. Discharge of poor quality effluent from sewage treatment works and poor quality water from mining and industrial activities may have a more severe

impact on water quality in the dry season than in the wet season (Nhapi and Tirivarombo, 2004). During the wet season, rainfall and surface water runoff dilutes the poor quality water that is discharged into the surface water resource. During the dry season, rivers and streams will be dry with the only water being from discharge activities. Due to the absence of a diluting source, i.e. water from rainfall, water quality in the dry season may in general be poorer.

### *2.3 Surface water characteristics*

The study area contains several tributaries, some that are smaller than others (Figure 2). To successfully allocate surface water monitoring points (Chapter 3 below), the tributaries within the study area and the significance of each tributary must be known. Tributaries are assigned order numbers based on various attributes associated with the watercourse (Strahler, 1957). These attributes include factors associated with size and complexity. The 1$^{st}$ order rivers are rivers that have no tributaries feeding them and are usually situated in the headwaters of a catchment (Cheidegger, 1965). Tributaries situated in the headwaters of a catchment area feeds into the 2$^{nd}$ to 4$^{th}$ order tributaries. If a 1$^{st}$ order tributary gets polluted and feeds into the 2$^{nd}$ to 4$^{th}$ order tributaries, any pollution within the 1$^{st}$ order tributaries will be transferred to the downstream tributaries (Cheidegger, 1965). The impact is usually cumulative as more than one 1$^{st}$ order tributary feeds into downstream tributaries. The 1$^{st}$ order tributaries in the study area are the Klipspruit, Groot-Bossiespruit, Rolspruit and several unnamed tributaries (DWA, 2012).

The order of the river increases as the size and complexity of the river increase (Strahler, 1957). The water quality within the 2$^{nd}$ to 4$^{th}$ order tributaries are expected to be worse than the 1$^{st}$ order tributaries due to cumulative water quality impacts (Cheidegger, 1965). According to the best practise guidelines for water monitoring systems published by the Department of Water Affairs and Forestry (DWAF), allocating monitoring points directly upstream and downstream to a specific pollution source and comparing the water qualities from these monitoring points is critical in determining pollution from a single pollution source (DWAF, 2007). The 2$^{nd}$ order rivers in the study area are the Grootspuit, Trichardspruit, Xspruit and some unnamed tributaries (DWA, 2012). The 3$^{rd}$ and 4$^{th}$ order tributaries in the study area are the Waterval River, Kleinspruit and parts of the Klipspruit and Trichardspruit (DWA, 2012).

### *2.4 Groundwater characteristics*

The 2526 Johannesburg 1:500 000 hydrogeological map series indicates that the geology of the study area can be divided into two categories. A part of the study area is

underlain by ultramatic / mafic intrusive rocks that consist of dolerite, diabase, gabbro, norite, carbonatite, anorthosite and pyroxenite (DWAF, 1999). The geology forms part of the Karoo Supergroup, which is characterised by yellow to white sandstone and also contains coal seams that is found in the Mpumalanga regions of South Africa (Barnard, 2000). A major coal mining operation within the study area is also indicative of the coal seam being present. Coal mining operations are characterised by acid mine drainage (Bester and Vermeulen, 2010) and regular water quality monitoring is therefore required to detect pollution. Parts of the study area is also underlain by predominantly arenaceous rocks consisting of sandstone (DWAF, 1999). The geology forms part of the Witwatersrand Supergroup, which is characterised by sandy soils (Barnard, 2000). No significant springs occur in the study area as a result of the geology type with very little information available on the water-bearing properties of the geology type (Barnard, 2000). Impact on natural springs are therefore anticipated to be limited from any pollution activities due to the absence of springs in the study area. The underlying aquifer is an intergranular and fractured aquifer and has been mainly characterised as a poor aquifer (DWAF, 1999). Intergranular aquifers are characterised by sand and gravel formations, characteristics also applicable to the Witwatersrand Supergroup mentioned above (Barnard, 2000). The fractured aquifer are characterised by hard and compacted rock similar to the geology type of the Karoo Supergroup (Barnard, 2000). The borehole yield of the intergranular and fractured aquifer of the study area is low with a median yield between 0.1 and 0.5 litres per second (DWAF, 1999). The EC of the aquifer in the study area is generally between 70 and 300 $mS.m^{-1}$ and F levels regularly exceed 1.5 $mg.\ell^{-1}$ (DWAF, 1999).

By knowing the hydrogeology, approximate borehole yield and general groundwater quality of the study area, groundwater quality monitoring can be applied with reference to the background conditions associated with the study area. Different hydrogeology may result in different background groundwater qualities based solely on the features associated with the hydrogeology (Barnard et al., 2013; Venter and van Vuren, 1997; Al-Hogaraty et al., 2008). Elevated levels of F within the study area can be expected (DWAF, 1999) because of natural conditions and not as a result of pollution. The low borehole yield of the study area also highlights the importance of protecting the groundwater resource within the area. Low borehole yield means little water availability for livestock watering, potable water and the ecological reserve.

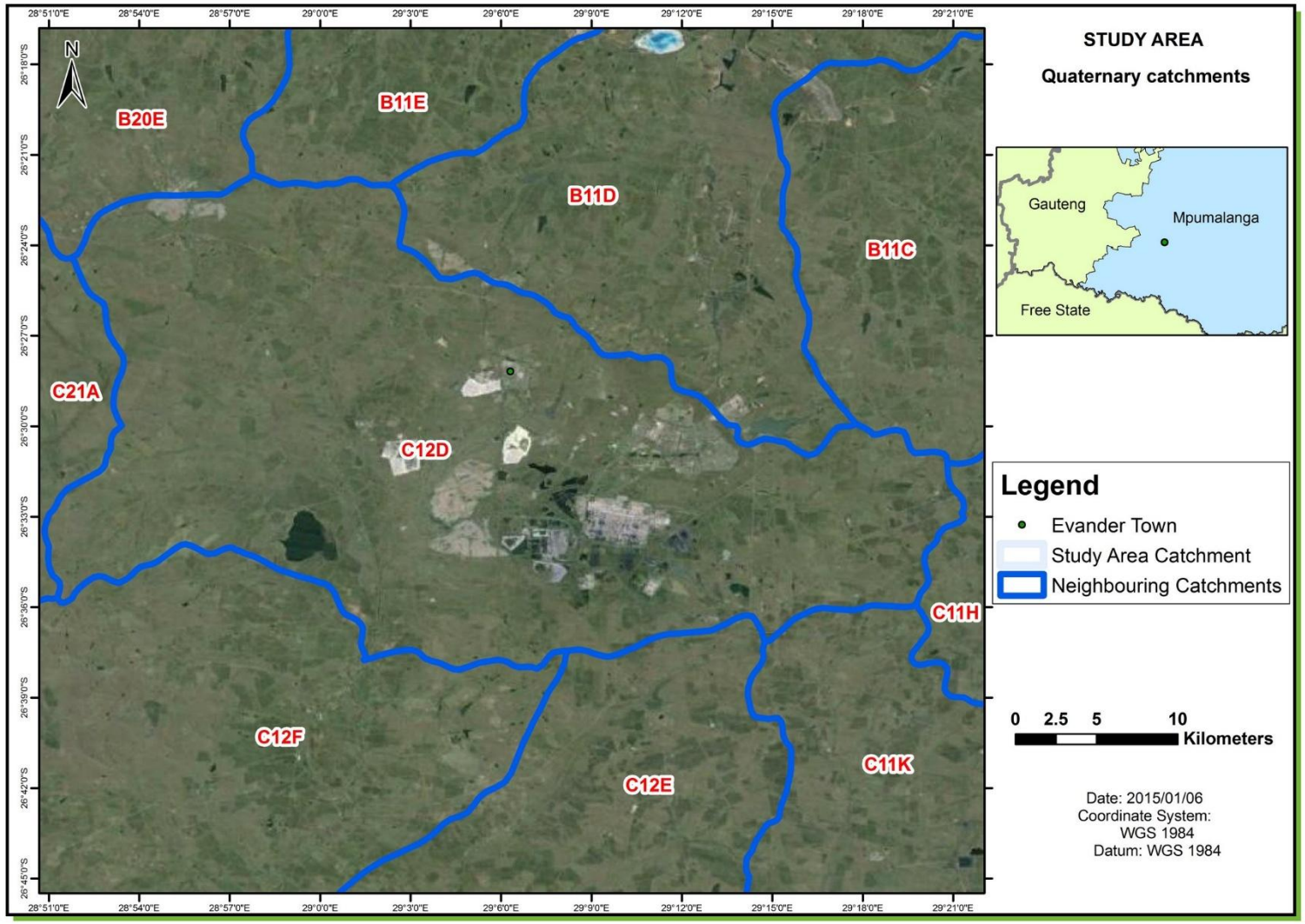


FIGURE 1: The study area of quaternary catchment C12D is bordered by nine other quaternary catchments. The study area is located in the Mpumalanga Province of South Africa, approximately 150 km east of Johannesburg and 300 km southwest of Nelspruit.

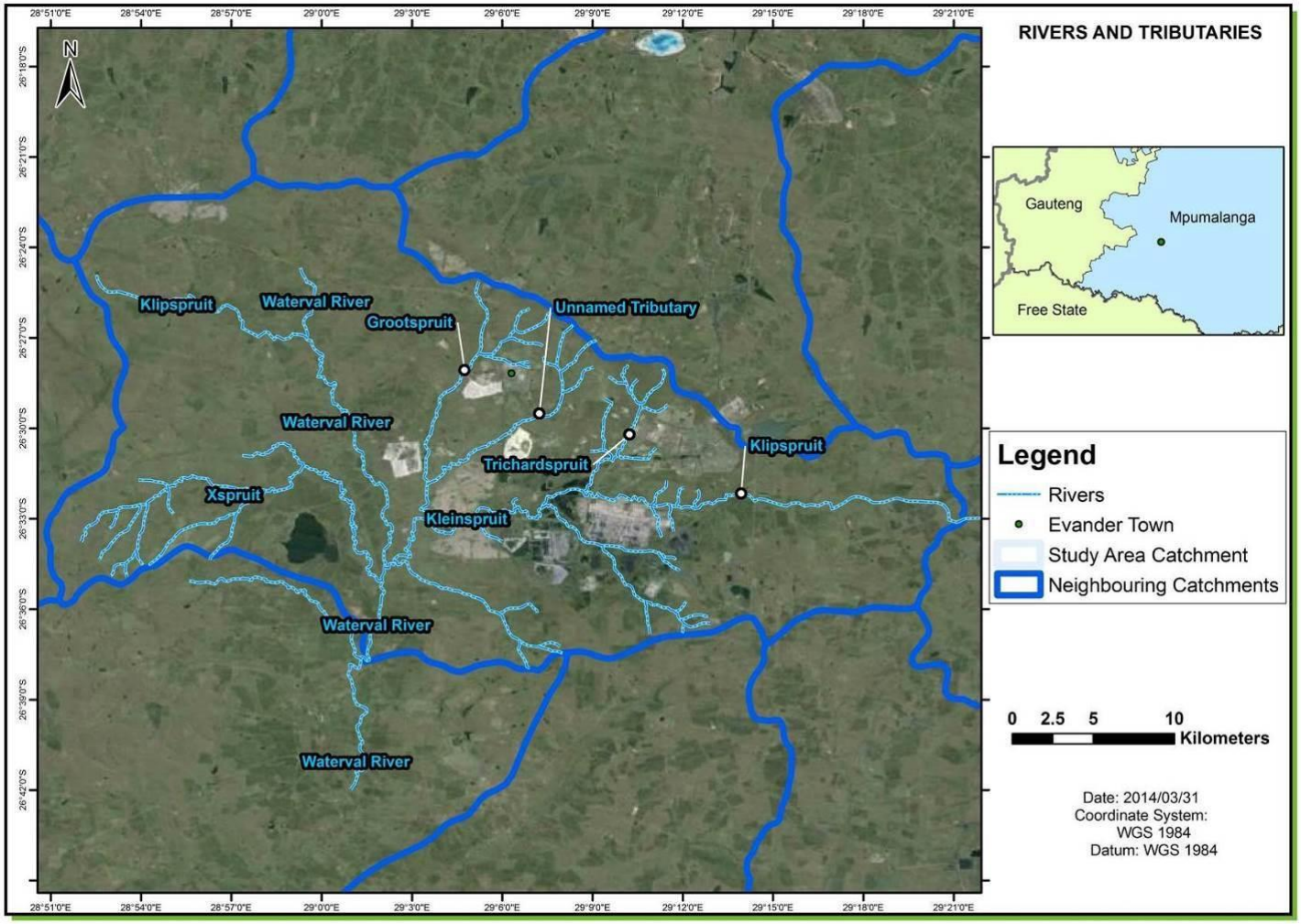


FIGURE 2: The study area contains several tributaries. The Klipsruit and several unnamed tributaries are situated in the headwaters of the catchment (1st order tributaries) and feeds into larger tributaries such as the Grootspruit, Trichardspruit and Waterval River (2nd to 4th order tributaries). The Waterval River exit the study area to the south into the adjacent quaternary catchment.

# Chapter 3: Determining upstream and downstream water monitoring points

## *3.1 Identifying pollution sources*

Before surface water and groundwater monitoring points are determined, the major pollution sources have to be identified (DWAF, 2007). Without knowing what the pollution sources are and what the extent of these activities are, placing monitoring points will be random and with no specific purpose (DWAF, 2007). Pollution sources were identified through a desktop study of the study area as well as through a site visit to the study area.

A desktop study of the area was conducted first to identify preliminary pollution sources. Due to the size of the study area, a desktop study allowed for the identification of potential pollution sources before conducting the site visit, reducing the time spent during the site visit. Topographical maps, with a scale of 1:50 000 and specific to the study area, were collected from the Chief Directorate at the Department of Land Affairs. The topographical maps from the study area contain specific information on the area such as the location of mining operations, agricultural activities and urban areas. A review of the topographical maps was undertaken to identify possible pollution sources. These pollution sources were noted at the time of the review so that it could be verified later with the site visit. The potential pollution sources that were identified using the topographical maps of the area were a gold mining operation, coal mining and petrochemical operation, the town of Secunda and agricultural activities.

Although potential pollution sources were identified during the desktop study, the extent of these activities could not be verified during the desktop phase. A site visit was conducted to the areas identified during the desktop study to verify the pollution sources. The site visit included a visit to all the areas identified in the desktop phase. An interview with the Environmental Manager of the gold mining operation was arranged to discuss additional pollution sources within the study area. The site visit was also used to identify the surface water resources, tributaries and rivers, which will be impacted on by the various pollution sources. All potential pollution sources identified during the desktop study, i.e. gold mining activities, town of Secunda, agricultural activities, coal mining and petrochemical activities, were confirmed during the site visit. An additional pollution source, a sewage treatment plant, and the location of the source were identified during the interview with the Environmental Manager. Refer to Figure 3 for the pollution sources identified.

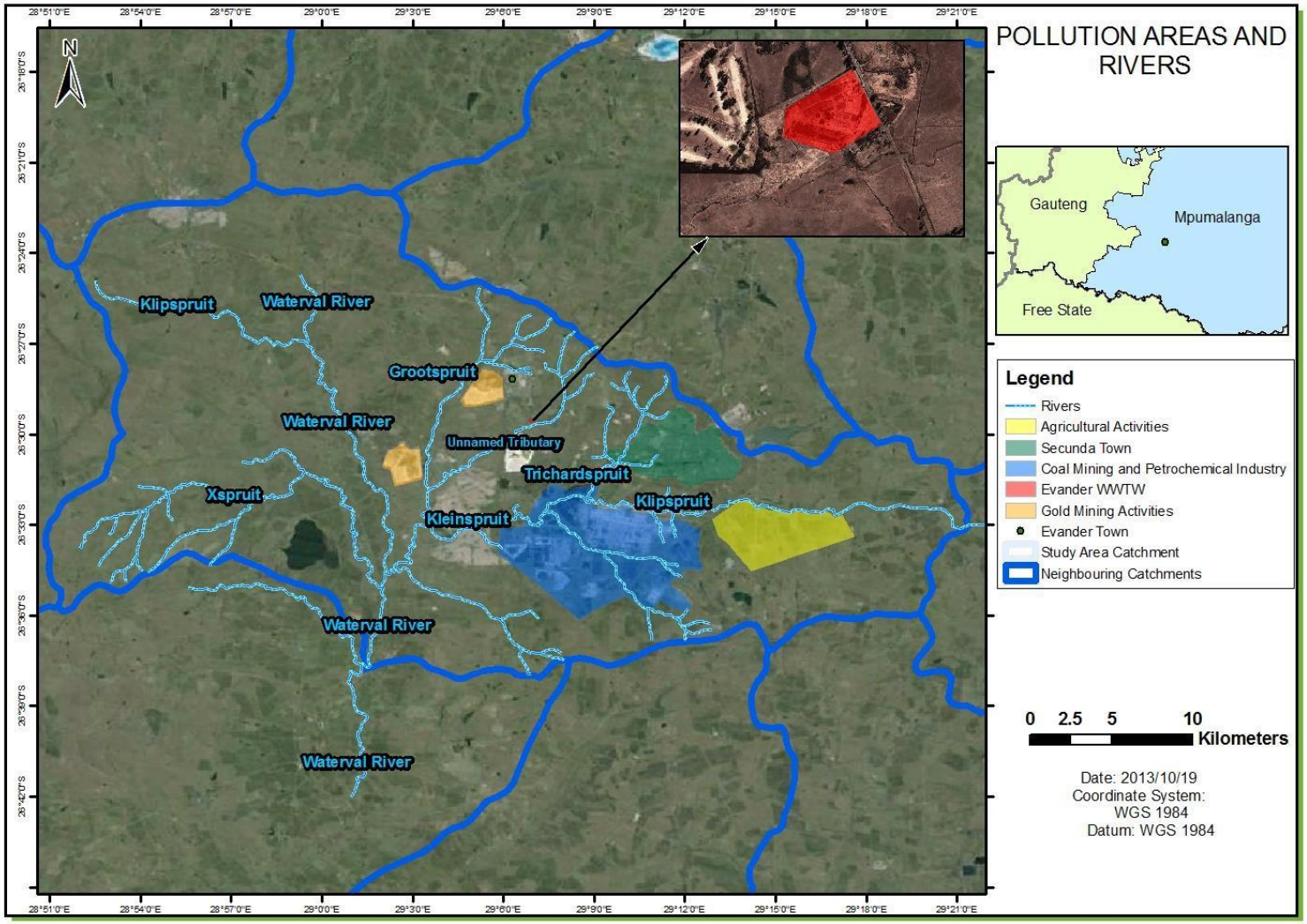


FIGURE 3: Different pollution sources were identified in relation to the relevant tributaries. The localities of the pollution sources will be used to allocate surface water and groundwater monitoring points.

Two areas of the gold mining activities were identified that may potentially affect water qualities of the study area. One of the areas is situated to the east of the Grootspruit and consists of a processing plant, gold slimes dam and process water dams (hereafter referred to as *Gold mining area A*). Spillages from the processing plant and process water dams may have an impact on the Grootspruit whereas storm water runoff from the slimes dam may affect the water quality in the Grootspruit. Furthermore, seepage from the slimes dam may affect the groundwater qualities of the study area.

The second area associated with the gold mining activities is situated to the east of the Waterval River and to the west of the Grootspruit (hereafter referred to as *Gold mining area B*). This area consist only of a gold slimes dam. Affected water runoff from the slimes dam may affect the water quality of both the Waterval River and the Grootspruit, as well as the groundwater quality of the area.

The coal mining and petrochemical industry covers a large area in the central part of the study area. Activities includes process water dams, mine residue deposits and processing activities. Separation of the coal mining and petrochemical industries would have given a more detailed description of impacts associated with each of the industries however, the specific coal mining and petrochemical industries in the study area are complexly linked and cannot be separated. Tributaries that may be affected are the Trichardspruit, Kleinspruit and Klipspruit. The activities associated with the coal mining and petrochemical industry may affect the water quality of the surface water and groundwater resources.

Some smaller activities were identified that can impact on surface water and groundwater resources. These activities include agricultural activities situated in the east of the study area, a sewage treatment plant situated close to an unnamed tributary of the Grootpsruit, and the town of Secunda that is situated in the north east of the study area.

### *3.2 Surface water monitoring localities*

To optimize surface water quality monitoring, the location of surface water monitoring points need to be specific to pollution sources (DWAF, 2007). The location of the pollution sources identified for the study area were used to select upstream and downstream surface water monitoring points in affected tributaries. The selection of monitoring points for the identified pollution sources were further done from a list of existing monitoring points in the study area. This allowed for the use of historic water quality data in optimizing water quality within the study area. The upstream surface water monitoring points will act as baseline water qualities for each pollution source. The downstream surface water monitoring points

will predict the impact of the specific pollution source on the surface water resource, after comparing the upstream and downstream water qualities (DWAF, 2007). A reference number, containing the prefix 'SW', was assigned for each of the surface water monitoring points. Refer to Figure 4 for an illustration of the surface water monitoring points in relation to the pollution areas and to Table 1 for a summary of the surface water monitoring points.

For *"Gold mining area A"*, a surface water monitoring point (SW01) upstream of the activities and a surface water monitoring point (SW02) downstream of the activities were selected in the Grootpsruit. The water quality from monitoring point SW01 will be used as background water quality and will be compared to water quality from monitoring point SW02 to determine the impact of *"Gold mining area A"* on the Grootspruit. The same principle was applied for selecting upstream and downstream surface water monitoring points for *"Gold mining area B"*. A surface water monitoring point (SW03) was selected upstream of the activities in the Grootspruit, to establish background water qualities, with a surface water monitoring point (SW04) selected downstream of the activities in the Grootspruit to monitor impact from activities on the surface water resource.

A water monitoring point upstream of the sewage treatment plant (SW05) was selected in an unnamed tributary feeding the Grootspruit to provide background water qualities. A water monitoring point (SW06) was selected immediately downstream of the sewage treatment plant to monitor impact. Surface water quality impacts associated with sewage treatment plants are mostly due to point source activities (e.g. discharge of treated effluent into the surface water resource) (Wiechers and Heynike, 1986). Surface water monitoring points were therefore selected as close as possible upstream and downstream of the sewage treatment plant. Selecting surface water monitoring points as close as possible to a pollution source, will yield more accurate water quality data for that specific pollution source.

The upstream water monitoring point (SW07) and the downstream surface water monitoring point (SW08) for the town of Secunda were selected in the Trichardspruit. The surface water monitoring point (SW09) upstream of the agricultural activities and the surface water monitoring point (SW10) downstream of the agricultural activities were selected in the Klipspruit. Both the town of Secunda and the agricultural activities are non-point source activities that will impact on the surface water resource (Wiechers and Heynike, 1986). Non-point source activities does not have a specific point of impact and therefore a greater distance between upstream and downstream surface water monitoring points can be used (Wiechers and Heynike, 1986).

The coal mining and petrochemical activities will have an impact on more than one tributary of the study area. The Trichardspruit and Klipspruit are situated upstream of the coal mining and petrochemical activities, with the tributaries joining downstream into the Kleinspruit. To ensure optimal placement of surface water monitoring points, an upstream surface water monitoring point was selected in the Klipspruit (SW10) and in the Trichardspruit (SW11). The downstream surface water monitoring point (SW12) was selected after the confluence of the Klipspruit and the Trichardspruit, in the Kleinspruit, to determine the impact of the coal mining and petrochemical industry on the surface water resource.

TABLE 1: A summary of the selected surface water monitoring points for the study area with their monitoring reference number and a short description of the monitoring points

| **Monitoring point reference number** | **Description** |
|---|---|
| SW01 | This monitoring point is situated in the Grootpsruit, upstream of *"Gold mining area A"*. |
| SW02 | This monitoring point is situated in the Grootpsruit, downstream of *"Gold mining area A"*. |
| SW03 | This monitoring point is situated in the Grootpsruit, upstream of *"Gold mining area B"*. |
| SW04 | This monitoring point is situated in the Grootpsruit, upstream of *"Gold mining area B"*. |
| SW05 | This monitoring point is situated upstream of the sewage treatment plant in an unnamed tributary of the Grootspruit. |
| SW06 | This monitoring point is situated downstream of the sewage treatment plant in an unnamed tributary of the Grootspruit. |
| SW07 | This monitoring points is situated in the Trichardspruit, upstream of the town of Secunda. |
| SW08 | This monitoring points is situated in the Trichardspruit, downstream of the town of Secunda. |
| SW09 | This monitoring point is situated upstream of the agricultural activities in the Klipspruit. |
| SW10 | This monitoring point is situated in the Klipspruit. It is both downstream of the agricultural activities and upstream of the coal mining and petrochemical activities. |
| SW11 | This monitoring point is located in the Trichardspruit, upstream of coal mining and petrochemical activities. |

| | |
|---|---|
| SW12 | This monitoring point is located in the Kleinspruit, downstream of coal mining and petrochemical activities. |

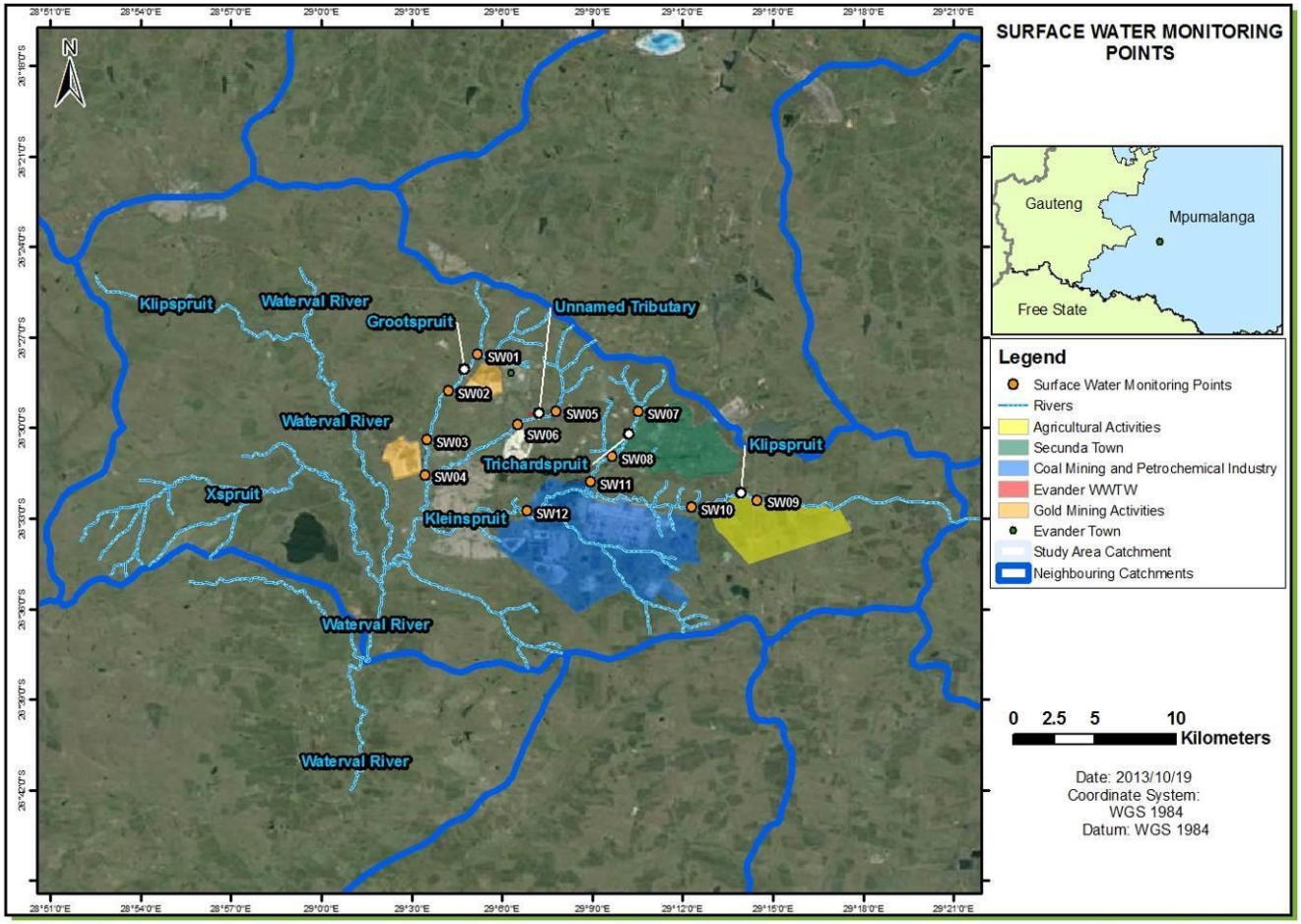


FIGURE 4: Upstream and downstream surface water monitoring points were determined and assigned based on the pollution areas identified. [*"Gold mining area A"* - SW01 and SW02 (in the Grootspruit); *"Gold mining area B"* - SW03 and SW04 (in the Grootspruit); Sewage treatment plant - SW05 and SW06 (in an unnamed tributary of the Grootspruit); Secunda town - SW07 and SW08 (in the Trichardspruit); Agricultural activities - SW09 and SW10 (in the Klipspruit); Coal mining and petrochemical activities – SW10, SW11 and SW12 (in the Klipspruit, Trichardspruit and Kleinspruit)]

### *3.3 Groundwater monitoring localities*

Groundwater monitoring points were selected with the same approach as for the surface water monitoring points. Groundwater monitoring points were selected upstream and downstream of a pollution source. The upstream groundwater monitoring points will be representative of the background water qualities of the area, with the downstream groundwater monitoring points determining the impact from each pollution source on the groundwater resource (DWAF, 2007).

#### *3.3.1 Groundwater flow direction*

To determine which side of a pollution area is upstream and downstream, the groundwater flow direction of the area is required. The groundwater flow direction in an area is determined by the hydraulic groundwater gradient within that area (Babiker and Gudmundsson, 2004). The groundwater levels within an area varies, creating a hydraulic gradient that determines groundwater flow directions. Due to the hydraulic gradient, the groundwater flow direction within an area is from a higher groundwater level to a lower groundwater level (Babiker and Gudmundsson, 2004). The presence of dykes and faults within an area impacts on groundwater flow. Dykes and faults transport groundwater to a surface discharge point such as a spring (Babiker and Gudmundsson, 2004). The determination of the groundwater flow direction within this study did not take in consideration the presence of dykes and faults. The effect of faults and dykes can in future be investigated for further optimization of groundwater quality monitoring.

When two boreholes are situated on the same elevation, groundwater flow can be determined by using only borehole depths. Groundwater will flow from a borehole where the groundwater level is closer to the surface to a borehole where the groundwater level is deeper, as a result of the hydraulic groundwater gradient (Babiker and Gudmundsson, 2004). Once the boreholes are situated on different elevations, borehole depths cannot be used for determining groundwater flow. In this case, the depth of the boreholes must be subtracted from the surface elevation to determine the elevation of the groundwater level in meters above mean sea level (mamsl). This will indicate which borehole is situated higher up from the hydraulic gradient, which is an indication of the direction of groundwater flow. Two different scenarios in Figure 5 and Figure 6 are used to illustrate the difference.

The depths and surface elevation data of boreholes in the study area and in adjacent quaternary catchments were requested and obtained from the Groundwater Database Archive (GDA) of the DWS. The GDA is a national database maintained by the DWS that contains groundwater monitoring data for each catchment in South Africa. Data that is recorded

includes coordinates, surface elevation, borehole depths and groundwater qualities. Groundwater monitoring data for a total of 1431 boreholes were collected from the GDA in an MS Office Excel spreadsheet.

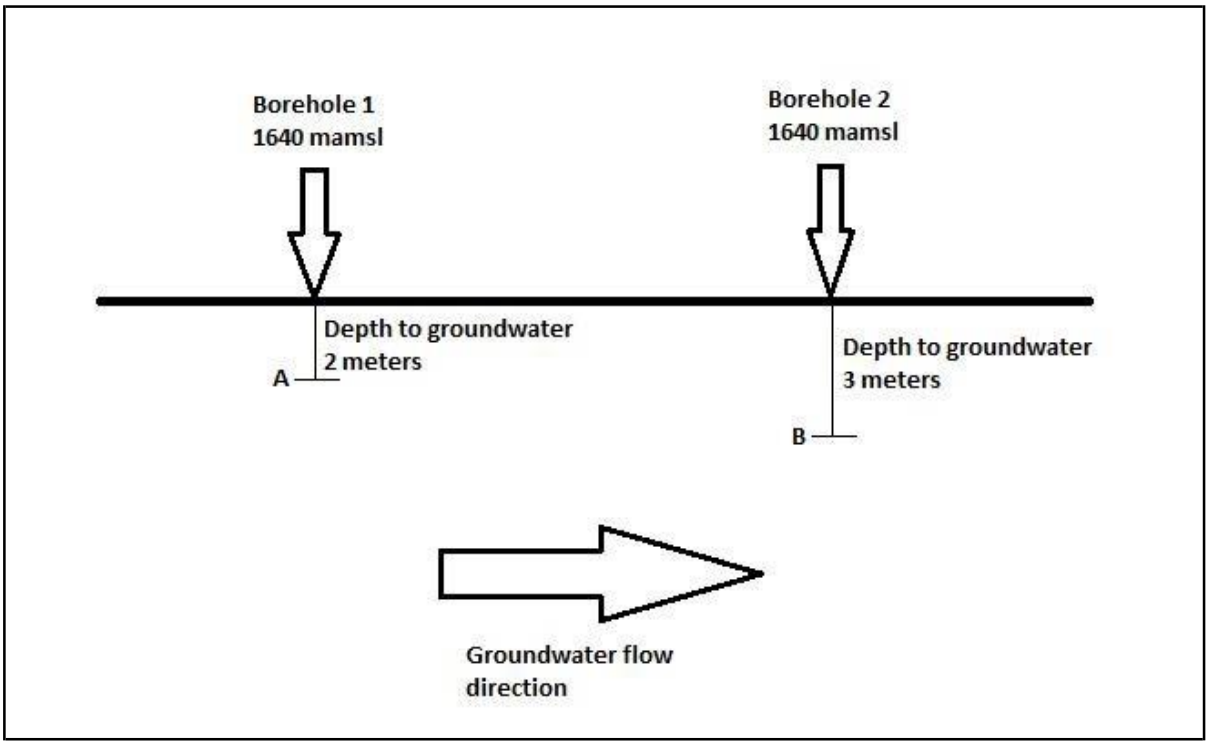


FIGURE 5: When two boreholes are situated on the same surface elevation, the groundwater flow is from point A to point B due to a higher groundwater level at point A.

In Figure 5, the direction of groundwater flow when two boreholes are situated on the same surface elevation is illustrated. Borehole 1 and borehole 2 are on a surface elevation of 1640 mamsl, with borehole depths of 2 meters and 3 meters respectively. Groundwater will flow from borehole 1, which has a shallow borehole level, to borehole 2, with the deeper borehole level, due to the hydraulic gradient created between the boreholes. A further test for groundwater flow direction is to subtract the borehole depths from the surface elevation. If the borehole depths are subtracted from the surface elevation, the groundwater elevation at point A will be 1638 mamsl and at point B 1637 mamsl. Groundwater flow direction will be from a higher groundwater level (borehole 1) to a lower groundwater level (borehole 2).

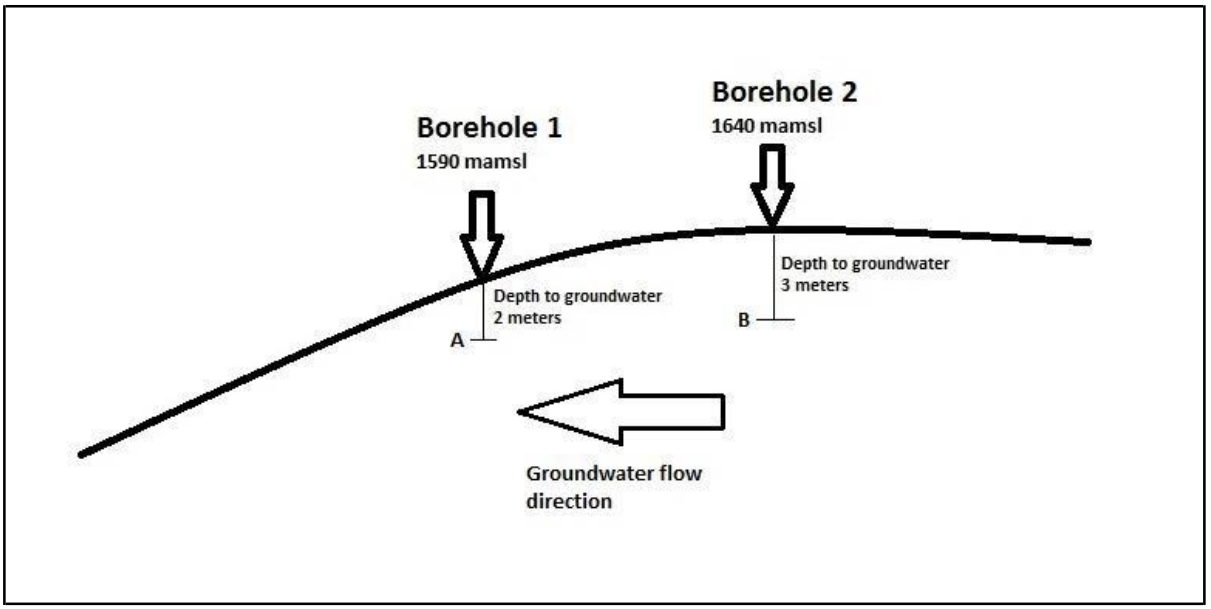


FIGURE 6: When two boreholes are situated at different surface elevation the direction of groundwater flow is from point B to point A due to a higher borehole level at point B.

In Figure 6, the direction of groundwater flow between borehole 1 and borehole 2 when they are situated at a surface elevation of 1590 mamsl and 1640 mamsl respectively is illustrated. Borehole 1 and borehole 2 have borehole depths of 2 meters and 3 meters respectively. Due to differences in surface elevation, borehole depths cannot be used in determining groundwater flow. If the borehole depths are subtracted from the surface elevation, the groundwater elevation at point A will be 1588 mamsl and at point B 1637 mamsl. Groundwater flow will be from a higher groundwater level to a lower groundwater level, which is from borehole 2 to borehole 1. The groundwater flow direction in figure 6 is opposite to the groundwater flow direction in Figure 5, although the borehole depths have remain the same.

To establish groundwater flow in the study area, the groundwater levels, in mamsl, for all boreholes obtained from the GDA were determined. To determine the water level of a borehole in mamsl, the depth of the borehole was subtracted from the general surface topography, in mamsl, of the borehole position. The water levels of all 1431 boreholes in the study area and adjacent quaternary catchments were determined using this technique and was recorded in an MS Office Excel spreadsheet. The water levels for the boreholes varied from 1208 mamsl to 1698 mamsl.

The Surfer® 8 modelling programme (http://www.ssg-surfer.com/html/surfer_details.html) was used to provide a model of groundwater levels throughout the entire study area so that groundwater flow direction can be determined. Surfer® 8 is a 3D surface and contouring mapping programme that runs under Microsoft Windows. The programme converts data into contour, surface, wireframe, vector, image, shaded relief and post maps. The programme also has a gridding function that allows for the production of maps from XYZ data. Surfer® 8 uses randomly dispersed data and interpolate the data onto a grid. The interpolated data are used to draw a map that gives a representation of the whole study area, instead of a scattered data set.

The water level data for the boreholes, calculated from the surface elevation and borehole depths, and each borehole's coordinates were imported into Surfer® 8. The automated programme used the available water level data from the MS Office Excel spreadsheet and interpolated data between the available water level data for a more detailed representation of water levels in the study area. Vectors were included onto the map to show the groundwater flow directions based on the water levels determined. Refer to Figure 7 for the groundwater flow of the study area.

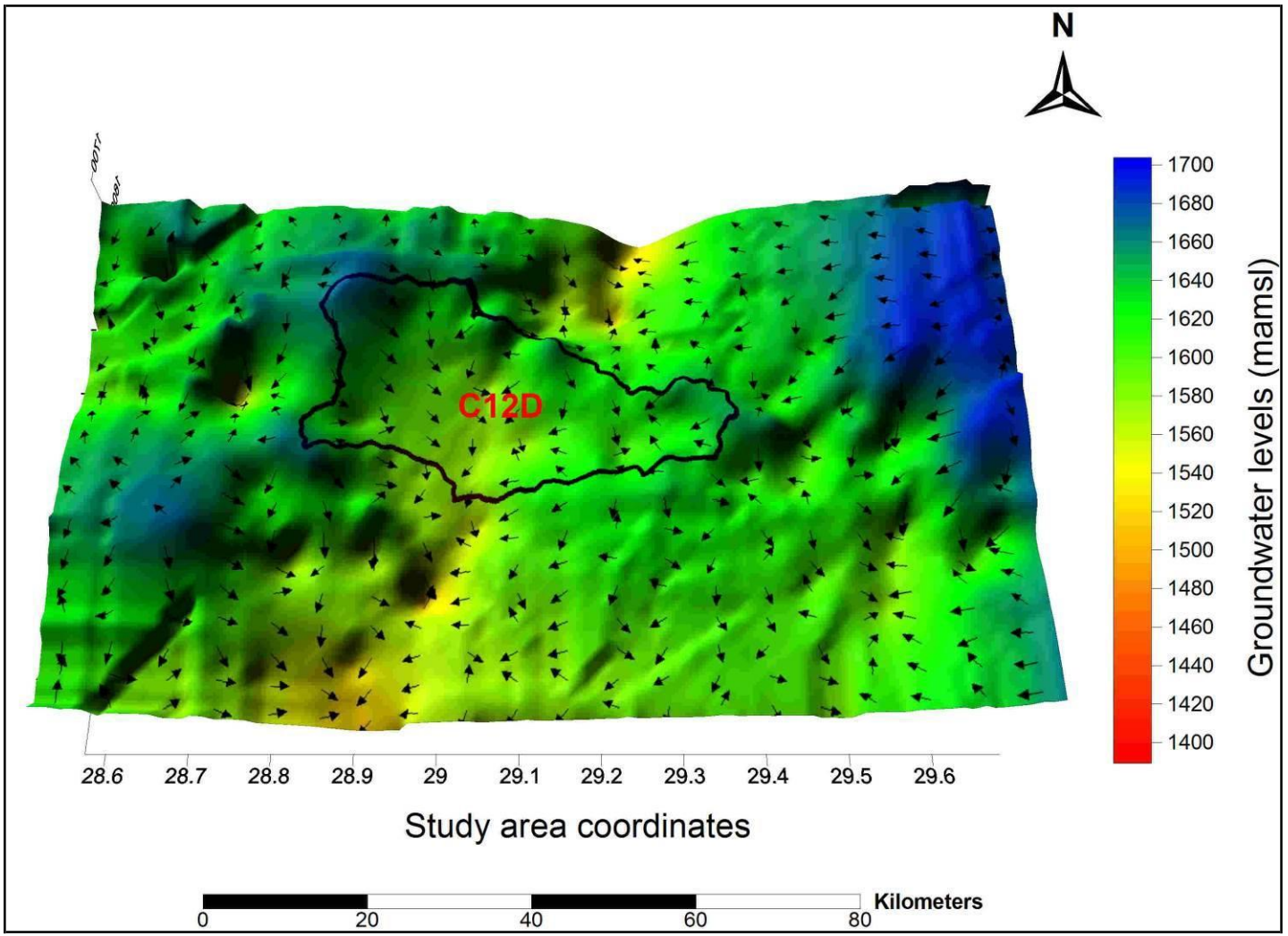


FIGURE 7: Using groundwater level data from the study area and adjacent quaternary catchments in Surfer® 8, the groundwater flow in the study area is mostly from the western and eastern sides of the study area towards the central part of the study area.

### *3.3.2 Surface and groundwater flow correlation*

To optimize the placement of groundwater monitoring localities, a correlation between groundwater levels and surface topography was investigated. If a correlation exist between groundwater levels and surface topography, surface topography can be used to estimate the groundwater flow direction and in turn to allocate upstream and downstream groundwater monitoring points.

To establish a correlation between groundwater levels and surface topography, a Bayesian correlation test was performed. The Bayesian correlation test indicates if two variables are related and how strong they are related (Wetzels and Wagenmakers, 2012). The Bayesian correlation was used above other correlation techniques primarily due to its simplicity. The Bayesian correlation is a test that is easily interpreted and it is a tool that can be used to predict future trends. The $r^2$ coefficient obtained from the correlation test is a measurement of the linear relationship between the two variables, where $r^2 = -1$ is an indication of a perfect negative correlation, $r^2 = 1$ indicates a perfect positive correlation, and $r^2 = 0$ indicates no correlation between the two variables (Wetzels and Wagenmakers, 2012). A significant score, p-value, was also calculated to determine the significance of the correlation. If a p-value of less than 0.05 is obtained, the correlation is statistically significant to the 95% confidence level.

The Bayesian correlation test was performed from a dataset comprising 1431 groundwater levels and their associated surface topography. There is a significant positive correlation between the groundwater levels (mamsl) and the surface elevation (mamsl), $r^2 = 0.9437$, $p < 0.001$ (Figure 8). Surface elevation data, as obtained from the GDA and imported into Surfer® 8, was used to plot surface water flow in the study area. The correlation between surface water flow and groundwater flow is further confirmed with the comparison of the surface water and groundwater flow maps (Figure 9).

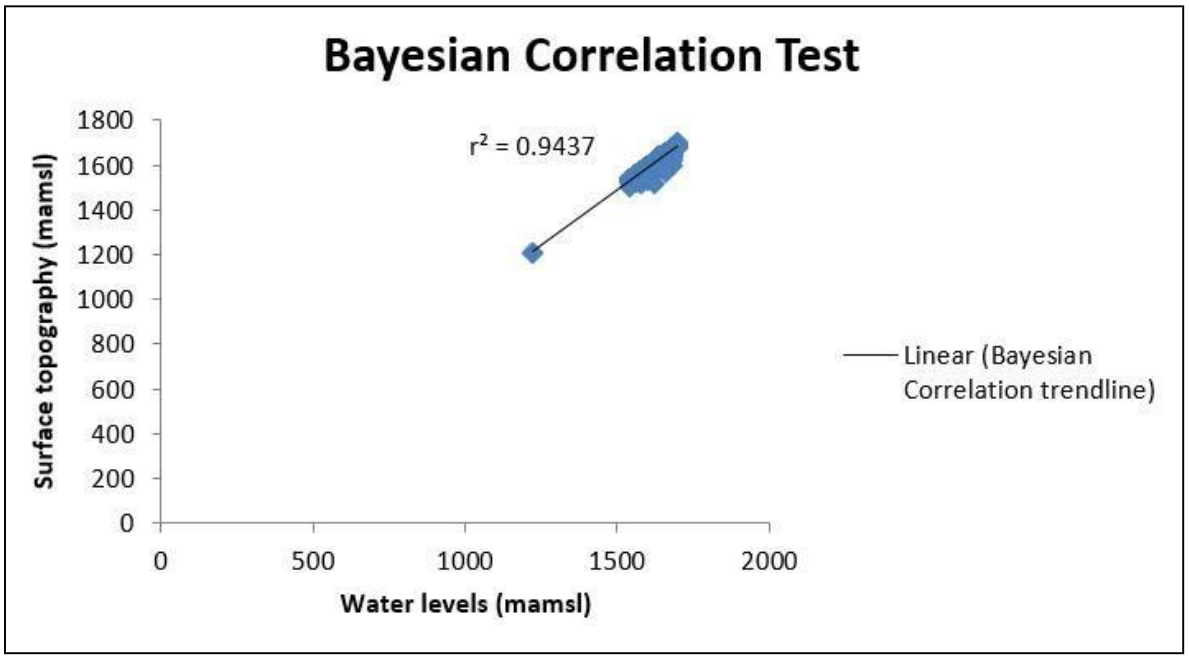


FIGURE 8: Correlation between surface topography (mamsl) and water levels (mamsl). A positive correlation indicates that groundwater levels increase as surface topography increases. It is a further indication that groundwater flow will be similar to surface water flow.

With a correlation established between groundwater levels and surface topography in the study area, groundwater quality monitoring can be optimized through placement of upstream and downstream groundwater monitoring points based only on surface water flow. Contours (5 meters apart) of the study area were used to determine surface water flow at each of the pollution areas identified (Figure 10). The direction of surface water flow can be determined by drawing a line perpendicular to two different contour intervals.

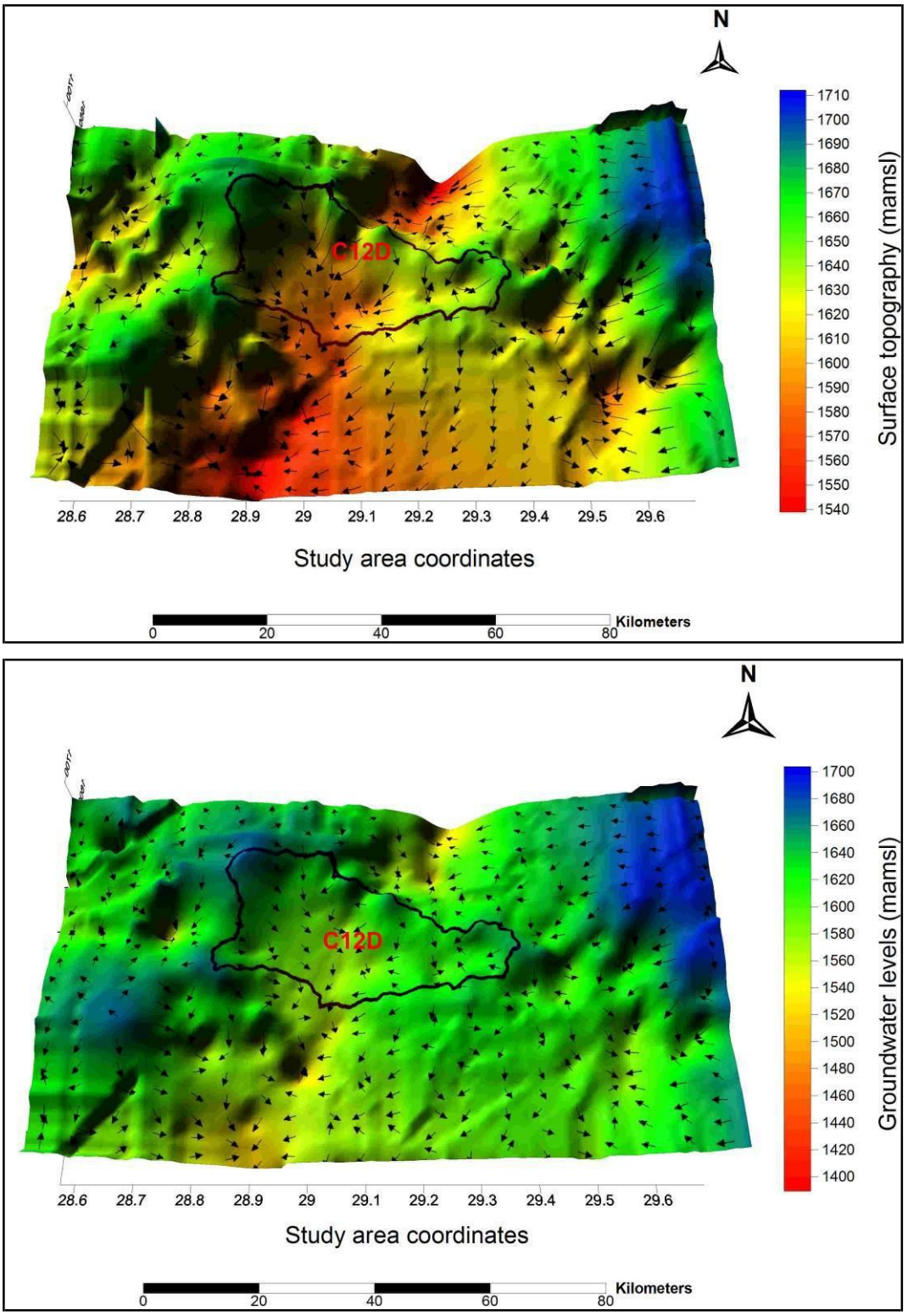


FIGURE 9: Top figure: Surface water flow is mainly from the western side and eastern side of the study area towards the middle of the study area. Bottom figure: Groundwater flow is similar to surface water flow (top figure) as it is mainly from the western side and eastern side of the study area to the middle of the study area.

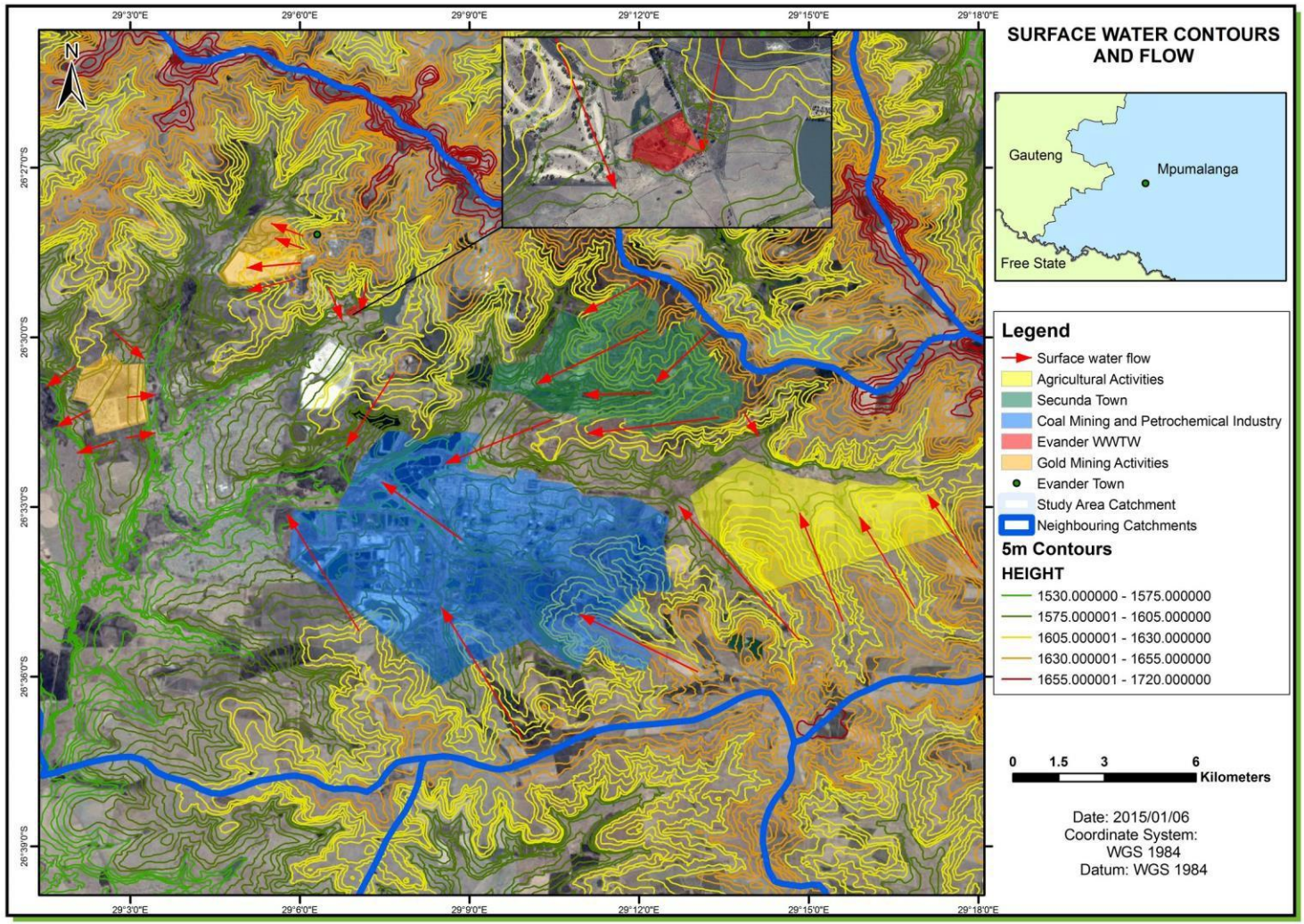


FIGURE 10: Perpendicular lines between contour intervals of 5 meters indicate the direction of surface water flow. It is assumed that groundwater flow within the study area is similar to the surface water flow due to the correlation between groundwater levels and surface topography.

### *3.3.3 Groundwater monitoring positions*

Upstream and downstream groundwater monitoring points were allocated specifically for pollution areas identified, similar to the allocation of surface water monitoring points, as a water quality monitoring optimization measure. The upstream groundwater monitoring points will provide background water qualities, where the downstream groundwater monitoring points will indicate the impact of each pollution source on the groundwater resource (DWAF, 2007). All groundwater monitoring points referred to in this section are proposed monitoring points. Existing groundwater monitoring points were not representative of upstream or downstream localities for pollution areas identified. A reference number, containing the prefix GW, was assigned for each of the groundwater monitoring points.

The groundwater flow direction at *"Gold mining area A"* is predominantly in a north, north-westerly direction. Based on the groundwater flow direction, two upstream groundwater monitoring points (GW01 and GW02) are allocated on the eastern side of the gold mining activities. Three downstream groundwater monitoring points (GW03, GW04 and GW05) are allocated to the western and north-western side of the mining activities to monitor groundwater impacts.

The "Gold mining area B" activities are situated on a watershed. A watershed is an area where two neighbouring drainage areas are separated (Strahler, 1957). The groundwater flow direction is therefore in two opposite directions (an easterly and westerly direction) as a result of the watershed. Upstream groundwater monitoring points (GW19 and GW20) are selected at the northern side of the mining area to act as background groundwater quality data. Two downstream groundwater monitoring points (GW23 and GW24) at the eastern side of the watershed and two downstream groundwater monitoring points (GW21 and GW22) at the western side of the watershed are selected to monitoring impact to the groundwater resource.

The groundwater flow direction at the sewage treatment plant is in a southerly direction. Due to the small size in activities at the sewage treatment plant, only one upstream groundwater monitoring point (GW17) is selected to the north of the plant and one downstream groundwater monitoring point (GW18) is selected as the downstream groundwater monitoring point.

The groundwater flow direction around the town of Secunda is predominantly in a west, south-westerly direction. Upstream groundwater monitoring boreholes are selected at the eastern side of Secunda (GW10, GW11 and GW12) between the urban activities and the

watershed situated further to the east. Downstream monitoring boreholes are allocated on the western side of Secunda (GW13, GW14 and GW15) to monitor any impact on the groundwater resource as a result of urban activities. An additional downstream groundwater monitoring borehole (GW16) is selected on the southern side of Secunda due to a small area where groundwater flow is to that direction.

The groundwater flow direction at the agricultural activities is in a north-westerly direction, in the direction of the Klipspruit. Two upstream groundwater monitoring boreholes (GW06 and GW07) are selected on the south-eastern side of the agricultural activities to monitor background groundwater qualities. Two downstream groundwater monitoring points (GW08 and GW09) are selected north and north-west of the agricultural activities. The downstream groundwater monitoring points are located south of the Klipspruit. Placing the downstream groundwater monitoring boreholes north of the Klipspruit will result in a misrepresentation of water quality for the agricultural activities, as the area north of the Klipspruit is downstream of the town of Secunda.

The groundwater flow direction at the coal mining and petrochemical activities is in several directions due to the large area that is occupied by the activities. The groundwater flow direction at the south of the activities are in a north-westerly direction. The groundwater flow direction is in a south-westerly direction at the northern and eastern parts of the coal mining and petrochemical activities. Three upstream groundwater monitoring points (GW25, GW26 and GW27) are selected to the south of the activities with one upstream groundwater monitoring points (GW28) selected to the north of the activities. Placing groundwater monitoring points both south and north of the activities results in optimal establishment of background groundwater qualities in an area that has groundwater flow in several directions. Three downstream groundwater monitoring points (GW29, GW30 and GW31) are selected to measure impact from the coal mining and petrochemical industry on the groundwater resource.

Refer to Figure 11 for an illustration of the groundwater monitoring points in relation to the pollution areas and to Table 2 for a summary of the groundwater monitoring points.

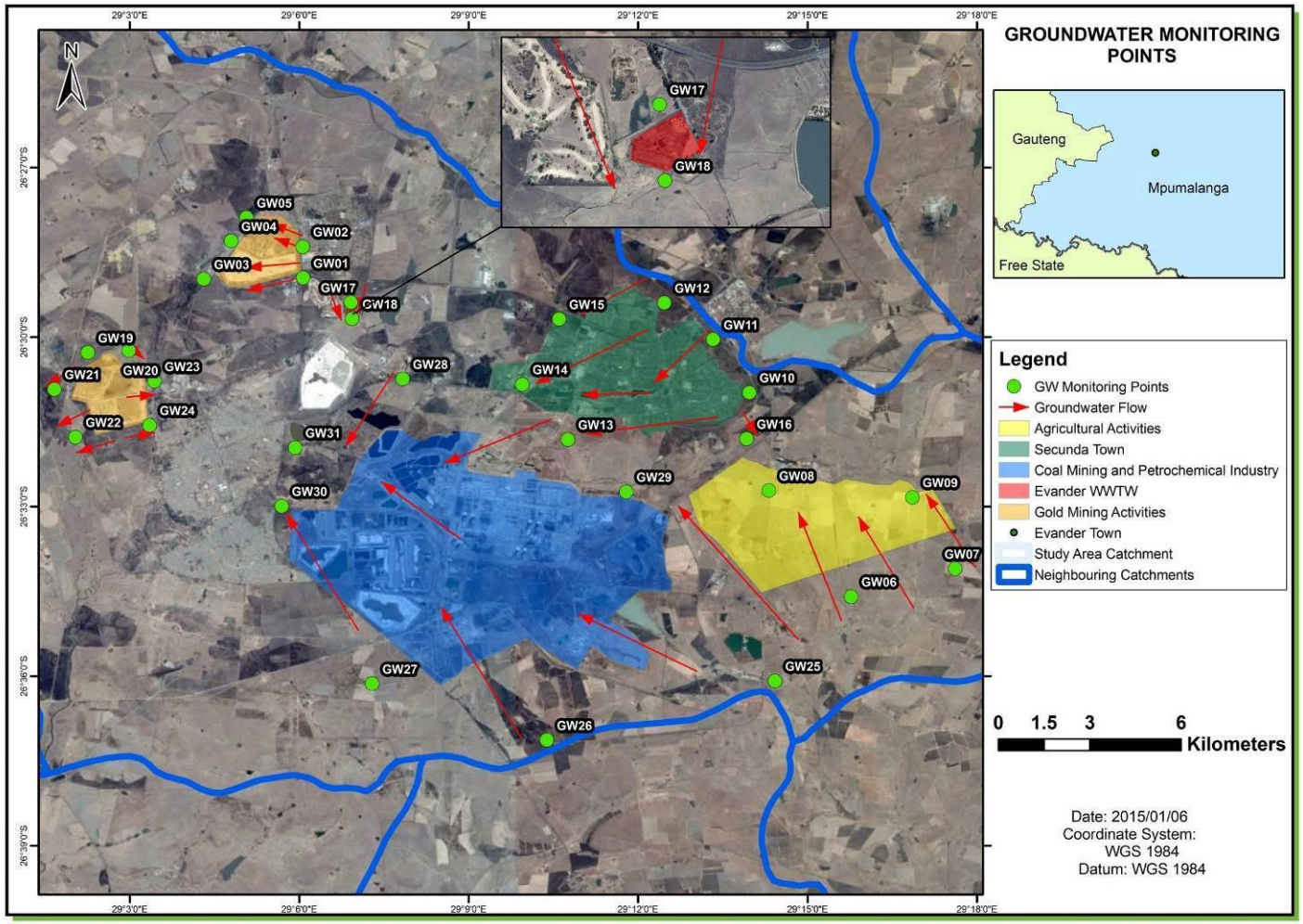


FIGURE 11: Upstream and downstream groundwater monitoring points were determined in relation to the pollution areas identified. [“Gold mining area A” – GW01 to GW05; “Gold mining area B” – GW19 to GW24; Sewage treatment plant – GW17 and GW18; Secunda town – GW10 to GW16; Agricultural activities – GW06 to GW09; Coal mining and petrochemical activities – GW25 to GW31]

TABLE 2: A summary of the selected groundwater monitoring points for the study area with their monitoring reference number, with a short description of the monitoring points.

| **Monitoring point reference number** | **Description** |
|---|---|
| GW01 and GW02 | The groundwater monitoring points is situated to the east and upstream of *"Gold mining area A"*. |
| GW03, GW04 and GW05 | The groundwater monitoring points is situated upstream and to the west and north-west of *"Gold mining area A"*. |
| GW06 and GW07 | The downstream groundwater monitoring points are situated to the south of the agricultural activities. |
| GW08 and GW09 | The upstream groundwater monitoring points are situated to the north of the agricultural activities but south of the Klipspruit. |
| GW10, GW11 and GW12 | The groundwater monitoring points are situated to the north-east of the town of Secunda and are selected as upstream groundwater monitoring boreholes. |
| GW13, GW14, GW15 and GW16 | The downstream groundwater monitoring points for the town of Secunda are situated to the west with one monitoring point (GW16) situated to the south. |
| GW17 | The groundwater monitoring point is situated upstream and to the north of the sewage treatment plant. |
| GW18 | The groundwater monitoring point is situated downstream and to the south of the sewage treatment plant. |
| GW19 and GW20 | The upstream groundwater monitoring points for *"Gold mining area B"* is situated to the north of the activities. |
| GW21, GW22, GW23, and GW24 | Due to the watershed at *"Gold mining area B"*, downstream groundwater monitoring points are selected both to the east and to the west of the activities. |
| GW25, GW26, GW27 and GW28 | Four upstream groundwater monitoring points are selected for the coal mining and petrochemical industry. The monitoring points are situated at to the south and to the north of the activities. |
| GW29, GW30 and GW31 | Two downstream groundwater monitoring points for the coal mining and petrochemical industry are selected to the west of the activities with one monitoring point situated to the north. |

# Chapter 4: Water quality variables and monitoring frequency

## *4.1 Data collection*

Unaccounted environmental factors, i.e. elevated levels of TDS as a result of dissolution of soil, may differ between study areas, which in turn may affect water quality of an area (Barnard et al., 2013; Venter and van Vuren, 1997; Al-Hogaraty et al., 2008). To eliminate unaccounted environmental factors and to accurately establish water quality variables to be monitored, an analysis of historic water quality data were conducted as part of investigating optimization of water quality monitoring within the study area. A comprehensive literature review on the impacts that the various pollution sources have on surface water and groundwater resources were also performed to compliment the water quality data obtained and to supplement where water quality data are lacking.

Water quality data for the study area were obtained from the gold mining activities situated within the study area. The gold mining activities are operational from as early as the 1960's and therefore an extensive water quality database were available for a large area within the study are. Water quality data were available for 21 surface water monitoring points and 47 groundwater monitoring points throughout the study area and included water quality data for the period from 1992 to 2012. Water quality data from the gold mining activities before 2002 was however incomplete and was lacking analysis of most of the water quality variables. The groundwater quality data from the gold mining activities were not applicable to the groundwater monitoring points selected for the study area and could therefore not be used in the analysis as it would have been an inaccurate representation of the different pollution sources. Surface water quality data were available in monthly intervals and groundwater quality data was available in quarterly intervals.

Water quality data were also requested from the DWS through the GDA. Although the database focuses on groundwater qualities, surface water qualities also formed part of the water quality data received. Water quality data for 34 surface water monitoring points were obtained from the GDA, with water quality data only available for 3 groundwater monitoring points throughout the study area. The groundwater quality data obtained for the 3 groundwater monitoring points were not applicable to the water monitoring points selected for the study area and was therefore not used in this study.

A total of eleven water quality variables (Ca, Mg, Na, Cl, $SO_4$, F, pH, EC, $NH_4$, $NO_3$ and TDS) were analysed and used for setting water quality variables to be monitored at each pollution source as well as setting monitoring frequency. The eleven water quality variables were selected based on the availability of water quality monitoring for the study area. Surface water quality data, as obtained from the gold mining activities and the GDA, and that was representative of the upstream and downstream surface water monitoring points selected for the study area, were plotted on graphs for the period between 2002 and 2012 (refer to Annexure A for all water quality variable graphs). Each graph represents an upstream and downstream surface water monitoring point for each of the pollution sources identified. As a reference, water quality data were compared to the Domestic Target Water Quality Range (DTWQR) provided by the DWS (refer to Table 3 for the guidelines). Water quality graphs were analysed for significant variations between upstream and downstream water qualities for each water quality variable and at each of the pollution sources. For this study, a significant variation was inferred when the downstream water qualities vary with more than 50% from the downstream water qualities, for more than five years of the study period. A 50% variation was selected as a conservative approach in detecting impact and to achieve the objectives of this study, and is not an indication of the severity of impact. If a variation was detected between upstream and downstream water qualities for a specific pollution source, impact from the specific pollution source on the surface water resource was assumed. The literature review was used to strengthen the variations between the upstream and downstream water qualities. The literature review was used as the only source in determining the groundwater quality variables to be impacted on by each pollution source, as there was no groundwater quality data applicable to the groundwater monitoring points established.

TABLE 3: The DTWQR as defined by the DWS. The DTWQR concentrations were used as a reference on the water quality graphs and in conjunction with the upstream and downstream water qualities of each pollution source.

| **Variable** | **Concentration** |
|---|---|
| Ca | 32 $mg.\ell^{-1}$ |
| Mg | 30 $mg.\ell^{-1}$ |
| Na | 100 $mg.\ell^{-1}$ |
| Cl | 100 $mg.\ell^{-1}$ |
| $SO_4$ | 200 $mg.\ell^{-1}$ |
| F | 1 $mg.\ell^{-1}$ |
| pH | 6 – 9 |

| | |
|---|---|
| EC | 70 $mS.m^{-1}$ |
| $NH_4$ | 1 $mg.\ell^{-1}$ |
| $NO_3$ | 6 $mg.\ell^{-1}$ |
| TDS | 450 $mg.\ell^{-1}$ |

Exceedance of the DTWQR specified for specific variables may have significant impacts on people and the environment (Department of Water Affairs and Forestry, 1996). By knowing the impacts of concentrations exceeding the DTWQR, efforts can be prioritized more effectively to the management of variables that have more severe impacts on human health and on the environment. Slight exceedance of the Ca and Mg DTWQR (32 – 80 $mg.\ell^{-1}$ and 30 – 50 $mg.\ell^{-1}$ respectively) will have no health effects however, larger exceedances of Ca (>80 $mg.\ell^{-1}$) and Mg (>400 $mg.\ell^{-1}$) will increase scaling problems and will result in diarrhoea respectively. Slight exceedances of the Na and Cl (100 – 200 $mg.\ell^{-1}$) DTWQR will result in the water becoming slightly salty with significant exceedances (>5000 $mg.\ell^{-1}$) resulting in severe salty taste and severe health implications such as disturbance of electrolyte balance.

Exceedance of the $SO_4$ DTWQR may result in diarrhoea, range of 200 – 400 $mg.\ell^{-1}$, with higher exceedances (>1000 $mg.\ell^{-1}$) resulting also in a very salty and bitter taste to the water. Slight exceedances of the F DTWQR (1.0 – 1.5 $mg.\ell^{-1}$) may result in slight damage of dental enamel, with large exceedances being lethal (>2000 $mg.\ell^{-1}$). Very acidic water (pH of less than 4) may result in severe health effects due to dissolved toxic metal ions, with very alkaline water (pH of more than 11) resulting in water tasting soapy. Severe exceedances of the TDS DTWQR (>3000 $mg.\ell^{-1}$) will result in water tasting extremely salty and bitter as well as the potential of disturbance of an adults body salt balance.

Low exceedances of $NH_4$ (1.0 - 2.0 $mg.\ell^{-1}$) and $NO_3$ (6 – 10 $mg.\ell^{-1}$) DTWQR may result in possible taste and odour deterioration, with high exceedances of $NH_4$ (>10 $mg.\ell^{-1}$) and $NO_3$ (>20 $mg.\ell^{-1}$) resulting in possible deaths of fish species in the receiving water environment and occurrence of Methaemoglobinaemia in infants respectively.

### *4.2 Surface water qualities*

#### *4.2.1 Gold mining activities*

The water quality data from the upstream and downstream surface water monitoring points at *"Gold mining area A"* (SW01 and SW02), showed significant variation between eight water quality variables (TDS, Na, EC, Ca, Cl, $SO_4$, F and Mg). The TDS concentration at SW01 stayed constant over the entire study period, with the TDS concentration reaching a

maximum of 781 mg.$\ell^{-1}$ in 2008 (Figure 12). The TDS concentration for SW01 was below the DTWQR for the entire study period, except for 2008 where the concentration exceeded the DTWQR. The TDS concentration at SW02 showed a steady increase between the period of 2002 and 2008, where it reached a maximum concentration of 2167 mg.$\ell^{-1}$. The TDS concentration for SW02 was above the DTWQR, which is 450 mg.$\ell^{-1}$, for the entire period between 2002 and 2012.

The Na concentration at SW01 where below the DTWQR for the entire study period, with the exception of 2008 where it reached an average concentration of 104 mg.$\ell^{-1}$, just exceeding the DTWQR of 100 mg.$\ell^{-1}$ (Figure 12). The Na concentration at SW02 where above the DTWQR for the entire study period, with a maximum and minimum Na concentration of 376 mg.$\ell^{-1}$ and 147 mg.$\ell^{-1}$ respectively.

The average EC at SW01 exceeded the DTWQR in 2002 and 2009 with a measurement of 73 mS.m$^{-1}$ and 71 mS.m$^{-1}$ respectively. The average EC for SW02 exceeded the DTWQR for the entire study period. It reached a maximum in 2008 with a measurement of 309 mS.m$^{-1}$ with the lowest average EC observed in 2010 with a measurement of 140 mS.m$^{-1}$.

The maximum Ca concentration at the upstream monitoring point, SW01, recorded for the study period was 60 mg.$\ell^{-1}$ (Figure 13). The Ca concentration at SW01 was below the DTWQR in 2010 and 2011 and exceeding the DTWQR for the rest of the study period. The lowest Ca concentration at SW02 was recorded in 2010, with a Ca concentration of 76 mg.$\ell^{-1}$. The highest Ca concentration was recorded in 2008 with a Ca concentration of 146 mg.$\ell^{-1}$.

The Cl concentration at SW01 recorded well below the DTWQR for the entire study period with a maximum Cl concentration of only 57 mg.$\ell^{-1}$ in 2002 (Figure 13). The Cl concentration at SW02 exceeded the DTWQR for the entire study period, with a maximum and minimum Cl concentration recorded in 2008 and 2010 respectively. The Cl concentration in 2008 and 2010 was 829 mg.$\ell^{-1}$ and 290 mg.$\ell^{-1}$ respectively.

The Mg concentration at SW01 exceeded the DTWQR for the periods of 2002, 2006, 2008 and 2009 (Figure 13). The maximum Mg concentration recorded at SW01 was 36 mg.$\ell^{-1}$ in 2006. The Mg concentration at SW02 exceeded the DTWQR for the entire study period, except for 2010 where the Mg concentration was recorded as 29 mg.$\ell^{-1}$.

The $SO_4$ concentrations at SW01 and SW02 where recorded below the DTWQR for the entire study period (Figure 14). The $SO_4$ concentration at SW02 did however record significantly higher than the $SO_4$ concentration at SW01. The maximum and minimum $SO_4$ concentrations during the study period at SW02 were 190.8 $mg.\ell^{-1}$ in 2008 and 75.9 $mg.\ell^{-1}$ in 2010 respectively.

The F concentration at SW01 was recorded below the DTWQR for entire study period, with a maximum F concentration of 0.82 $mg.\ell^{-1}$ in 2005 (Figure 14). The F concentration at SW02 in turn exceeded the DTWQR for most periods in the study period, with the exception of 2003, 2004, 2006 and 2007. The maximum and minimum F concentrations during the study period at SW02 were recorded as 1.5 $mg.\ell^{-1}$ in 2008 and 0.89 $mg.\ell^{-1}$ in 2007 respectively.

A 50% variation were observed between upstream and downstream TDS, Na, EC, Ca, $SO_4$ and Cl concentrations for the entire study period. A 50% variation between upstream and downstream Mg concentrations were observed in 2002 to 2007, 2009 and 2011 to 2012. No significant variation between upstream and downstream Mg concentrations were observed in 2008 and 2010. A 50% variation was observed between upstream and downstream F concentrations for the entire study period, except for 2005, 2007 and 2012. Based on the significant variation determined between eight upstream and downstream water quality variables, impact from *"Gold mining area A"* on these variables in the Grootspruit is confirmed.

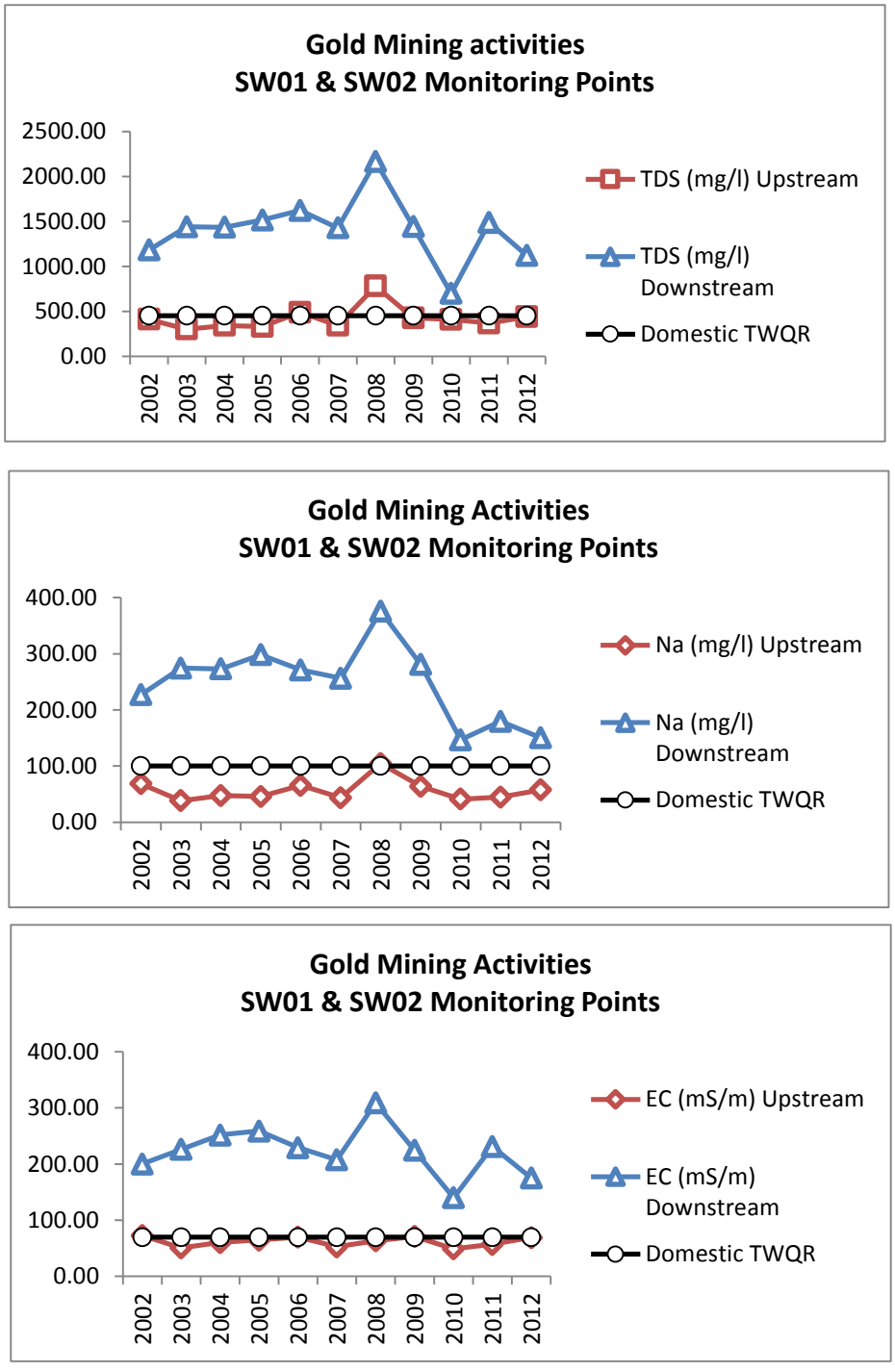


FIGURE 12: Comparison of TDS concentration (top figure), Na concentration (middle figure) and EC (bottom figure) for upstream and downstream monitoring points, SW01 and SW02, over the period 2002 to 2012. A significant variation (50%) between upstream and downstream TDS, EC and Na concentrations were determined over the entire period indicating impact from "*Gold mining area A*".

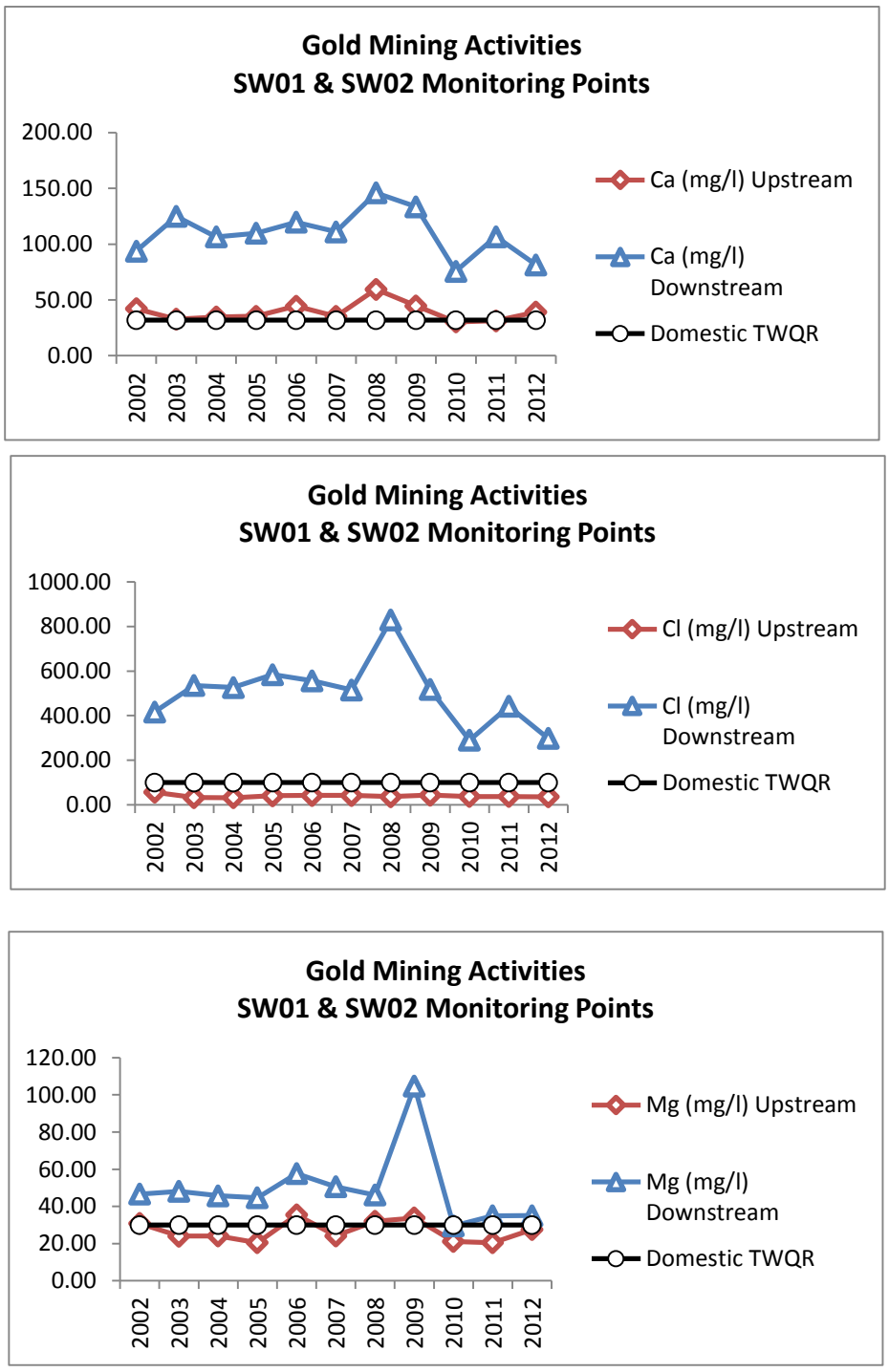


FIGURE 13: Comparison of Ca (top figure), Cl concentration (middle figure) and Mg concentration (bottom figure) for upstream and downstream water monitoring points, SW01 and SW02, between 2002 and 2012. A 50% variation in Ca and Cl concentrations between upstream and downstream monitoring points where determined for the entire study period. A significant variation (50%) between upstream and downstream Mg concentrations were only recorded for 2002 to 2007, 2009 and 2011 to 2012.

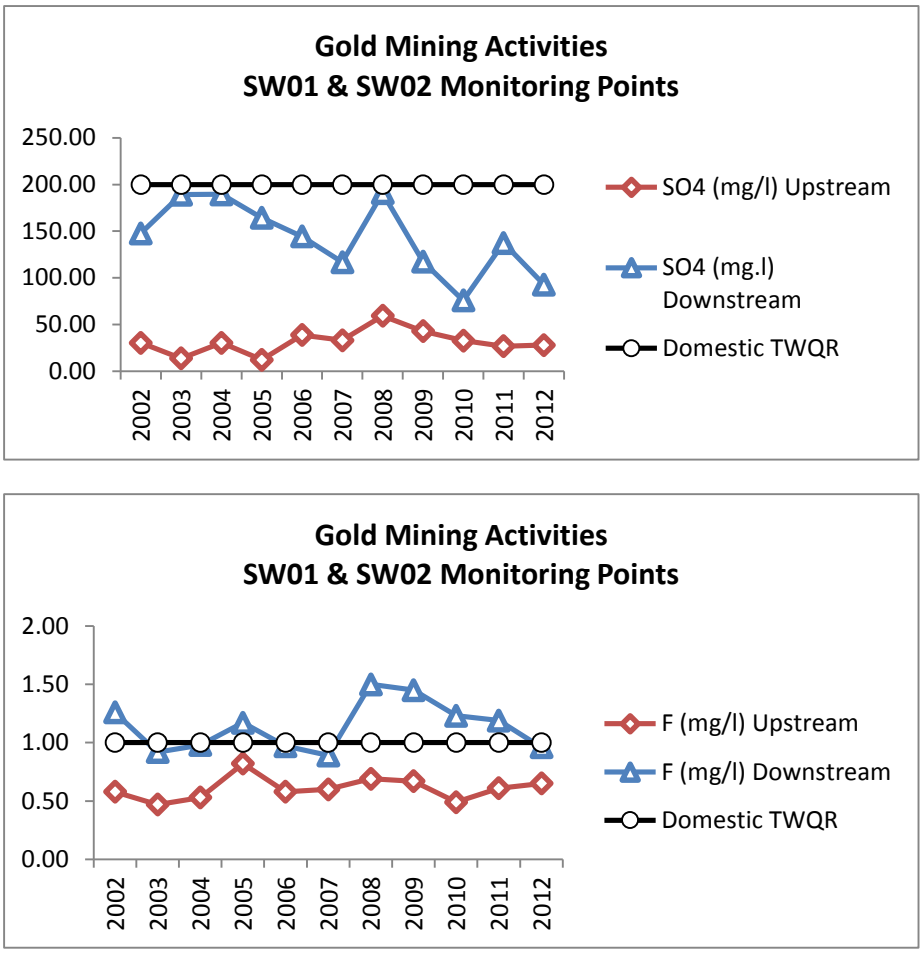


FIGURE 14: Comparison of $SO_4$ concentration (top figure) and F concentration (bottom figure) for upstream and downstream water monitoring points, SW01 and SW02, over the period 2002 to 2012. A significant variation (50%) between upstream and downstream $SO_4$ concentrations were recorded for entire study period with only no significant variation between upstream and downstream F concentrations recorded for 2005, 2007 and 2012.

The comparison between the upstream and downstream water quality data for the monitoring points at *"Gold mining area B"* (SW03 and SW04), shows no significant variation between any water quality variables. This is an indication that activities at *"Gold mining area B"* does not have a significant impact on the Grootspruit.

Literature confirms the conclusion from the historic water quality data analysis above in that gold mining activities will always have an impact on surface water qualities (Barnard et al., 2013; Venter and van Vuren, 1997). Specific activities associated with gold mining that can impact on surface water qualities include the disposal of mining waste in the form of slimes (Nengovhela et al., 2007) and the disposal of waste rock material (Luis et al., 2009). Acid mine drainage is usually associated with gold mining activities. Acid mine drainage occurs when there is a formation of sulphuric acid that leads to a low pH, high $SO_4$ content and high

EC levels (Luis et al., 2009). The main water quality variables that are impacted on by gold mining activities are $SO_4$, EC and pH (Barnard et al., 2013; Luis et al., 2009). TDS can also be impacted on by gold mining activities (Barnard et al., 2013).

Based on the historic water quality analysis and the available literature, TDS, F, Na, Ca, EC, Cl, Mg, $SO_4$ and pH should be included in the water monitoring programme for the gold mining activities to ensure optimisation of surface water quality monitoring in the study area.

*4.2.2 Sewage treatment plant*

A significant variation in Ca, $NO_3$, Na, Cl, F, EC, TDS and $NH_4$ concentrations were recorded at the upstream and downstream monitoring points (SW05 and SW06) of the sewage treatment plant. The Ca concentration at SW05 showed a steady decrease over the study period, from 28 mg.$\ell^{-1}$ in 2002 to 20 mg.$\ell^{-1}$ in 2012 (Figure 15). The Ca concentration at SW05 was also under the DTWQR of 32 mg.$\ell^{-1}$ for the entire study period. The Ca concentrations at SW06 showed an opposite trend than SW05, exceeding the DTWQR and increasing over the study period, from 29 mg.$\ell^{-1}$ in 2002 to 36 mg.$\ell^{-1}$ in 2012.

The $NO_3$ concentration recorded at SW05 showed little variation throughout the study period, with a maximum and minimum $NO_3$ concentrations of 1.2 mg.$\ell^{-1}$ and 0.3 mg.$\ell^{-1}$ respectively (Figure 15). The $NO_3$ concentration at SW06 showed a rapid increase from 2002 to 2007 where it reached a maximum concentration of 12.3 mg.$\ell^{-1}$. The $NO_3$ concentration decreased from 10.9 mg.$\ell^{-1}$ in 2008 to 6.5 mg.$\ell^{-1}$ in 2012.

The Na concentration at SW05 decreased from a maximum concentration of 56.1 mg.$\ell^{-1}$ in 2004 to a concentration of 19.9 mg.$\ell^{-1}$ in 2012, staying below the DTWQR for the entire study period (Figure 16). The Na concentration at SW06 stayed constant from 2002 to 2006 where after the concentration slightly increased to a maximum concentration of 57.5 mg.$\ell^{-1}$ in 2012. The Na concentration at SW06 recorded well below the DTWQR but varied significant from the upstream monitoring point SW05.

A decrease in Cl concentration at SW05, 39.2 mg.$\ell^{-1}$ to 17.1 mg.$\ell^{-1}$, was recorded from 2002 to 2012, staying below the DTWQR (Figure 16). The Cl concentration recorded at SW06 were similar for all years throughout the study period, except for 2009 when the Cl concentration increase to 165 mg.$\ell^{-1}$ and above the DTWQR.

The F concentration at SW05 recorded below the DTWQR for the study period with a maximum and minimum concentration of 0.76 mg.$\ell^{-1}$ in 2004 and 0.36 mg.$\ell^{-1}$ in 2010 respectively (Figure 16). The F concentration at SW06 started at 1.29 mg.$\ell^{-1}$ in 2002, decreased to 0.7 mg.$\ell^{-1}$ in 2005 where after it increased again to its maximum concentration of 1.4 mg.$\ell^{-1}$ in 2008. The F concentration then decreased again to 0.8 mg.$\ell^{-1}$ in 2012.

The EC at SW05 showed a general decrease over the study period, from 46.7 mS.m$^{-1}$ in 2002 to 31 mS.m$^{-1}$ in 2012, and staying below the DTWQR (Figure 17). In contrast, the EC at SW06 showed a general increase over the study period, from 55.8 mS.m$^{-1}$ in 2002 to 74 mS.m$^{-1}$ in 2012, exceeding the DTWQR in 2012. The same water quality trend was observed for TDS concentrations at SW05 and SW06 (Figure 17). TDS concentrations at SW05 decrease from 266.3 mg.$\ell^{-1}$ in 2002 to 206 mg.$\ell^{-1}$ in 2012 where as TDS concentrations at SW06 increased from 295.7 mg.$\ell^{-1}$ in 2002 to 472.8 mg.$\ell^{-1}$ in 2012.

The $NH_4$ concentration at SW05 was below the DTWQR for the entire study period, with a maximum and minimum $NH_4$ concentration of 0.4 mg.$\ell^{-1}$ and 0.06 mg.$\ell^{-1}$ respectively (Figure 15). The $NH_4$ concentration at SW06 between 2002 and 2005 recorded above the DTWQR, with a maximum $NH_4$ concentration of 4.2 mg.$\ell^{-1}$ in 2002. The $NH_4$ concentration decreased drastically in 2006 to 1 mg.$\ell^{-1}$ and stayed below the DTWQR until 2011. In 2012, the $NH_4$ concentration at SW06 increase to 5.8 mg.$\ell^{-1}$ for the maximum $NH_4$ concentration for the study period.

A 50% variation was observed between upstream and downstream $NO_3$ concentrations for the entire study period, with 50% variation between upstream and downstream Na and F concentration recorded for 2002 and between 2006 and 2012. For the Ca concentrations, a 50% variation between upstream and downstream data were observed for 6 study years, 2006 and from 2008 to 2012. A 50% variation between upstream and downstream Cl concentration was observed for 2002 and 2006 to 2012, 50% variation in 2006 and 2008 to 2012 for EC, and 50% variation in TDS concentration from 2008 to 2012. A 50% variation was also observed between upstream and downstream NH4 concentrations for 7 years, 2002 to 2007 and for 2012. Based on the significant variations determined for Ca, $NO_3$, Na, Cl, F, EC, TDS and $NH_4$ concentrations, the impact from the sewage treatment plant on these variables in the unnamed tributary of the Grootspruit is confirmed.

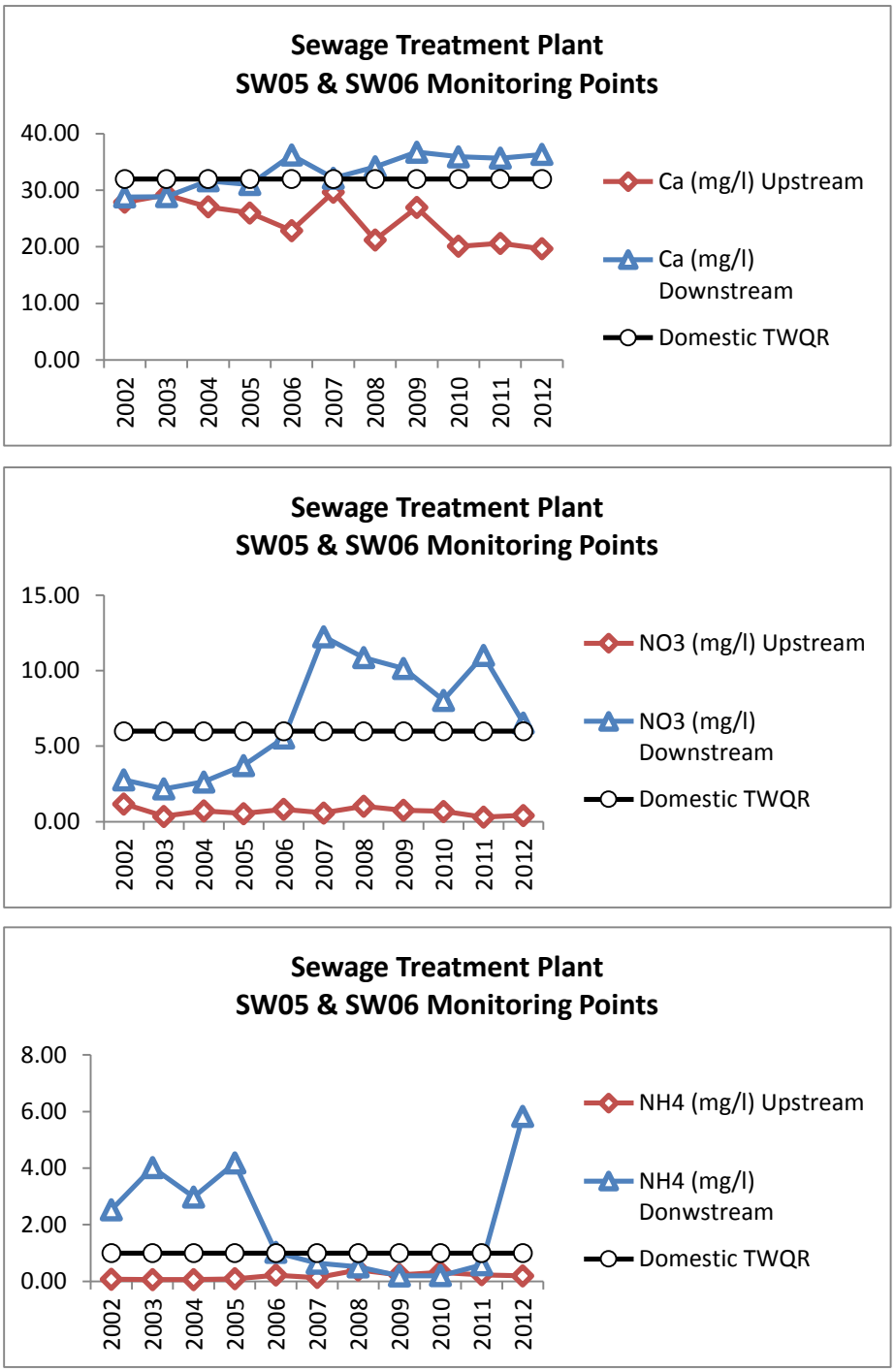


FIGURE 15: Comparison of Ca concentrations (top figure), $NO_3$ concentrations (middle figure) and $NH_4$ concentrations (bottom figure) for upstream and downstream water monitoring points, SW05 and SW06, between the period of 2002 and 2012. A significant variation in Ca concentration was observed for 2006 and from 2008 to 2012, with a significant variation in $NO_3$ concentrations for the entire study period. A significant variation in $NH_4$ concentration was observed for 2002 to 2007 and for 2012.

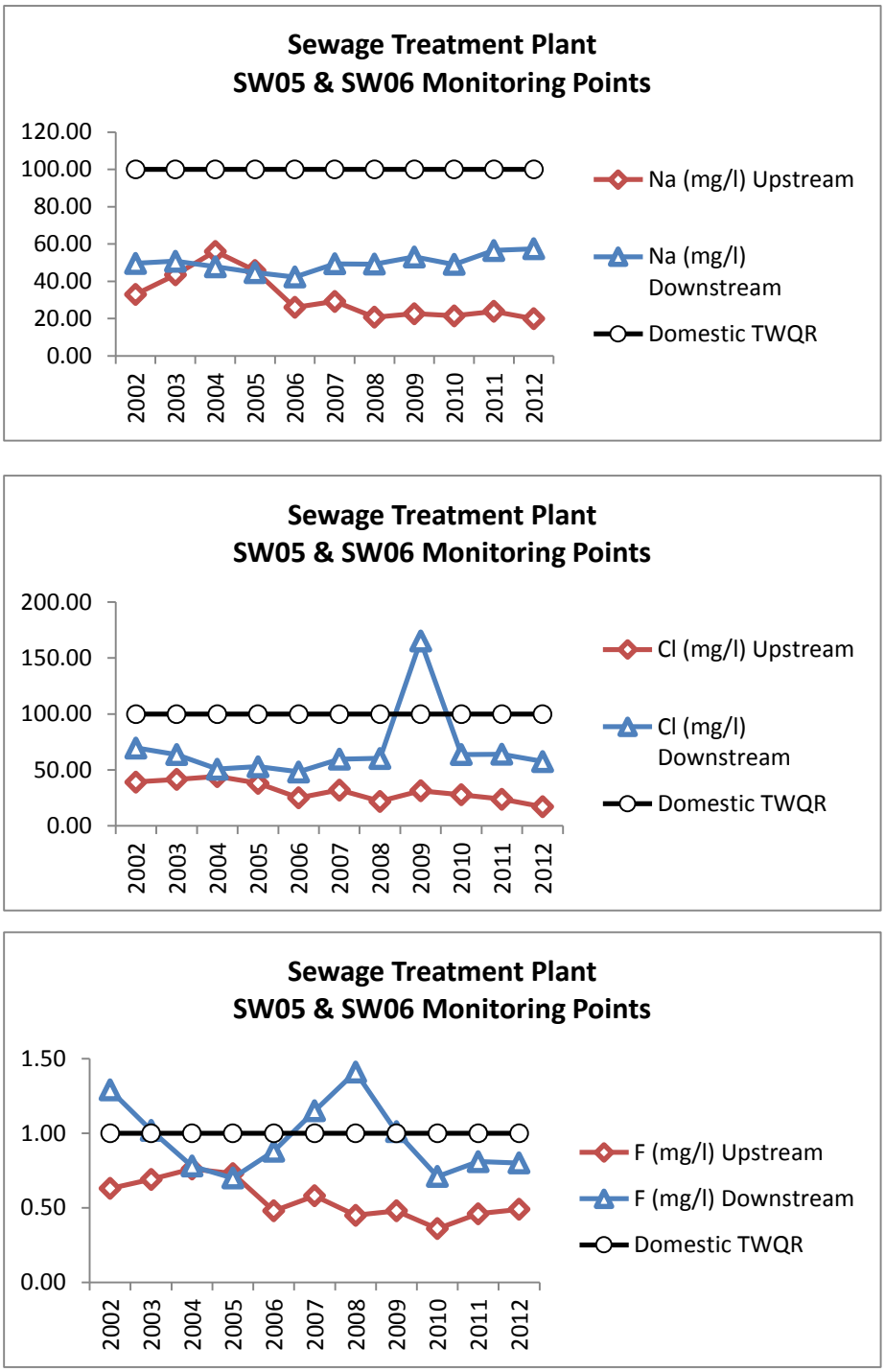


FIGURE 16: Comparison of Na concentrations (top figure), Cl concentrations (middle figure) and F concentrations (bottom figure) for upstream and downstream water monitoring points, SW05 and SW06, between the period of 2002 and 2012. A significant variation in Na and F concentrations were observed for 2002 and from 2006 to 2012. A significant variation in Cl concentration was observed for 2002 and for 2006 to 2012.

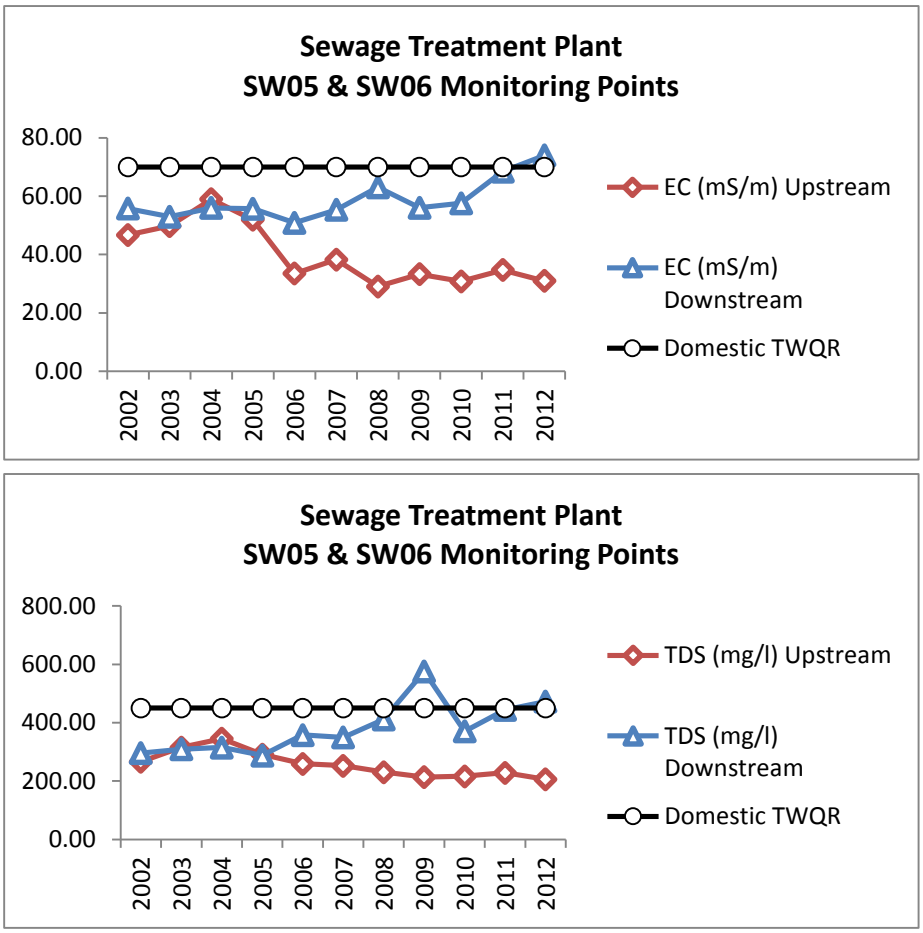


FIGURE 17: Comparison of EC (top figure) and TDS concentrations (bottom figure) for upstream and downstream water monitoring points, SW05 and SW06, between the period of 2002 and 2012. A significant variation in EC were observed for 2006 and from 2008 to 2012, with significant variation in TDS concentration from 2008 to 2012.

Literature confirms the impact from sewage treatment plants on $NO_3$ and $NH_4$ concentrations. High concentrations of $NO_3$ and $NH_4$ as a result of ammonium nitrate being totally of partially dissolved can be expected from untreated sewage effluent released into a surface water resource (Morrison et al., 2001; Nhapi and Tirivarombo, 2004). The discharge of untreated sewage effluent can also contribute to an increase in oxygen demand and nutrient loading that may eventually result in eutrophication (Jones and Lee, 1984; Morrison et al., 2001; Nhapi and Tirivarombo, 2004). When a water resource is used for potable water supply, eutrophication of the water resource is of special concern (Jones and Lee, 1984). Untreated sewage effluent usually contains high amounts of dissolved salts (Morrison et al., 2001). EC is a good indicator of the salt concentration in water and therefore a high salt load is usually associated with a high EC (Morrison et al., 2001).

Based on the historic water quality analysis and the available literature, Ca, Na, Cl, F, TDS, $NO_3$, $NH_4$ and EC should be included in the water monitoring programme for the sewage treatment plant to ensure optimisation of surface water quality monitoring in the study area.

### *4.2.3 Town of Secunda*

Upstream surface water quality data were absent for 2005 and 2009. A significant variation between upstream and downstream monitoring points (SW07 and SW08) was recorded for only Cl concentrations. The Cl concentrations at both the upstream and downstream monitoring points were however below the DTWQR. The maximum and minimum Cl concentrations at SW07 were 34.3 mg.$\ell^{-1}$ and 19 mg.$\ell^{-1}$ respectively (Figure 18). For SW08, the maximum and minimum Cl concentrations were 61.4 mg.$\ell^{-1}$ and 33 mg.$\ell^{-1}$ respectively.

A 50% variation was observed between upstream and downstream Cl concentrations for 2003, 2004, 2006, 2007, 2011 and 2012. Based on the significant variation determined for Cl concentrations, impact from the town of Secunda on Cl concentrations in the Trichardspruit is confirmed.

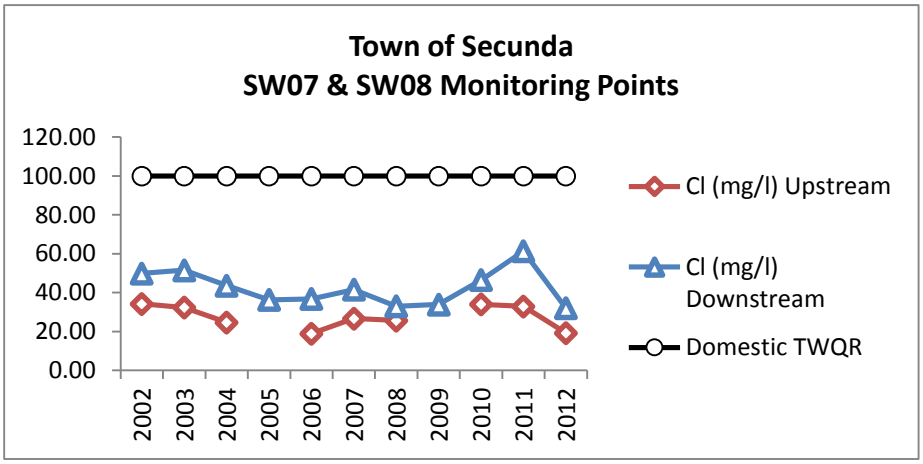


FIGURE 18: Comparison of Cl concentrations for upstream and downstream water monitoring points, SW07 and SW08, between the period of 2002 and 2012. A significant variation in Cl concentration was observed for 2003, 2004, 2006, 2007, 2011 and 2012.

Literature on the impact of urban areas on surface water resources are limited. The impacts of urban areas on surface water resources are mostly linked to other pollution activities such as agricultural activities and sewage treatment plants. Agricultural activities and sewage treatment plants were considered separately as a source of pollution in this

study and therefore no focus will be placed on these activities as part of this literature review. A study conducted by Vos and Roos (2005) looked at the impact from urban activities on an urban surface water resource before and after rainfall events. This study concluded that urban activities impact on $NO_3$ and $NH_4$ concentrations, especially after the first heavy rainfall event. A possible cause for the increase in the $NO_3$ concentrations in the surface water resource after a rainfall event has been identified as storm sewers overflowing into the surface water resource due to the increase of water pressure during the rainfall event (Vos and Roos, 2005). The increase in $NH_4$ concentrations may be as a result of mineralisation of waste and other organic matter that ends up in the surface water resource during a rainfall event (Vos and Roos, 2005). The results from the study also showed impacts on the pH of the surface water resource, with a higher pH in the winter periods than the summer periods.

Based on the historic water quality analysis and the available literature, Cl, $NO_3$, $NH_4$ and pH should be included in the water monitoring programme for the town of Secunda to ensure optimisation of surface water quality monitoring in the study area.

### *4.2.4 Agricultural activities*

Upstream and downstream water quality data were only available for the period between 2002 and 2006 and for the year 2008. No TDS concentrations were available for monitoring points SW09 and SW10. No significant variation for any water quality variable between SW09 and SW10 were observed from the available water quality data.

Although no significant variation was observed between upstream and downstream monitoring points at the agricultural activities, available literature do give an indication of water quality variables that may be impacted on by agricultural activities. The main impact on surface water qualities from agricultural activities is associated with eutrophication of the surface water resources (Walmsley et al., 1987). Eutrophication is as a result of nutrient loading from agricultural activities that results in an increase in oxygen demand (Jones and Lee, 1984; Morrison et al., 2001; Nhapi and Tirivarombo, 2004). The main agricultural activities that are responsible for eutrophication in surface water resources are feedlots, meat processing activities, milk processing activities and runoff from cultivated and uncultivated lands (Wiechers and Heynike, 1986). Highly enriched waters contains high concentrations of nitrogen that is represented in $NO_3$ and $NH_4$ (Walmsley et al., 1987).

Based only on the available literature, $NO_3$ and $NH_4$ should be included in the water monitoring programme for the agricultural activities to ensure optimisation of surface water quality monitoring in the study area.

### *4.2.5 Coal mining and petrochemical activities*

TDS concentrations for the surface water monitoring points SW11 and SW12 were absent for the entire study period. A significant variation between the upstream and downstream monitoring points (SW10, SW11 and SW12) was recorded for $SO_4$, $NH_4$ and $NO_3$ concentrations. The $SO_4$ concentration at the upstream monitoring points situated in the Klipspruit (SW10) showed an increase from 47.7 mg.$\ell^{-1}$ in 2003 to 147.7 mg.$\ell^{-1}$ in 2006, but remained within the DTWQR (Figure 19). The $SO_4$ concentration at the upstream monitoring point situated in the Trichardspruit (SW11) remained constant and below the DTWQR, with a maximum and minimum $SO_4$ concentration of 61.7 mg.$\ell^{-1}$ and 37.7 mg.$\ell^{-1}$ respectively. The $SO_4$ concentration at the downstream monitoring point (SW12) also remained constant throughout most of the study period with only a slight increase in concentration to 133.8 mg.$\ell^{-1}$ in 2009.

The $NH_4$ concentration at SW10 remained below the DTWQR for the entire study period (Figure 20). The $NH_4$ concentration at SW11 showed variation between years with the maximum $NH_4$ concentration recorded as 1.25 mg.$\ell^{-1}$. The upstream $NH_4$ concentration at SW11 was also higher than the downstream $NH_4$ concentration at SW12 in 2003, 2006 and 2012. This might be an indication of other pollution sources impacting on the SW11 monitoring point. The $NH_4$ concentration at SW12 increase from 0.29 mg.$\ell^{-1}$ in 2004 to 1.25 mg.$\ell^{-1}$ in 2009 where after it decreased to 0.18 mg.$\ell^{-1}$ in 2012.

The $NO_3$ concentrations at SW10 and SW11 stayed constant throughout the study period and within the DTWQR (Figure 19). The $NO_3$ concentrations at SW10 and SW11 measured a maximum of 1.15 mg.$\ell^{-1}$ in 2002 and 1.25 mg.$\ell^{-1}$ in 2003 respectively. The $NO_3$ concentration at SW12 showed a maximum and minimum concentration of 9.5 mg.$\ell^{-1}$ in 2008 and 1.79 mg.$\ell^{-1}$ in 2011 respectively. The $NO_3$ concentration only exceeded the DTWQR in 2008.

A 50% variation in $SO_4$ concentrations was observed between the upstream monitoring point SW11 and downstream monitoring point SW12 for the entire study period, except for 2002. A 50% variation was also observed between SW10 and SW12 $NO_3$ concentrations and between SW11 and SW12 $NO_3$ concentrations for the entire study period. Only a 50%

variation was observed between SW11 and SW12 $NH_4$ concentrations in the year 2004 and between 2007 and 2011. Based on the significant variation determined for $SO_4$, $NO_3$ and $NH_4$ concentrations, impact from the coal mining and petrochemical industries on these variables are confirmed.

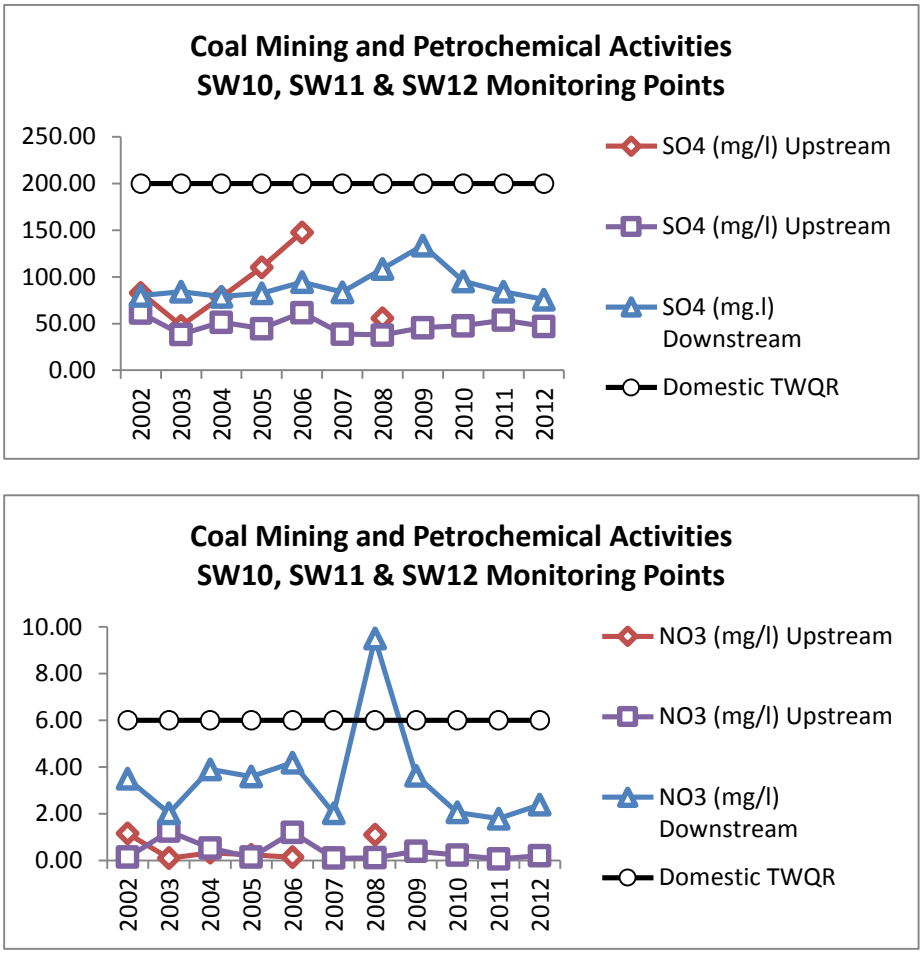


FIGURE 19: Comparison of $SO_4$ concentration (top figure) and $NO_3$ concentration (bottom figure) for upstream and downstream monitoring points, SW10, SW11 and SW12, over the period 2002 to 2012. A significant variation (50%) in $NO_3$ concentrations between SW10 and SW12 and between SW11 and SW12 were determined over the study period. A significant variation in $SO_4$ concentration between SW11 and SW12 was observed for the study period, except for 2002. No significant variation was observed between SW10 and SW12.

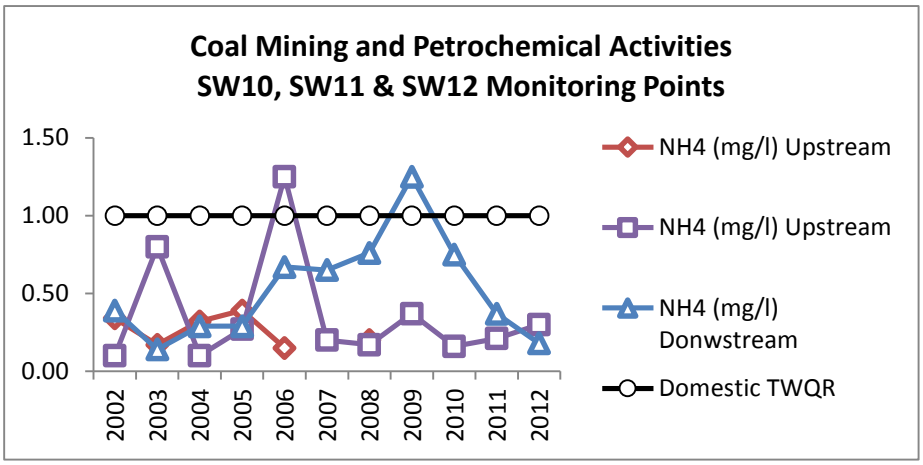


FIGURE 20: Comparison of $SO_4$ concentrations for upstream and downstream water monitoring points, SW10, SW11 and SW128, between the period of 2002 and 2012. A significant variation (50%) in $NH_4$ concentrations between SW11 and SW12 were recorded in the year 2004 and between 2007 and 2011, indicating impact from the coal mining and petrochemical activities on the surface water resource.

The impact of the coal mining activities on $SO_4$ concentrations are confirmed by the available literature. Coal mining activities will most likely have an impact on the $SO_4$ concentrations and pH levels of a surface water resource due to the high risk of acid mine drainage formation from such activities (Bester and Vermeulen, 2010; Barnes and Vermeulen, 2012). The formation of acid mine drainage can be summarised with the following three reactions (Nengovhela et al., 2007; Barnes and Vermeulen, 2012; Luis et al., 2009; Kang et al., 2001; Tiwary, 2001):

**Step 1:** Pyrite reacts with water and oxygen, forming dissolved ferrous iron, acidity and $SO_4$.

$4FeS_{2(s)} + 14O_{2(g)} + 4H_2O_{(l)} \rightarrow 4Fe^{2+}_{(aq)} + 8SO_4^{2-}{}_{(aq)} + 8H^+_{(aq)}$

The reaction initiates once pyrite has come into contact with oxygen and water.

**Step 2:** Ferrous iron is oxidised to ferric iron.

$4Fe^{2+}_{(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O_{(l)}$

Constructed silt traps/ponds and aerobic wetlands promote this reaction.

**Step 3:** Ferric iron is hydrolysed to insoluble iron hydroxide (yellow boy).

$4Fe^{3+}_{(aq)} + 12\ H_2O_{(l)} \rightarrow 4Fe(OH)^3_{(s)} + 12H^+_{(aq)}$

Acid mine drainage formation, as presented in the three formulas above, results in elevated $SO_4$ concentrations and a decrease in the pH of a surface water resource. Coal mining and petrochemical activities may also impact on Cl, Mg and Na concentrations of a surface water resource (Bester and Vermeulen, 2010; Kang et al., 2001).

Based on the historic water quality analysis and the available literature, $SO_4$, $NO_3$, $NH_4$, Na, pH, Cl, Mg, K and pH should be included in the water monitoring programme for the coal mining and petrochemical activities to ensure optimisation of surface water quality monitoring in the study area.

### *4.3 Groundwater qualities*

No groundwater qualities obtained from the gold mining activities and from the GDA could be used for groundwater quality comparison. The groundwater qualities obtained were incomplete and not applicable to the groundwater monitoring points selected for the study area. Only a literature review was therefore conducted to determine groundwater quality variables to be monitored and the frequency of groundwater monitoring.

#### *4.3.1 Gold mining activities*

Pyrite containing rock, which is a feature of some gold mines in South Africa, results in the formation of acid mine drainage when reacting with water and oxygen (Luis et al., 2009). Acid mine drainage formation and the associated negative groundwater quality features are as a result of the formation of sulphuric acid from the reactions between pyrite rock and oxygen and water. Acid mine drainage formation can be summarised through three formulas as highlighted by Nengovhela et al. (2007), Barnes and Vermeulen (2012), Luis et al. (2009), Kang et al. (2001) and Tiwary (2001) and as illustrated in the surface water section above. Acid mine drainage leads to a low pH, high $SO_4$ concentration and high EC in groundwater resources (Luis et al., 2009; Barnard et al., 2013). The impact of gold mining activities on groundwater resources is further highlighted by Armah (2014) in a case study conducted in the gold mining regions of Ghana. The study concluded that gold mining activities will result in high EC and $NO_3$ concentrations in groundwater resources.

To ensure optimization of groundwater quality monitoring at the gold mining activities, pH, $SO_4$, EC and $NO_3$ must be included in the groundwater monitoring programme for the study area.

### *4.3.2 Sewage treatment plant*

Treated effluent released from sewage[1] treatment plants into surface water resources may impact on groundwater resources if not adequately treated. Inadequate treatment of sewage at a sewage treatment plant may be as a result of poor maintenance and upkeep, or due to the lack of financial support and technical knowledge. The treated effluent released into the surface water resource will seep through to the underlying aquifer and in turn impact on groundwater qualities (Kroeger et al., 2006). Elevated $NO_3$ and $NH_4$ concentrations in the groundwater resource downstream of the sewage treatment plant can therefore be expected (Kroeger et al., 2006; Morrison et al., 2001; Nhapi and Tirivarombo, 2004).

To ensure optimization of groundwater quality monitoring at the sewage treatment plant, $NO_3$ and $NH_4$ must be included in the groundwater monitoring programme for the study area.

### *4.3.3 Town of Secunda*

Studies conducted by Al-Hogaraty et al. (2008), in the northern United Arab Emirates, and by Kelly (2008), identified several point sources and non-points sources of groundwater pollution as a result of urbanisation. Point sources include tyre disposal sites, hospitals, clinics, petrol storage tanks and industrial factories such as fertiliser and cement factories. Non-point sources include old sewerage systems, such as pit latrines, leakage from new sewerage systems into the groundwater aquifers and polluted storm water runoff from roads. An activity associated with urban areas that can have a significant impact in groundwater qualities are the disposal of waste at a landfill site. Groundwater pollution from landfill sites may result from leaching of contaminants from the waste disposed at the landfill sites (Husain et al., 1989; Al-Hogaraty et al., 2008). The level of groundwater pollution are influenced by the age of the landfill site as well as the climate in which the landfill site is situated (Husain et al., 1989).

Leachate from landfill sites and contamination as a result of point and non-point sources of pollution may lead to elevated concentrations of Cl, $SO_4$, Na, Ca, TDS, $NO_3$ and $NH_4$ in the groundwater resource (Al-Hogaraty et al., 2008; Kelly, 2008; Husain et al., 1989). To ensure optimization of groundwater quality monitoring at the town of Secunda, all water quality variables listed above must be included in the water monitoring programme for the study area.

[1] Sewage refers to the waste that is generated whereas sewerage refers to the facilities that conveys the sewage.

### *4.3.4 Agricultural activities*

Agriculture is recognised as the leading non-point source polluter to surface water and groundwater resources (Liu and Hallberg, 2002). Agricultural activities throughout the world are associated with the use of large quantities of fertiliser or the disposal of manure from feedlots (Jayasingha et al., 2011). Fertilisers are applied to infertile soils as part of crop cultivation activities and due to this practise high concentrations of $NO_3$ are found in groundwater resources in close proximity to these activities (Jayasingha et al., 2011; Khanif et al., 1984; Liu and Hallberg, 2002; Kraft et al., 2008). Intense agricultural activities make use of high quantities of fertilizer on cultivated land as well as intense watering to prevent the ground from becoming dry (Jayasingha et al., 2011). The combined effect of applying high quantities of fertiliser and intense watering result in leaching of $NO_3$ into the groundwater resource, resulting in groundwater pollution. Consuming water with high concentrations of $NO_3$ can have severe health implications such as developing methaemoglobinemia and cancer (Khanif et al., 1984).

To ensure optimization of groundwater quality monitoring at the agricultural activities, $NO_3$ must be included in the water monitoring programme for the study area.

### *4.3.5 Coal mining and petrochemical activities*

Water found in opencast coal mines and underground water in close proximity to coal mining activities generally contains high concentrations of TDS, $SO_4$ and $NO_3$ (Tiwary, 2001). The major source of groundwater pollution from coal mining activities are seepage from waste dumps such as overburden dumps, waste rock dumps and tailings dumps (Tiwary, 2001). Similar to gold mining activities, acid mine drainage formation may result from coal mining activities. Acid mine drainage results in a decrease in pH and an increase in $SO_4$ concentrations, due to the formation of sulphuric acid when pyrite rock comes in contact with oxygen and water (Tiwary, 2001; Cook and Fritz, 2002).

To ensure optimization of groundwater quality monitoring at the coal mining and petrochemical activities, TDS, $SO_4$, $NO_3$ and pH must be included in the water monitoring programme for the study area.

## *4.4 Water quality variables and monitoring frequency*

The results from the background water quality analysis and the literature review enables the optimization of water quality monitoring in the study area through setting water quality variables to be monitored and also setting the frequency of monitoring. Water quality

variables that showed significant variation between upstream and downstream water monitoring points and water quality variables that have been identified by literature to be of concern are selected for more frequent water quality monitoring, i.e. monthly water quality monitoring. More frequent water quality monitoring for variables that are impacted on by the different pollution sources will allow for early detection of pollution events and in turn allow for quick remediation activities to take place. Water quality variables not selected for monthly monitoring have been selected for annual water monitoring to maintain background water qualities in the study area.

In Table 4 and Table 5 below, a summary of the surface water and groundwater quality variables to be monitored in the study area, including the frequency of monitoring of each water quality variable, are presented.

TABLE 4: A summary of the surface water quality variables to be monitored on a monthly and quarterly bases for each surface water monitoring point. Grey highlighted cells indicate water quality variables that needs to be monitored on a monthly basis. Clear cells were not identified to be impacted on and needs to be monitored on an annual basis.

| Surface water monitoring point reference | Ca | Mg | Na | Cl | $SO_4$ | F | pH | EC | $NH_4$ | $NO_3$ | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **SW01 and SW02** | | | | | | | | | | | |
| **SW03 and SW04** | | | | | | | | | | | |
| **SW05 and SW06** | | | | | | | | | | | |
| **SW07 and SW08** | | | | | | | | | | | |
| **SW09** | | | | | | | | | | | |
| **SW10, SW11 and SW12** | | | | | | | | | | | |

TABLE 5: A summary of the groundwater quality variables to be monitored on a monthly and quarterly bases for each groundwater monitoring point. Grey highlighted cells indicate water quality variables that needs to be monitored on a monthly basis. Clear cells were not identified to be impacted on and needs to be monitored on an annual basis.

| Groundwater monitoring points reference numbers | Ca | Mg | Na | Cl | $SO_4$ | F | pH | EC | $NH_4$ | $NO_3$ | TDS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| GW01, GW02, GW03, GW04 and GW05 | | | | | | | | | | | |
| GW06, GW07, GW08 and GW09 | | | | | | | | | | | |
| GW10, GW11, GW12, GW13, GW14, GW15 and GW16 | | | | | | | | | | | |
| GW17 and GW18 | | | | | | | | | | | |
| GW19, GW20, GW21, GW22, GW23 and GW24 | | | | | | | | | | | |
| GW25, GW26, GW27, GW28, GW29, GW30 and GW31 | | | | | | | | | | | |

# Chapter 5: Conclusion and recommendations

## *5.1 General*

Water is one of the most sought after natural resource in South Africa and the world today (Barnes and Vermeulen, 2012). Government, as the custodians of water, has the responsibility of protecting this resource in South Africa. Water quality monitoring is one measure to achieve the goals in protecting our water resources (Roux et al., 1993). A CMA can, as part of this responsibility, assist in protecting and regulating the water in South Africa. The CMA, and its associated roles and responsibilities, is yet to be established for the study area, however, one of the possible roles and responsibilities that could be assigned to the CMA for the study area is to implement and maintain water quality monitoring. Water quality monitoring can however be very complex due to the different pollution sources and the large scale of activities within a specific area. Water quality monitoring can be implemented in the study area by the CMA to achieve four different objectives (Roux et al., 1999). Water quality monitoring can be implemented in the study area to monitor water quality trends within the catchment or to measure performance towards water resource quality objectives that are specified by the DWS for the study area. Water quality monitoring can also be used for compliance monitoring, i.e. to verify compliance to water quality limits specified in a water use license. It can also be used as impact assessment monitoring, to monitor why the quality of a water resource is what it is. Optimization of water quality monitoring in the study area will allow for achieving any of the different water quality monitoring objectives in a fast and effective manner. Water quality monitoring can also be simplified for a specific area through optimization of the water quality monitoring.

Quaternary catchment C12D was used as study area to illustrate optimization of water quality monitoring in a typical quaternary catchment in the Mpumalanga Province of South Africa. The results from this study have shown optimization of water quality monitoring in the study area and these results can be used by the CMA for future water quality monitoring. Three optimization principles have been identified in this study that can be applied by the CMA in the study area.

## *5.2 Pollution areas*

Five major pollution sources were identified in the study area that may have an impact on surface water and groundwater qualities. The results from this study have identified five major pollution activities namely gold mining, agricultural activities, a sewage treatment

plant, town of Secunda and coal mining and petrochemical activities. Through identifying the main pollution sources of the study area, the CMA can implement impact assessment monitoring and compliance monitoring at these pollution areas (Roux et al., 1999).

### *5.3 Selecting surface and groundwater monitoring points*

Surface water and groundwater monitoring points were selected in this study specifically for each pollution source identified and can be used by the CMA to continue water quality monitoring within the study area. A total of 12 surface water monitoring points were selected upstream and downstream of the pollution sources identified within the tributaries most likely to be impacted on. A significant positive correlation between groundwater flow and surface water flow was also established in the study area. It optimizes water quality monitoring through allowing the CMA to use surface water flow as an indication for groundwater flow, therefore simplifying groundwater flow direction determination around new pollution sources identified. A total of 31 groundwater monitoring points were selected upstream and downstream of the pollution sources identified. Additional surface water and groundwater monitoring points need to be selected when new pollution sources are identified within the study area.

### *5.4 Water quality variables and frequency of monitoring*

The water quality variables and frequency of monitoring determined in this study were based on historic water quality data and a literature review. According to Barnard et al. (2013), environmental factors of a specific area will affect the water quality of that area, irrespective of the pollution sources within the area. The water qualities to be monitored in the study area is therefore representative of the specific pollution sources identified as well as possible unaccounted environmental factors that may affect water quality (Barnard et al., 2013; Venter and van Vuren, 1997; Al-Hogaraty et al., 2008). Determining specific water quality variables to be monitored also allows for the CMA to focus on water quality variables of concern, reduce time spent on analysis as well as costs incurred.

Based on this, historic surface water quality data were used to establish significant variations between upstream and downstream surface water monitoring points. A significant variation in TDS, Na, EC, Ca, Cl, $SO_4$, F and Mg concentrations were recorded between the upstream and downstream monitoring points at the gold mining area. Water qualities analysed upstream and downstream of the sewage treatment plant showed significant variations in Ca, $NO_3$, Na, Cl, F, EC, TDS and $NH_4$ concentrations between the two monitoring points. Only Cl concentrations showed a significant variation between upstream and downstream monitoring points selected for monitoring at the town of Secunda, with no significant variation at the

monitoring points selected at the agricultural activities. The water quality data for the coal mining and petrochemical activities showed a significant variation between upstream and downstream monitoring points for $SO_4$, $NH_4$ and $NO_3$ concentrations. The water qualities that showed a significant variation between upstream and downstream monitoring points, together with water quality variables identified as part of the literature review, are to be monitored on a more frequent basis to optimize surface water quality monitoring.

No historic groundwater data were available to determine variation between upstream and downstream groundwater quality variables. The literature review identified pH, $SO_4$, EC and $NO_3$ concentrations in groundwater to be impacted on by gold mining activities, with TDS, $SO_4$, pH and $NO_3$ concentrations in groundwater to be impacted on by the coal mining and petrochemical activities. Only $NO_3$ concentrations were identified as a variable in groundwater impacted on by agricultural activities. The sewage treatment plant can impact on $NO_3$ and $NH_4$ concentrations in groundwater, with the town of Secunda having a significant impact on Cl, $SO_4$, Na, Ca, TDS, $NO_3$ and $NH_4$ concentrations in the groundwater.

### *5.5 Conclusion*

In conclusion, the results from this study can assist the CMA of the study area to optimize water quality monitoring through three activities identified. Firstly, the major pollution sources of the study area have been identified and the upstream and downstream surface water monitoring points have been selected. Other pollution sources are bound to exist within the study area. It is recommended that smaller pollution sources are identified to further optimize water quality monitoring within the study area.

Secondly, a correlation was established between the groundwater flow direction and the surface water flow direction. This will allow the CMA to use surface topography as an indication of the groundwater flow direction of the study area. The upstream and downstream groundwater monitoring points have also been selected for the identified pollution sources. It is recommended that additional studies be conducted to determine the presence of dykes and faults in the study area and the impact it may have on groundwater flow directions. The presence of dykes and faults may impact on the direction of groundwater flow and is therefore a component worth considering for future optimization of water quality monitoring in the study area (Babiker and Gudmundsson, 2004).

Thirdly, water quality variables specific to the pollution sources identified were determined through assessing historic water quality data and establishing a significant

variation between upstream and downstream water qualities. Where water quality data was lacking, available literature was used in determining water quality variables to be monitored. For future optimization of water quality monitoring within the study area, other water quality monitoring techniques can also be incorporated. Assessing the chemical attributes of water can only be considered an initial assessment of water quality (Roux et al., 1993). Bio-monitoring is an indicator of overall environmental health as biological communities are all influenced by physical and chemical attributes of a water resource, and can be included as a measure to optimize water quality monitoring within the study area (Roux et al., 1993). It is further recommended that a groundwater quality dataset is incorporated within the GDA to enable the CMA to assess water quality trends. A detailed surface water quality data set is available from the GDA, however, a groundwater quality data set was absent.

An investigation into strategies that will improve water quality is recommended as a possible future study that will supplement this dissertation.

Through optimisation of water quality monitoring in the study area, the CMA can assist water users in efficient allocation of resources (both financial and human resources). This will have a direct positive financial implication on the water user. Optimisation of water quality monitoring in the study area will also enable the CMA to keep people or industries liable for pollution as a more clear and detailed understanding of the water qualities would be established. This may ultimately have a positive effect on the water quality of the area.

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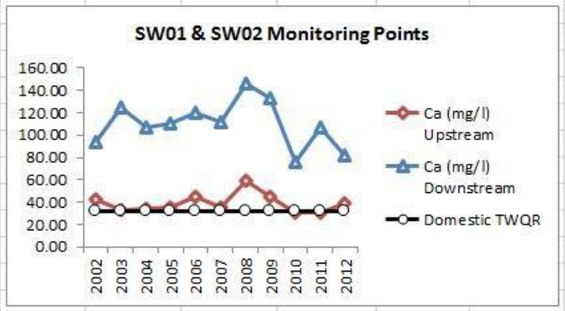
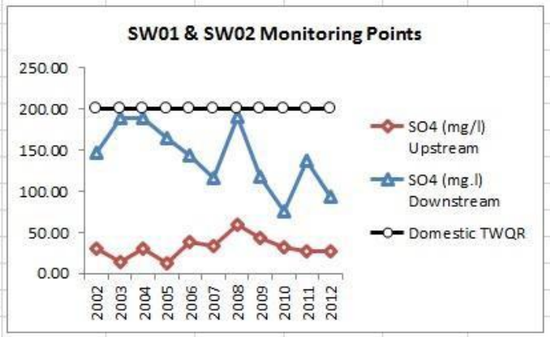
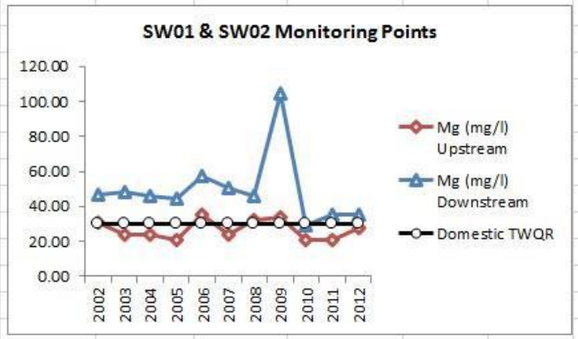
# Annexure A

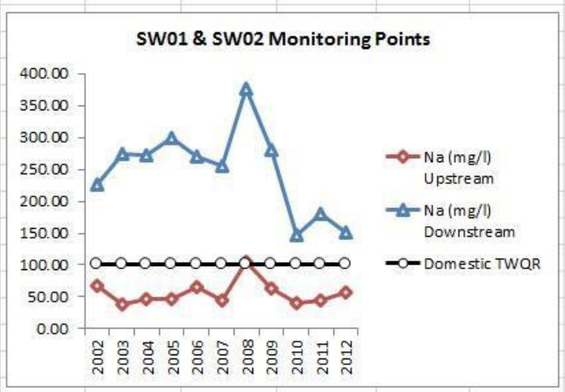
Water monitoring data

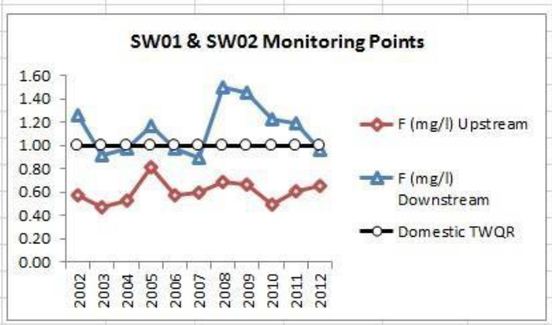
| Year | Ca (SW01) | Ca (SW02) | Ca (TWQR) | Mg (SW01) | Mg (SW02) | Mg (TWQR) | Na (SW01) | Na (SW02) | Na (TWQR) | Cl (SW01) | Cl (SW02) | Cl (TWQR) | SO4 (SW01) | SO4 (SW02) | SO4 (TWQR) | F (SW01) | F (SW02) | F (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 42.12 | 93.82 | 32.00 | 30.89 | 46.68 | 30.00 | 68.50 | 227.04 | 100.00 | 57.13 | 417.02 | 100.00 | 30.45 | 147.61 | 200.00 | 0.58 | 1.26 | 1.00 |
| 2003 | 32.76 | 124.98 | 32.00 | 24.04 | 48.13 | 30.00 | 38.38 | 274.54 | 100.00 | 32.78 | 535.09 | 100.00 | 13.88 | 189.14 | 200.00 | 0.47 | 0.92 | 1.00 |
| 2004 | 34.68 | 106.49 | 32.00 | 24.10 | 45.76 | 30.00 | 47.47 | 272.97 | 100.00 | 32.00 | 526.42 | 100.00 | 30.45 | 189.47 | 200.00 | 0.53 | 0.98 | 1.00 |
| 2005 | 35.39 | 109.90 | 32.00 | 20.45 | 44.71 | 30.00 | 45.76 | 298.42 | 100.00 | 40.82 | 583.74 | 100.00 | 12.26 | 164.35 | 200.00 | 0.82 | 1.17 | 1.00 |
| 2006 | 44.50 | 119.74 | 32.00 | 35.50 | 57.67 | 30.00 | 65.53 | 271.08 | 100.00 | 42.52 | 556.66 | 100.00 | 38.82 | 144.46 | 200.00 | 0.58 | 0.97 | 1.00 |
| 2007 | 35.19 | 111.09 | 32.00 | 24.22 | 50.63 | 30.00 | 43.62 | 256.28 | 100.00 | 42.59 | 515.70 | 100.00 | 33.23 | 116.88 | 200.00 | 0.60 | 0.89 | 1.00 |
| 2008 | 59.58 | 146.05 | 32.00 | 32.04 | 46.15 | 30.00 | 104.47 | 375.91 | 100.00 | 37.24 | 829.27 | 100.00 | 59.36 | 190.83 | 200.00 | 0.69 | 1.50 | 1.00 |
| 2009 | 44.72 | 133.58 | 32.00 | 33.83 | 104.76 | 30.00 | 63.89 | 280.90 | 100.00 | 43.96 | 518.57 | 100.00 | 42.93 | 117.43 | 200.00 | 0.67 | 1.45 | 1.00 |
| 2010 | 30.25 | 75.76 | 32.00 | 21.16 | 29.52 | 30.00 | 41.03 | 146.71 | 100.00 | 37.91 | 290.26 | 100.00 | 32.83 | 75.92 | 200.00 | 0.49 | 1.23 | 1.00 |
| 2011 | 31.26 | 106.63 | 32.00 | 20.47 | 34.96 | 30.00 | 44.62 | 179.62 | 100.00 | 37.77 | 441.89 | 100.00 | 26.89 | 137.33 | 200.00 | 0.61 | 1.19 | 1.00 |
| 2012 | 39.05 | 81.46 | 32.00 | 27.60 | 35.09 | 30.00 | 57.59 | 150.38 | 100.00 | 36.33 | 298.29 | 100.00 | 28.00 | 92.87 | 200.00 | 0.65 | 0.96 | 1.00 |

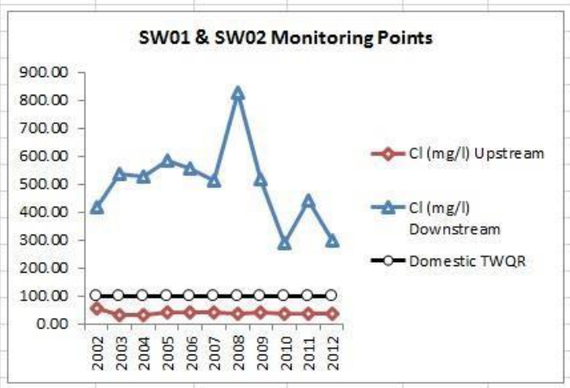


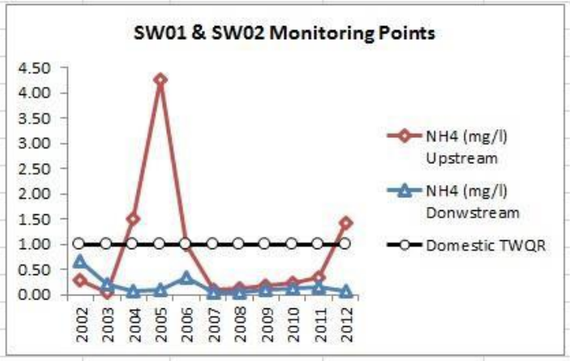



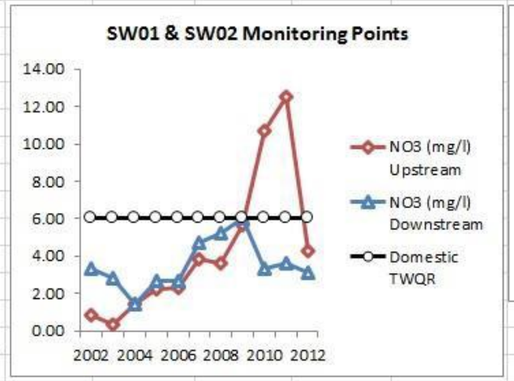



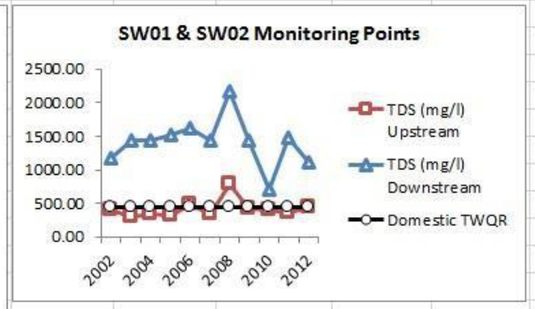



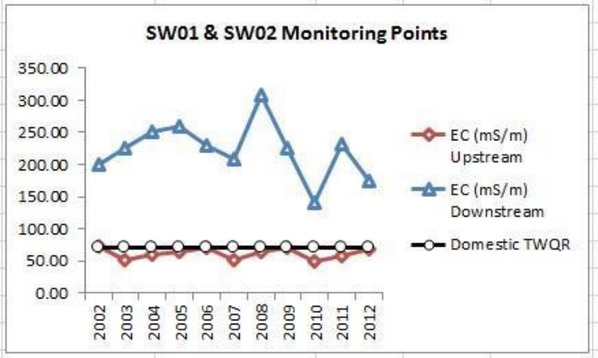



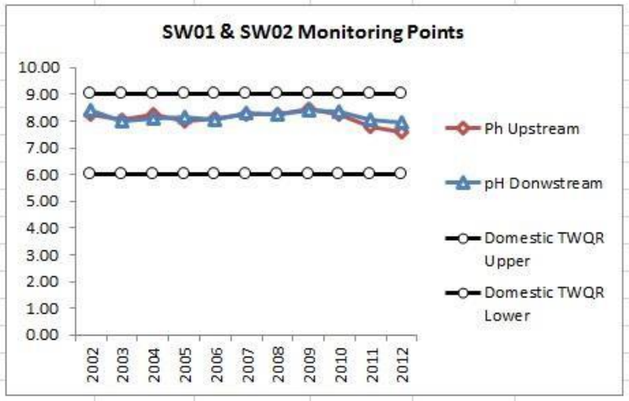
| Year | pH (SW01) | pH (SW02) | pH (TWQR) Lower | pH (TWQR) upper | EC (SW01) | EC (SW02) | EC (TWQR) | NH4 (SW01) | NH4 (SW02) | NH4 (TWQR) | NO3 (SW01) | NO3 (SW02) | NO3 (TWQR) | TDS (SW01) | TDS (SW02) | TDS (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 8.24 | 8.40 | 6.00 | 9.00 | 72.78 | 200.08 | 70.00 | 0.30 | 0.66 | 1.00 | 0.82 | 3.32 | 6.00 | 410.67 | 1182.00 | 450.00 |
| 2003 | 8.07 | 8.01 | 6.00 | 9.00 | 50.74 | 226.24 | 70.00 | 0.06 | 0.20 | 1.00 | 0.30 | 2.81 | 6.00 | 300.80 | 1440.44 | 450.00 |
| 2004 | 8.24 | 8.12 | 6.00 | 9.00 | 60.22 | 251.76 | 70.00 | 1.52 | 0.08 | 1.00 | 1.46 | 1.45 | 6.00 | 342.67 | 1434.91 | 450.00 |
| 2005 | 8.01 | 8.14 | 6.00 | 9.00 | 64.80 | 258.76 | 70.00 | 4.27 | 0.10 | 1.00 | 2.24 | 2.64 | 6.00 | 329.78 | 1516.36 | 450.00 |
| 2006 | 8.10 | 8.04 | 6.00 | 9.00 | 70.05 | 229.17 | 70.00 | 0.99 | 0.34 | 1.00 | 2.28 | 2.65 | 6.00 | 487.67 | 1621.67 | 450.00 |
| 2007 | 8.26 | 8.31 | 6.00 | 9.00 | 52.53 | 207.58 | 70.00 | 0.11 | 0.06 | 1.00 | 3.85 | 4.69 | 6.00 | 341.45 | 1429.25 | 450.00 |
| 2008 | 8.27 | 8.28 | 6.00 | 9.00 | 63.34 | 308.95 | 70.00 | 0.12 | 0.05 | 1.00 | 3.65 | 5.21 | 6.00 | 781.60 | 2167.00 | 450.00 |
| 2009 | 8.46 | 8.39 | 6.00 | 9.00 | 70.99 | 224.53 | 70.00 | 0.19 | 0.11 | 1.00 | 5.67 | 6.03 | 6.00 | 426.33 | 1443.00 | 450.00 |
| 2010 | 8.27 | 8.35 | 6.00 | 9.00 | 49.08 | 140.19 | 70.00 | 0.23 | 0.12 | 1.00 | 10.69 | 3.33 | 6.00 | 408.67 | 698.75 | 450.00 |
| 2011 | 7.82 | 8.05 | 6.00 | 9.00 | 57.03 | 231.08 | 70.00 | 0.35 | 0.15 | 1.00 | 12.52 | 3.65 | 6.00 | 368.08 | 1486.92 | 450.00 |
| 2012 | 7.59 | 7.94 | 6.00 | 9.00 | 69.00 | 175.18 | 70.00 | 1.42 | 0.09 | 1.00 | 4.29 | 3.08 | 6.00 | 438.19 | 1121.67 | 450.00 |



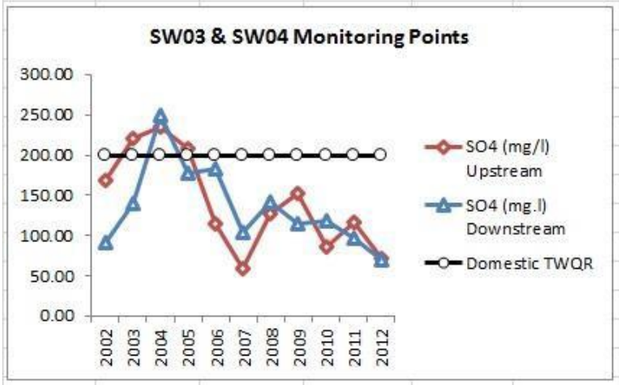



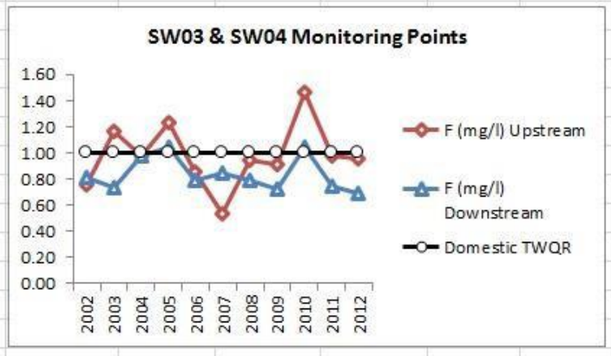



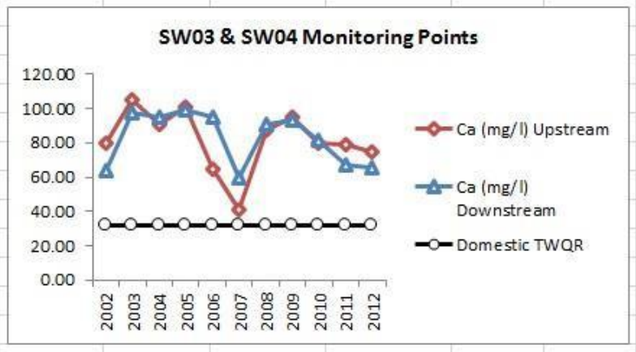



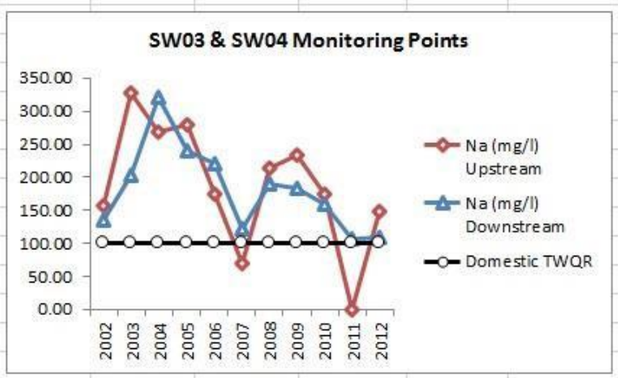



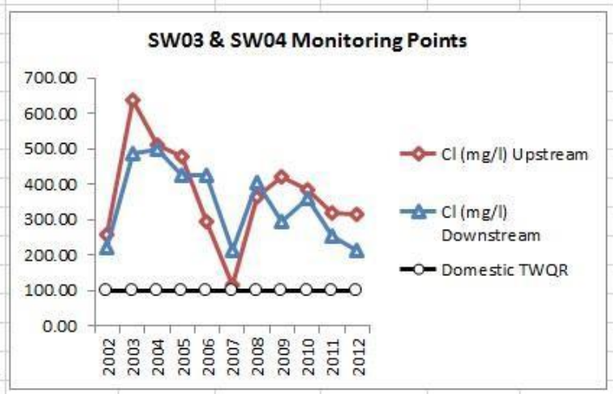
| Year | Ca (SW03) | Ca (SW04) | Ca (TWQR) | Mg (SW03) | Mg (SW04) | Mg (TWQR) | Na (SW03) | Na (SW04) | Na (TWQR) | Cl (SW03) | Cl (SW04) | Cl (TWQR) | SO4 (SW03) | SO4 (SW04) | SO4 (TWQR) | F (SW03) | F (SW04) | F (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 80.05 | 64.17 | 32.00 | 32.41 | 29.17 | 30.00 | 157.37 | 135.44 | 100.00 | 259.80 | 220.90 | 100.00 | 168.84 | 90.57 | 200.00 | 0.76 | 0.81 | 1.00 |
| 2003 | 105.15 | 97.89 | 32.00 | 45.81 | 51.22 | 30.00 | 328.19 | 202.60 | 100.00 | 639.08 | 487.50 | 100.00 | 220.59 | 139.95 | 200.00 | 1.17 | 0.74 | 1.00 |
| 2004 | 91.18 | 95.38 | 32.00 | 39.80 | 49.99 | 30.00 | 269.65 | 321.00 | 100.00 | 509.61 | 497.93 | 100.00 | 234.99 | 249.45 | 200.00 | 0.98 | 0.98 | 1.00 |
| 2005 | 100.73 | 99.31 | 32.00 | 30.39 | 29.40 | 30.00 | 280.46 | 240.96 | 100.00 | 478.81 | 427.32 | 100.00 | 208.42 | 178.14 | 200.00 | 1.23 | 1.05 | 1.00 |
| 2006 | 64.80 | 94.68 | 32.00 | 29.78 | 43.81 | 30.00 | 174.37 | 220.92 | 100.00 | 297.07 | 426.11 | 100.00 | 114.70 | 183.66 | 200.00 | 0.86 | 0.79 | 1.00 |
| 2007 | 41.54 | 59.73 | 32.00 | 20.00 | 23.22 | 30.00 | 69.35 | 121.96 | 100.00 | 115.35 | 213.27 | 100.00 | 58.44 | 104.55 | 200.00 | 0.53 | 0.85 | 1.00 |
| 2008 | 87.69 | 90.76 | 32.00 | 34.78 | 42.41 | 30.00 | 214.90 | 190.30 | 100.00 | 363.89 | 405.81 | 100.00 | 127.33 | 141.95 | 200.00 | 0.94 | 0.79 | 1.00 |
| 2009 | 94.63 | 93.25 | 32.00 | 126.48 | 31.27 | 30.00 | 233.45 | 183.68 | 100.00 | 420.83 | 295.43 | 100.00 | 152.26 | 114.40 | 200.00 | 0.91 | 0.72 | 1.00 |
| 2010 | 79.78 | 81.84 | 32.00 | 34.99 | 41.47 | 30.00 | 175.11 | 159.00 | 100.00 | 385.96 | 359.14 | 100.00 | 85.88 | 117.70 | 200.00 | 1.47 | 1.04 | 1.00 |
| 2011 | 79.04 | 67.42 | 32.00 | 40.80 | 34.57 | 30.00 | 142..99 | 106.42 | 100.00 | 318.15 | 253.35 | 100.00 | 116.60 | 97.27 | 200.00 | 0.98 | 0.75 | 1.00 |
| 2012 | 74.49 | 65.52 | 32.00 | 34.13 | 30.91 | 30.00 | 148.53 | 108.87 | 100.00 | 316.56 | 212.65 | 100.00 | 72.01 | 70.65 | 200.00 | 0.96 | 0.69 | 1.00 |

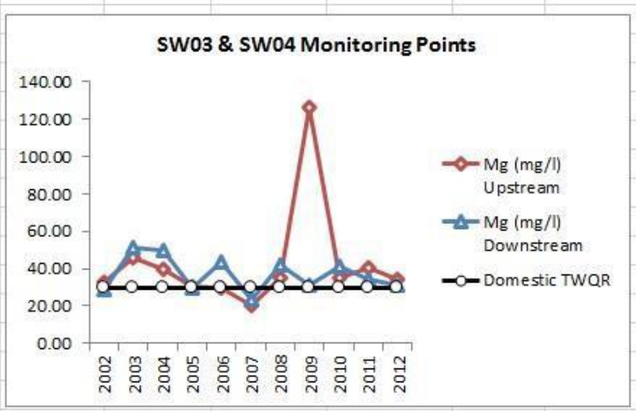


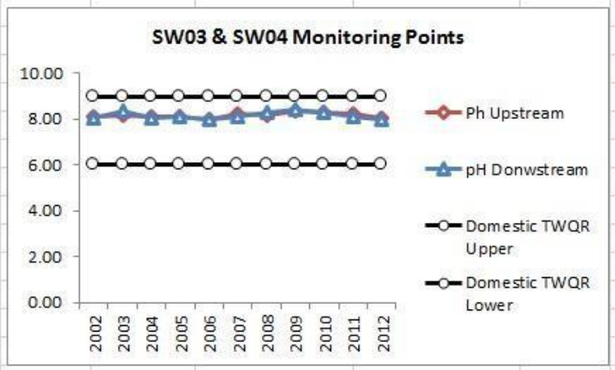



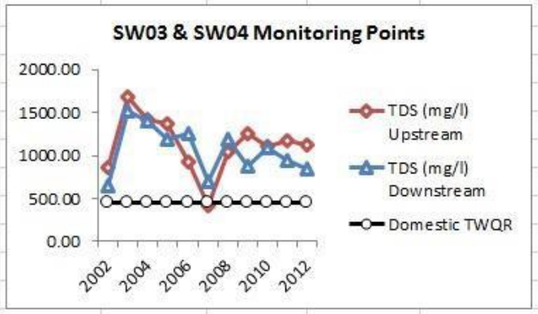



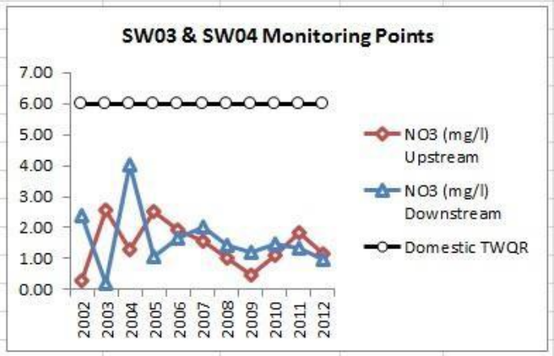



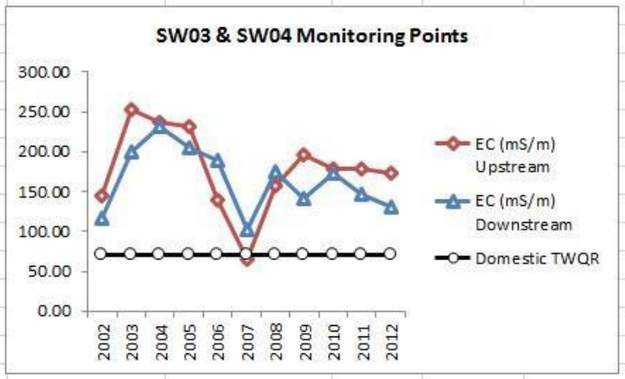



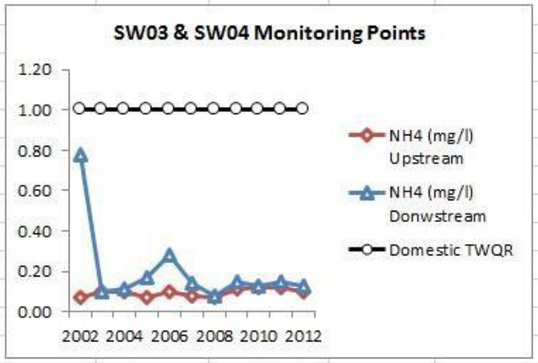
| Year | pH (SW03) | pH (SW04) | pH (TWQR) Lower | pH (TWQR) upper | EC (SW03) | EC (SW04) | EC (TWQR) | NH4 (SW03) | NH4 (SW04) | NH4 (TWQR) | NO3 (SW03) | NO3 (SW04) | NO3 (TWQR) | TDS (SW03) | TDS (SW04) | TDS (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 8.14 | 8.03 | 6.00 | 9.00 | 144.66 | 117.17 | 70.00 | 0.07 | 0.78 | 1.00 | 0.28 | 2.37 | 6.00 | 855.55 | 653.33 | 450.00 |
| 2003 | 8.20 | 8.38 | 6.00 | 9.00 | 252.70 | 199.20 | 70.00 | 0.10 | 0.10 | 1.00 | 2.56 | 0.20 | 6.00 | 1689.00 | 1512.00 | 450.00 |
| 2004 | 8.09 | 8.07 | 6.00 | 9.00 | 236.42 | 230.95 | 70.00 | 0.10 | 0.11 | 1.00 | 1.31 | 4.03 | 6.00 | 1420.00 | 1412.00 | 450.00 |
| 2005 | 8.12 | 8.13 | 6.00 | 9.00 | 231.20 | 205.30 | 70.00 | 0.07 | 0.17 | 1.00 | 2.51 | 1.08 | 6.00 | 1372.80 | 1187.20 | 450.00 |
| 2006 | 8.01 | 7.97 | 6.00 | 9.00 | 139.43 | 188.34 | 70.00 | 0.10 | 0.28 | 1.00 | 1.91 | 1.65 | 6.00 | 926.33 | 1262.22 | 450.00 |
| 2007 | 8.26 | 8.10 | 6.00 | 9.00 | 65.07 | 102.50 | 70.00 | 0.08 | 0.14 | 1.00 | 1.57 | 2.00 | 6.00 | 409.67 | 704.00 | 450.00 |
| 2008 | 8.20 | 8.28 | 6.00 | 9.00 | 157.32 | 174.16 | 70.00 | 0.07 | 0.08 | 1.00 | 1.02 | 1.44 | 6.00 | 1047.11 | 1186.67 | 450.00 |
| 2009 | 8.34 | 8.41 | 6.00 | 9.00 | 196.43 | 141.96 | 70.00 | 0.11 | 0.15 | 1.00 | 0.47 | 1.19 | 6.00 | 1253.33 | 881.14 | 450.00 |
| 2010 | 8.29 | 8.31 | 6.00 | 9.00 | 177.91 | 173.93 | 70.00 | 0.12 | 0.13 | 1.00 | 1.12 | 1.49 | 6.00 | 1102.67 | 1095.67 | 450.00 |
| 2011 | 8.22 | 8.12 | 6.00 | 9.00 | 179.22 | 146.33 | 70.00 | 0.12 | 0.15 | 1.00 | 1.85 | 1.35 | 6.00 | 1171.00 | 944.33 | 450.00 |
| 2012 | 8.08 | 7.98 | 6.00 | 9.00 | 173.50 | 131.29 | 70.00 | 0.10 | 0.13 | 1.00 | 1.16 | 0.99 | 6.00 | 1117.33 | 850.00 | 450.00 |



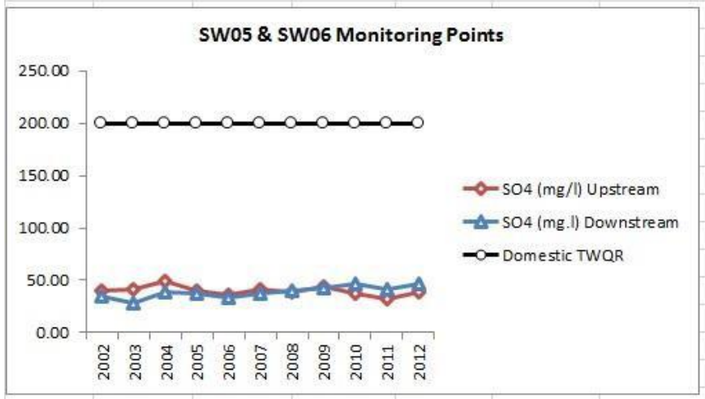



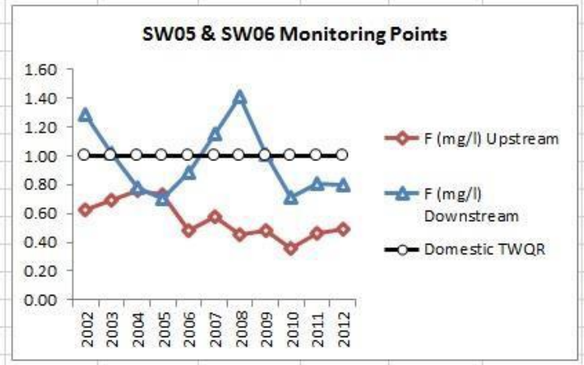



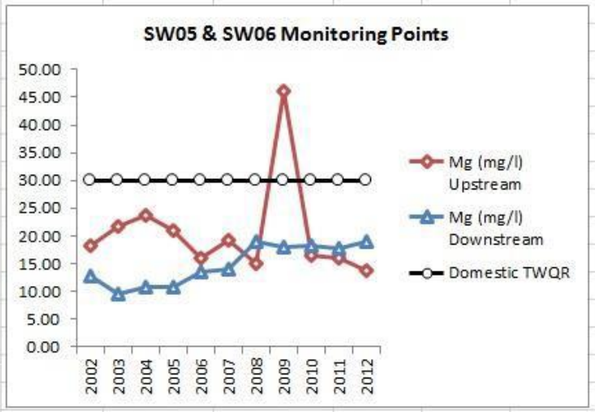



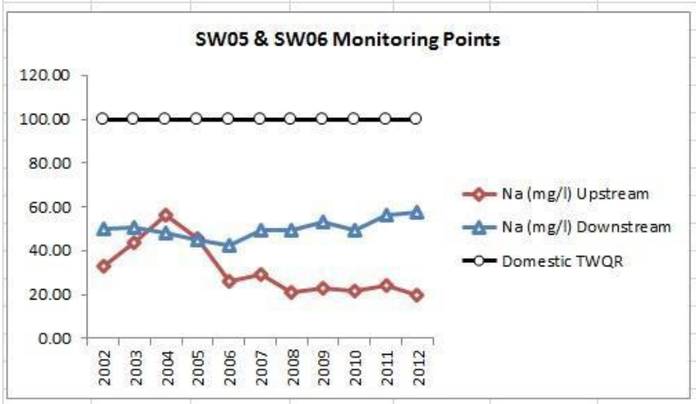



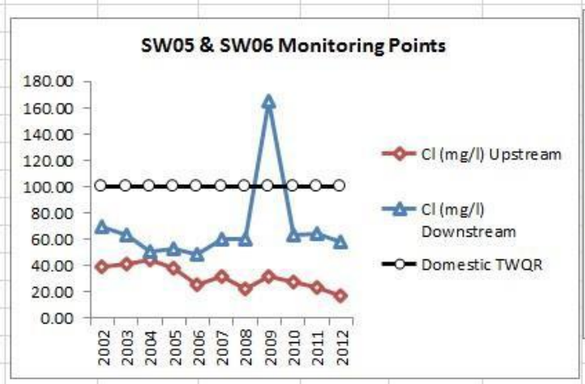
| Year | Ca (SW05) | Ca (SW06) | Ca (TWQR) | Mg (SW05) | Mg (SW06) | Mg (TWQR) | Na (SW05) | Na (SW06) | Na (TWQR) | Cl (SW05) | Cl (SW06) | Cl (TWQR) | SO4 (SW05) | SO4 (SW06) | SO4 (TWQR) | F (SW05) | F (SW06) | F (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 27.88 | 28.80 | 32.00 | 18.27 | 12.72 | 30.00 | 33.07 | 49.66 | 100.00 | 39.19 | 69.61 | 100.00 | 39.39 | 35.00 | 200.00 | 0.63 | 1.29 | 1.00 |
| 2003 | 29.19 | 28.87 | 32.00 | 21.72 | 9.53 | 30.00 | 43.45 | 50.84 | 100.00 | 41.58 | 63.78 | 100.00 | 41.62 | 27.98 | 200.00 | 0.69 | 1.02 | 1.00 |
| 2004 | 27.05 | 31.65 | 32.00 | 23.75 | 10.78 | 30.00 | 56.11 | 47.86 | 100.00 | 44.12 | 50.77 | 100.00 | 49.24 | 38.96 | 200.00 | 0.76 | 0.78 | 1.00 |
| 2005 | 25.98 | 31.00 | 32.00 | 20.86 | 10.90 | 30.00 | 45.77 | 44.75 | 100.00 | 38.10 | 52.98 | 100.00 | 39.38 | 37.06 | 200.00 | 0.73 | 0.70 | 1.00 |
| 2006 | 22.85 | 36.22 | 32.00 | 15.92 | 13.61 | 30.00 | 26.04 | 42.37 | 100.00 | 25.09 | 48.24 | 100.00 | 36.22 | 34.02 | 200.00 | 0.48 | 0.88 | 1.00 |
| 2007 | 29.66 | 32.12 | 32.00 | 19.34 | 13.91 | 30.00 | 29.26 | 49.39 | 100.00 | 32.03 | 59.66 | 100.00 | 40.87 | 37.04 | 200.00 | 0.58 | 1.15 | 1.00 |
| 2008 | 21.21 | 34.12 | 32.00 | 14.92 | 19.10 | 30.00 | 20.78 | 49.21 | 100.00 | 21.90 | 60.30 | 100.00 | 39.10 | 40.47 | 200.00 | 0.45 | 1.41 | 1.00 |
| 2009 | 26.94 | 36.74 | 32.00 | 45.98 | 17.92 | 30.00 | 22.69 | 53.09 | 100.00 | 31.42 | 165.35 | 100.00 | 43.63 | 42.12 | 200.00 | 0.48 | 1.01 | 1.00 |
| 2010 | 20.10 | 35.92 | 32.00 | 16.58 | 18.33 | 30.00 | 21.51 | 49.07 | 100.00 | 27.78 | 63.76 | 100.00 | 37.04 | 46.92 | 200.00 | 0.36 | 0.71 | 1.00 |
| 2011 | 20.61 | 35.66 | 32.00 | 15.88 | 17.78 | 30.00 | 23.91 | 56.58 | 100.00 | 23.84 | 64.01 | 100.00 | 32.10 | 41.02 | 200.00 | 0.46 | 0.81 | 1.00 |
| 2012 | 19.65 | 36.33 | 32.00 | 13.65 | 19.00 | 30.00 | 19.93 | 57.48 | 100.00 | 17.14 | 57.65 | 100.00 | 38.69 | 46.96 | 200.00 | 0.49 | 0.80 | 1.00 |

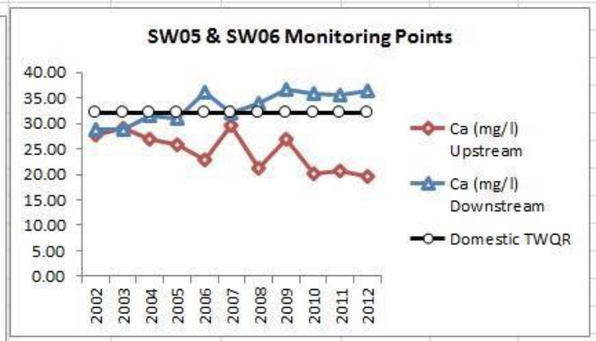


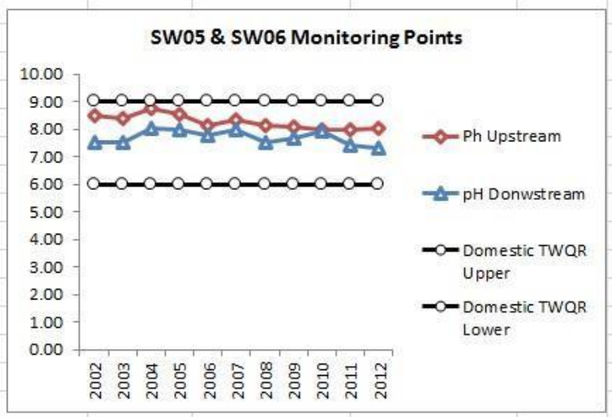



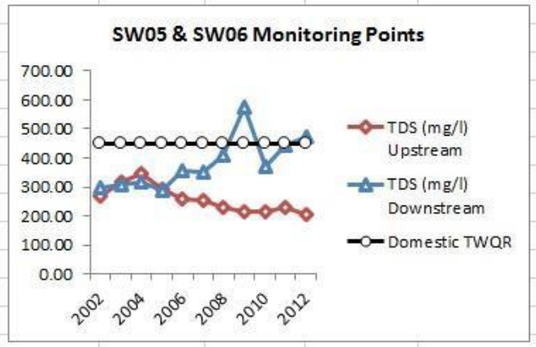



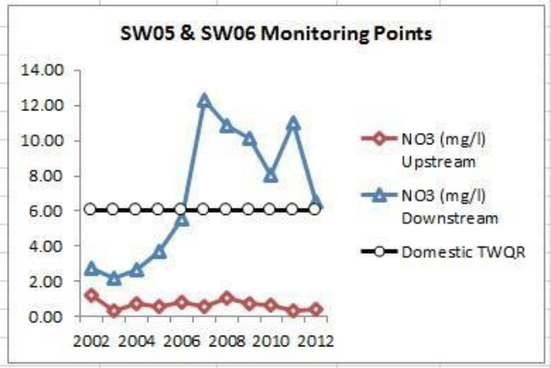



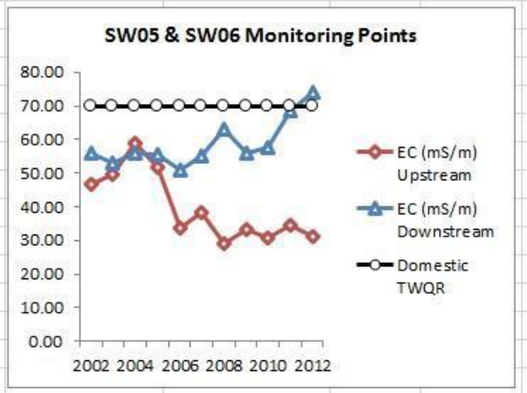



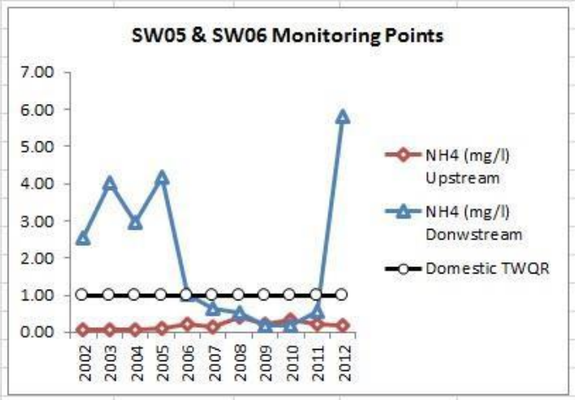
| Year | pH (SW05) | pH (SW06) | pH (TWQR) Lower | pH (TWQR) upper | EC (SW05) | EC (SW06) | EC (TWQR) | NH4 (SW05) | NH4 (SW06) | NH4 (TWQR) | NO3 (SW05) | NO3 (SW06) | NO3 (TWQR) | TDS (SW05) | TDS (SW06) | TDS (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 8.50 | 7.55 | 6.00 | 9.00 | 46.73 | 55.76 | 70.00 | 0.07 | 2.53 | 1.00 | 1.18 | 2.77 | 6.00 | 266.33 | 295.67 | 450.00 |
| 2003 | 8.38 | 7.55 | 6.00 | 9.00 | 49.78 | 52.98 | 70.00 | 0.06 | 4.02 | 1.00 | 0.36 | 2.18 | 6.00 | 315.00 | 309.33 | 450.00 |
| 2004 | 8.74 | 8.03 | 6.00 | 9.00 | 58.93 | 55.99 | 70.00 | 0.06 | 2.98 | 1.00 | 0.72 | 2.64 | 6.00 | 345.33 | 315.00 | 450.00 |
| 2005 | 8.54 | 7.98 | 6.00 | 9.00 | 51.93 | 55.69 | 70.00 | 0.09 | 4.18 | 1.00 | 0.54 | 3.73 | 6.00 | 291.00 | 287.67 | 450.00 |
| 2006 | 8.17 | 7.79 | 6.00 | 9.00 | 33.48 | 50.88 | 70.00 | 0.22 | 1.02 | 1.00 | 0.82 | 5.55 | 6.00 | 259.33 | 358.00 | 450.00 |
| 2007 | 8.35 | 8.01 | 6.00 | 9.00 | 38.23 | 55.33 | 70.00 | 0.13 | 0.64 | 1.00 | 0.58 | 12.26 | 6.00 | 252.45 | 349.58 | 450.00 |
| 2008 | 8.14 | 7.54 | 6.00 | 9.00 | 29.05 | 63.02 | 70.00 | 0.40 | 0.51 | 1.00 | 1.02 | 10.88 | 6.00 | 230.67 | 411.33 | 450.00 |
| 2009 | 8.07 | 7.68 | 6.00 | 9.00 | 33.29 | 56.04 | 70.00 | 0.23 | 0.19 | 1.00 | 0.76 | 10.16 | 6.00 | 213.67 | 575.67 | 450.00 |
| 2010 | 7.98 | 7.94 | 6.00 | 9.00 | 30.78 | 57.56 | 70.00 | 0.32 | 0.20 | 1.00 | 0.68 | 8.05 | 6.00 | 216.33 | 370.58 | 450.00 |
| 2011 | 7.97 | 7.42 | 6.00 | 9.00 | 34.71 | 68.43 | 70.00 | 0.23 | 0.58 | 1.00 | 0.30 | 11.02 | 6.00 | 228.67 | 444.08 | 450.00 |
| 2012 | 8.05 | 7.35 | 6.00 | 9.00 | 30.97 | 73.96 | 70.00 | 0.19 | 5.83 | 1.00 | 0.42 | 6.54 | 6.00 | 206.00 | 472.75 | 450.00 |



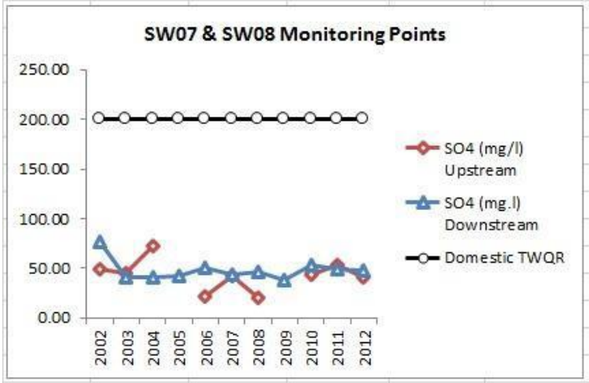



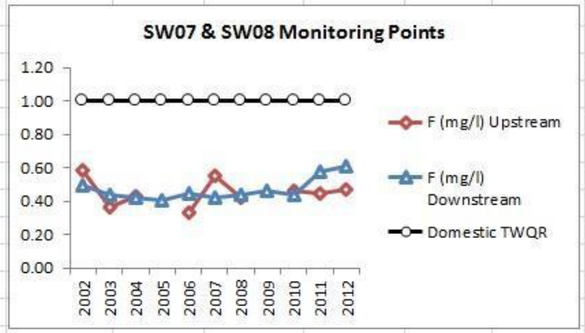



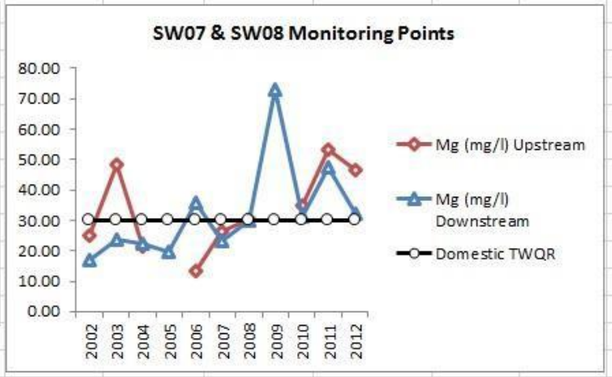



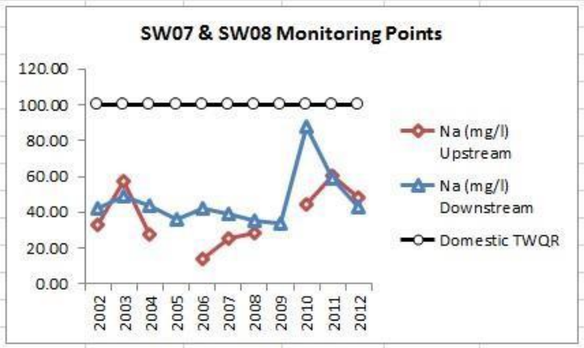



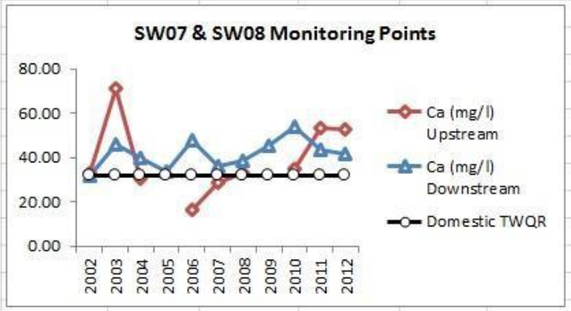
| Year | Ca (SW07) | Ca (SW08) | Ca (TWQR) | Mg (SW07) | Mg (SW08) | Mg (TWQR) | Na (SW07) | Na (SW08) | Na (TWQR) | Cl (SW07) | Cl (SW08) | Cl (TWQR) | SO4 (SW07) | SO4 (SW08) | SO4 (TWQR) | F (SW07) | F (SW08) | F (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 32.95 | 32.08 | 32.00 | 25.01 | 16.93 | 30.00 | 32.94 | 42.44 | 100.00 | 34.30 | 49.86 | 100.00 | 48.55 | 77.37 | 200.00 | 0.59 | 0.50 | 1.00 |
| 2003 | 70.99 | 46.11 | 32.00 | 48.26 | 23.69 | 30.00 | 57.63 | 48.64 | 100.00 | 32.40 | 51.58 | 100.00 | 44.50 | 41.58 | 200.00 | 0.37 | 0.44 | 1.00 |
| 2004 | 30.97 | 39.73 | 32.00 | 21.38 | 22.39 | 30.00 | 27.97 | 43.34 | 100.00 | 24.75 | 43.64 | 100.00 | 72.40 | 41.46 | 200.00 | 0.43 | 0.42 | 1.00 |
| 2005 |  | 33.94 | 32.00 |  | 19.63 | 30.00 |  | 36.26 | 100.00 |  | 36.33 | 100.00 |  | 41.83 | 200.00 |  | 0.41 | 1.00 |
| 2006 | 16.52 | 48.15 | 32.00 | 13.44 | 35.92 | 30.00 | 14.30 | 41.86 | 100.00 | 19.00 | 36.82 | 100.00 | 21.40 | 50.22 | 200.00 | 0.33 | 0.45 | 1.00 |
| 2007 | 28.54 | 36.43 | 32.00 | 26.34 | 23.13 | 30.00 | 25.31 | 38.99 | 100.00 | 26.70 | 41.58 | 100.00 | 42.80 | 44.04 | 200.00 | 0.55 | 0.42 | 1.00 |
| 2008 | 33.15 | 38.97 | 32.00 | 30.45 | 29.93 | 30.00 | 28.80 | 35.10 | 100.00 | 25.71 | 33.01 | 100.00 | 19.76 | 46.24 | 200.00 | 0.42 | 0.44 | 1.00 |
| 2009 |  | 45.29 | 32.00 |  | 73.03 | 30.00 |  | 33.44 | 100.00 |  | 33.93 | 100.00 |  | 37.57 | 200.00 |  | 0.46 | 1.00 |
| 2010 | 34.67 | 54.30 | 32.00 | 34.92 | 31.36 | 30.00 | 44.34 | 87.91 | 100.00 | 34.01 | 46.53 | 100.00 | 44.04 | 53.51 | 200.00 | 0.46 | 0.44 | 1.00 |
| 2011 | 53.26 | 43.61 | 32.00 | 53.40 | 47.22 | 30.00 | 60.28 | 59.22 | 100.00 | 32.94 | 61.36 | 100.00 | 53.78 | 49.54 | 200.00 | 0.45 | 0.58 | 1.00 |
| 2012 | 52.57 | 41.82 | 32.00 | 46.51 | 32.02 | 30.00 | 48.04 | 42.71 | 100.00 | 19.28 | 32.14 | 100.00 | 40.61 | 48.40 | 200.00 | 0.47 | 0.61 | 1.00 |

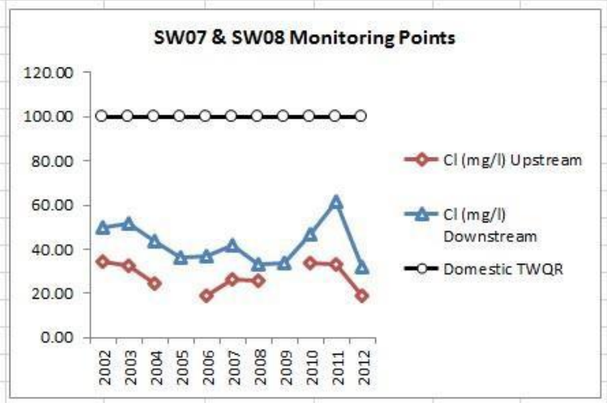


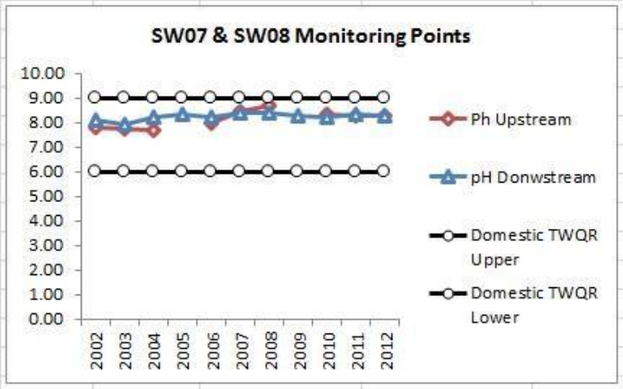



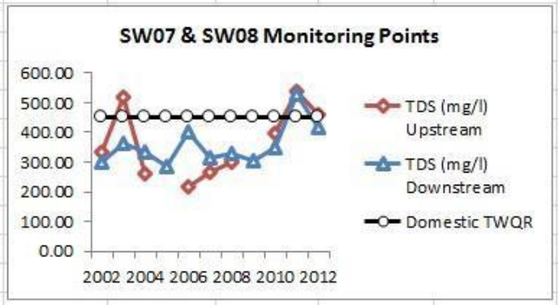



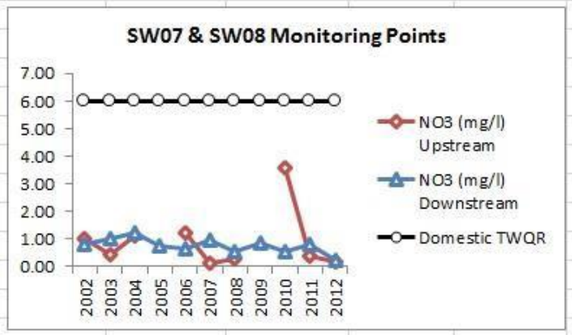



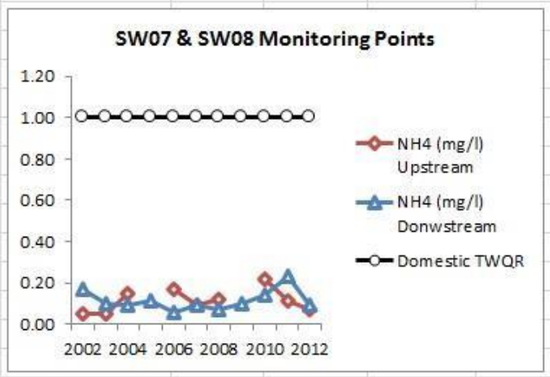



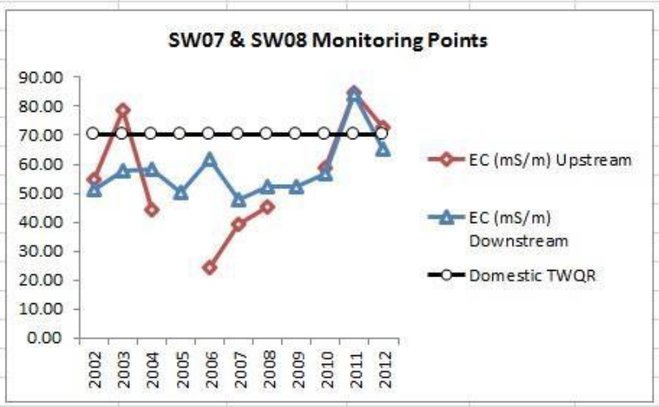
| Year | pH (SW07) | pH (SW08) | pH (TWQR) Lower | pH (TWQR) upper | EC (SW07) | EC (SW08) | EC (TWQR) | NH4 (SW07) | NH4 (SW08) | NH4 (TWQR) | NO3 (SW07) | NO3 (SW08) | NO3 (TWQR) | TDS (SW07) | TDS (SW08) | TDS (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 7.82 | 8.12 | 6.00 | 9.00 | 55.00 | 51.36 | 70.00 | 0.05 | 0.17 | 1.00 | 1.00 | 0.78 | 6.00 | 332.00 | 301.09 | 450.00 |
| 2003 | 7.76 | 7.94 | 6.00 | 9.00 | 78.50 | 57.71 | 70.00 | 0.05 | 0.10 | 1.00 | 0.45 | 1.03 | 6.00 | 520.00 | 362.33 | 450.00 |
| 2004 | 7.71 | 8.21 | 6.00 | 9.00 | 44.31 | 58.27 | 70.00 | 0.15 | 0.09 | 1.00 | 1.10 | 1.23 | 6.00 | 262.00 | 335.64 | 450.00 |
| 2005 | | 8.36 | 6.00 | 9.00 | | 50.41 | 70.00 | | 0.11 | 1.00 | | 0.74 | 6.00 | | 287.67 | 450.00 |
| 2006 | 8.00 | 8.21 | 6.00 | 9.00 | 24.30 | 61.69 | 70.00 | 0.17 | 0.06 | 1.00 | 1.20 | 0.66 | 6.00 | 216.00 | 402.33 | 450.00 |
| 2007 | 8.47 | 8.43 | 6.00 | 9.00 | 39.40 | 47.73 | 70.00 | 0.09 | 0.09 | 1.00 | 0.10 | 0.94 | 6.00 | 268.00 | 314.67 | 450.00 |
| 2008 | 8.69 | 8.38 | 6.00 | 9.00 | 45.05 | 52.08 | 70.00 | 0.12 | 0.07 | 1.00 | 0.30 | 0.53 | 6.00 | 302.00 | 329.00 | 450.00 |
| 2009 | | 8.29 | 6.00 | 9.00 | | 52.36 | 70.00 | | 0.10 | 1.00 | | 0.85 | 6.00 | | 303.64 | 450.00 |
| 2010 | 8.32 | 8.25 | 6.00 | 9.00 | 58.63 | 56.69 | 70.00 | 0.22 | 0.14 | 1.00 | 3.60 | 0.53 | 6.00 | 397.00 | 348.67 | 450.00 |
| 2011 | 8.31 | 8.35 | 6.00 | 9.00 | 84.90 | 84.29 | 70.00 | 0.11 | 0.23 | 1.00 | 0.40 | 0.78 | 6.00 | 536.92 | 527.82 | 450.00 |
| 2012 | 8.27 | 8.27 | 6.00 | 9.00 | 72.48 | 65.28 | 70.00 | 0.07 | 0.09 | 1.00 | 0.17 | 0.22 | 6.00 | 459.33 | 415.20 | 450.00 |



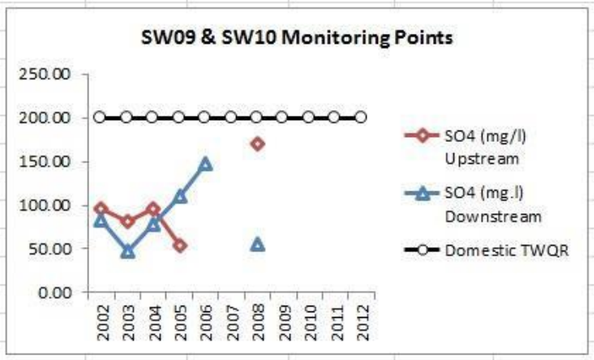



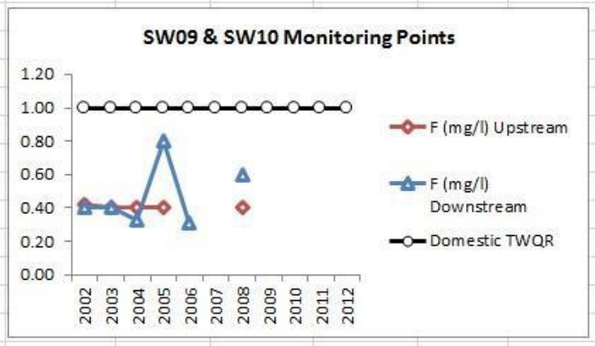



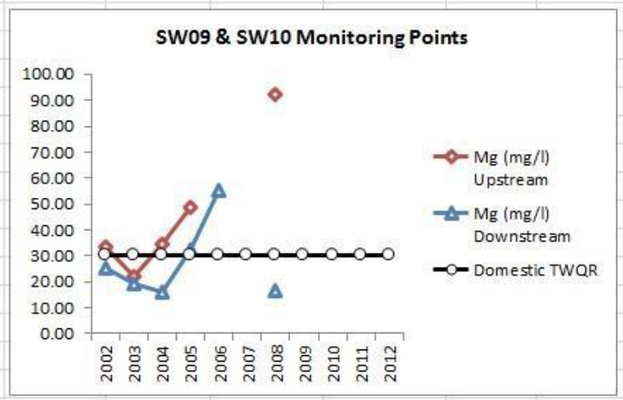



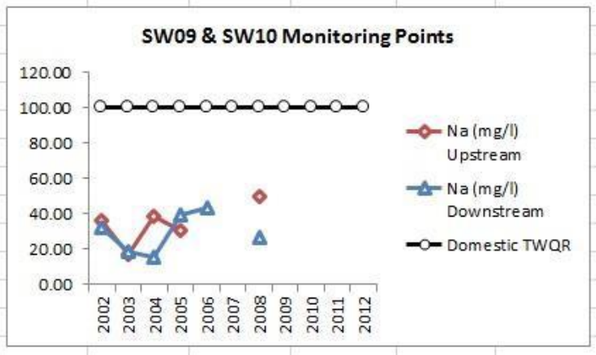



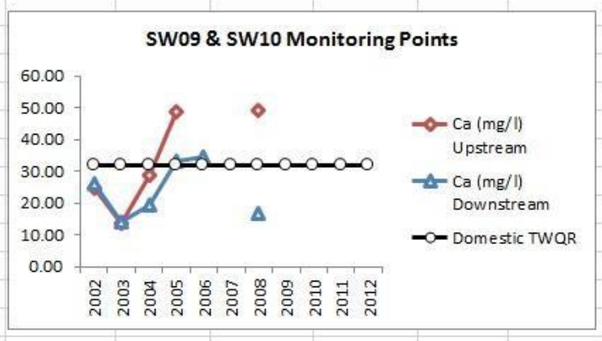
| Year | Ca (SW09) | Ca (SW10) | Ca (TWQR) | Mg (SW09) | Mg (SW10) | Mg (TWQR) | Na (SW09) | Na (SW10) | Na (TWQR) | Cl (SW09) | Cl (SW10) | Cl (TWQR) | SO4 (SW09) | SO4 (SW10) | SO4 (TWQR) | F (SW09) | F (SW10) | F (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 25.00 | 26.13 | 32.00 | 33.24 | 25.52 | 30.00 | 36.24 | 32.40 | 100.00 | 31.40 | 27.83 | 100.00 | 95.20 | 83.00 | 200.00 | 0.42 | 0.40 | 1.00 |
| 2003 | 13.50 | 14.07 | 32.00 | 22.07 | 19.10 | 30.00 | 17.13 | 18.34 | 100.00 | 11.33 | 9.67 | 100.00 | 80.67 | 47.67 | 200.00 | 0.40 | 0.40 | 1.00 |
| 2004 | 28.62 | 19.40 | 32.00 | 34.66 | 15.93 | 30.00 | 39.04 | 15.10 | 100.00 | 36.40 | 15.67 | 100.00 | 96.60 | 78.33 | 200.00 | 0.40 | 0.33 | 1.00 |
| 2005 | 48.73 | 33.30 | 32.00 | 48.50 | 32.34 | 30.00 | 30.32 | 39.30 | 100.00 | 61.67 | 28.14 | 100.00 | 54.67 | 110.29 | 200.00 | 0.40 | 0.80 | 1.00 |
| 2006 | | 34.79 | 32.00 | | 55.05 | 30.00 | | 43.81 | 100.00 | | 31.36 | 100.00 | | 147.73 | 200.00 | | 0.31 | 1.00 |
| 2007 | | | 32.00 | | | 30.00 | | | 100.00 | | | 100.00 | | | 200.00 | | | 1.00 |
| 2008 | 49.40 | 16.90 | 32.00 | 92.10 | 16.30 | 30.00 | 49.70 | 27.00 | 100.00 | 42.00 | 13.00 | 100.00 | 171.00 | 56.00 | 200.00 | 0.40 | 0.60 | 1.00 |
| 2009 | | | 32.00 | | | 30.00 | | | 100.00 | | | 100.00 | | | 200.00 | | | 1.00 |
| 2010 | | | 32.00 | | | 30.00 | | | 100.00 | | | 100.00 | | | 200.00 | | | 1.00 |
| 2011 | | | 32.00 | | | 30.00 | | | 100.00 | | | 100.00 | | | 200.00 | | | 1.00 |
| 2012 | | | 32.00 | | | 30.00 | | | 100.00 | | | 100.00 | | | 200.00 | | | 1.00 |

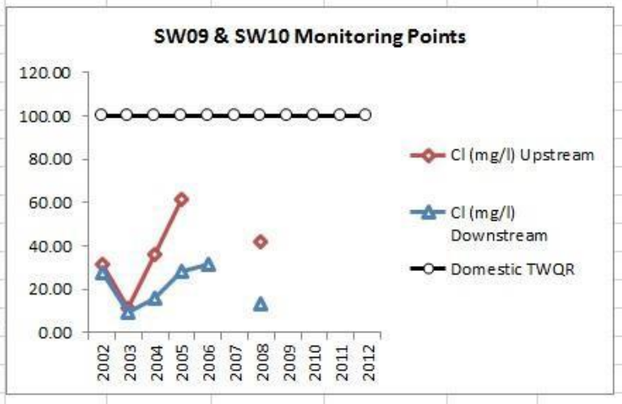


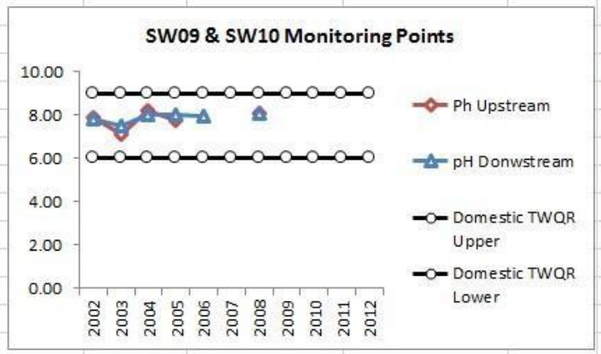



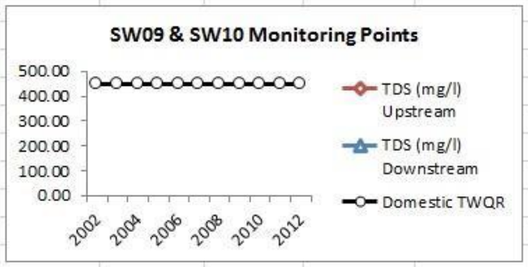



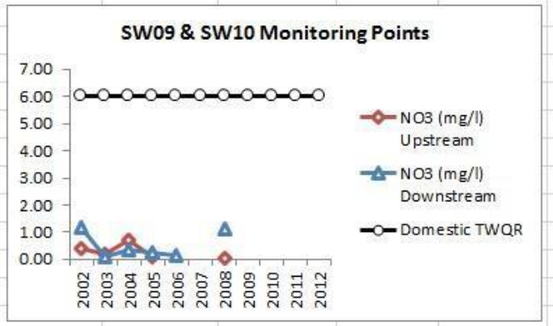



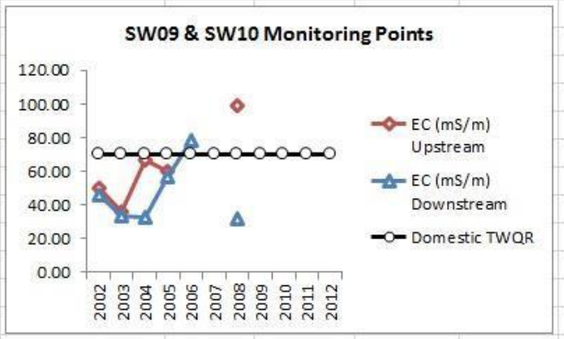



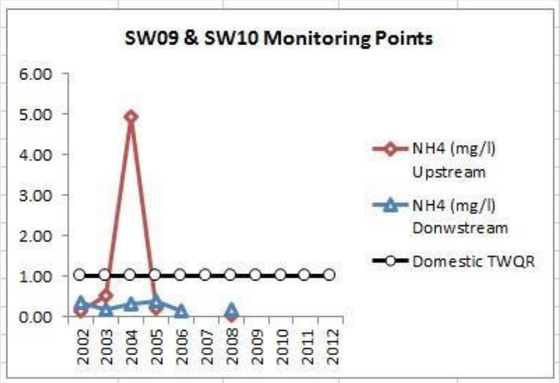
| Year | pH (SW09) | pH (SW10) | pH (TWQR) Lower | pH (TWQR) upper | EC (SW09) | EC (SW10) | EC (TWQR) | NH4 (SW09) | NH4 (SW10) | NH4 (TWQR) | NO3 (SW09) | NO3 (SW10) | NO3 (TWQR) | TDS (SW09) | TDS (SW10) | TDS (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 7.90 | 7.83 | 6.00 | 9.00 | 49.80 | 46.17 | 70.00 | 0.16 | 0.34 | 1.00 | 0.39 | 1.15 | 6.00 | | | 450.00 |
| 2003 | 7.13 | 7.53 | 6.00 | 9.00 | 35.67 | 33.67 | 70.00 | 0.53 | 0.17 | 1.00 | 0.22 | 0.10 | 6.00 | | | 450.00 |
| 2004 | 8.24 | 8.03 | 6.00 | 9.00 | 66.80 | 32.67 | 70.00 | 4.95 | 0.32 | 1.00 | 0.69 | 0.33 | 6.00 | | | 450.00 |
| 2005 | 7.77 | 8.03 | 6.00 | 9.00 | 60.33 | 56.86 | 70.00 | 0.23 | 0.39 | 1.00 | 0.10 | 0.24 | 6.00 | | | 450.00 |
| 2006 | | 7.98 | 6.00 | 9.00 | | 78.73 | 70.00 | | 0.15 | 1.00 | | 0.14 | 6.00 | | | 450.00 |
| 2007 | | | 6.00 | 9.00 | | | 70.00 | | | 1.00 | | | 6.00 | | | 450.00 |
| 2008 | 8.10 | 8.10 | 6.00 | 9.00 | 99.00 | 32.00 | 70.00 | 0.05 | 0.20 | 1.00 | 0.05 | 1.10 | 6.00 | | | 450.00 |
| 2009 | | | 6.00 | 9.00 | | | 70.00 | | | 1.00 | | | 6.00 | | | 450.00 |
| 2010 | | | 6.00 | 9.00 | | | 70.00 | | | 1.00 | | | 6.00 | | | 450.00 |
| 2011 | | | 6.00 | 9.00 | | | 70.00 | | | 1.00 | | | 6.00 | | | 450.00 |
| 2012 | | | 6.00 | 9.00 | | | 70.00 | | | 1.00 | | | 6.00 | | | 450.00 |



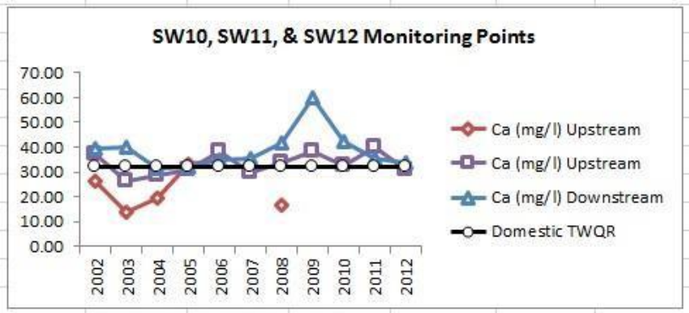



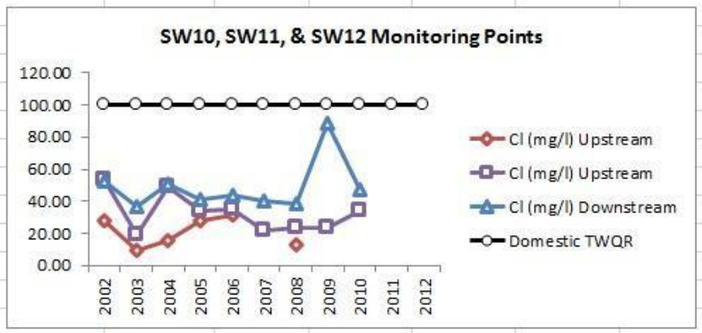



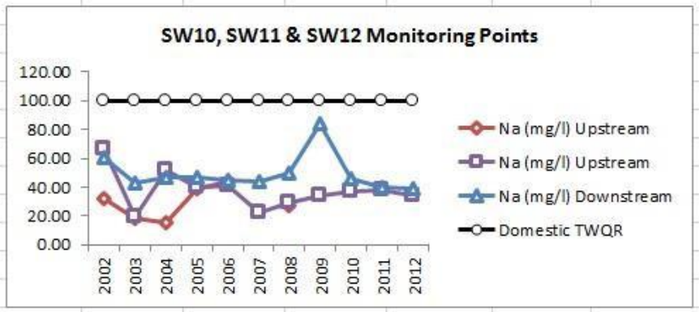



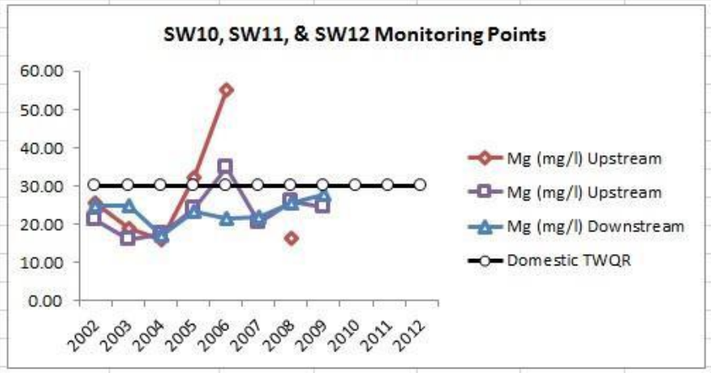



| Year | Ca (SW10) | Ca (SW11) | Ca (SW12) | Ca (TWQR) | Mg (SW10) | Mg (SW11) | Mg (SW12) | Mg (TWQR) | Na (SW10) | Na (SW11) | Na (SW12) | Na (TWQR) | Cl (SW10) | Cl (SW11) | Cl (SW12) | Cl (TWQR) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 26.13 | 37.45 | 39.37 | 32.00 | 25.52 | 21.12 | 24.97 | 30.00 | 32.40 | 66.35 | 60.87 | 100.00 | 27.83 | 53.17 | 52.17 | 100.00 |
| 2003 | 14.07 | 26.51 | 40.24 | 32.00 | 19.10 | 16.04 | 24.67 | 30.00 | 18.34 | 19.82 | 43.04 | 100.00 | 9.67 | 19.22 | 36.55 | 100.00 |
| 2004 | 19.40 | 28.63 | 31.23 | 32.00 | 15.93 | 17.43 | 17.10 | 30.00 | 15.10 | 51.52 | 46.87 | 100.00 | 15.67 | 49.33 | 50.43 | 100.00 |
| 2005 | 33.30 | 30.77 | 31.90 | 32.00 | 32.34 | 24.04 | 23.31 | 30.00 | 39.30 | 40.28 | 46.71 | 100.00 | 28.14 | 34.33 | 40.78 | 100.00 |
| 2006 | 34.79 | 38.08 | 34.71 | 32.00 | 55.05 | 34.68 | 21.68 | 30.00 | 43.81 | 41.02 | 45.38 | 100.00 | 31.36 | 35.07 | 43.71 | 100.00 |
| 2007 |  | 29.80 | 35.48 | 32.00 |  | 20.26 | 21.74 | 30.00 |  | 22.18 | 43.79 | 100.00 |  | 22.00 | 40.00 | 100.00 |
| 2008 | 16.90 | 33.79 | 41.66 | 32.00 | 16.30 | 25.93 | 25.62 | 30.00 | 27.00 | 28.78 | 49.75 | 100.00 | 13.00 | 23.90 | 38.90 | 100.00 |
| 2009 |  | 38.54 | 59.95 | 32.00 |  | 24.57 | 27.91 | 30.00 |  | 34.28 | 84.00 | 100.00 |  | 23.71 | 88.57 | 100.00 |
| 2010 |  | 32.62 | 42.04 | 32.00 |  |  |  | 30.00 |  | 36.82 | 45.78 | 100.00 |  | 34.00 | 47.00 | 100.00 |
| 2011 |  | 40.28 | 35.22 | 32.00 |  |  |  | 30.00 |  | 38.12 | 40.48 | 100.00 |  |  |  | 100.00 |
| 2012 |  | 31.17 | 33.72 | 32.00 |  |  |  | 30.00 |  | 34.59 | 38.95 | 100.00 |  |  |  | 100.00 |



| Year | SO4 (SW10) | SO4 (SW11) | SO4 (SW12) | SO4 (TWQR) | F (SW10) | F (SW11) | F (SW12) | F (TWQR) | pH (SW10) | pH (SW11) | pH (SW12) | pH (TWQR) Lower | pH (TWQR) upper |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2002 | 83.00 | 61.33 | 80.00 | 200.00 | 0.40 | 0.57 | 0.78 | 1.00 | 7.83 | 8.17 | 8.02 | 6.00 | 9.00 |
| 2003 | 47.67 | 38.44 | 84.15 | 200.00 | 0.40 | 0.44 | 0.67 | 1.00 | 7.53 | 7.73 | 7.65 | 6.00 | 9.00 |
| 2004 | 78.33 | 51.50 | 79.00 | 200.00 | 0.33 | 0.43 | 0.59 | 1.00 | 8.03 | 8.33 | 8.13 | 6.00 | 9.00 |
| 2005 | 110.29 | 44.56 | 82.44 | 200.00 | 0.80 | 0.67 | 0.69 | 1.00 | 8.03 | 8.09 | 7.73 | 6.00 | 9.00 |
| 2006 | 147.73 | 61.71 | 94.43 | 200.00 | 0.31 | 0.41 | 0.54 | 1.00 | 7.98 | 8.18 | 7.80 | 6.00 | 9.00 |
| 2007 | | 38.80 | 83.67 | 200.00 | | 0.35 | 0.52 | 1.00 | | 7.74 | 7.58 | 6.00 | 9.00 |
| 2008 | 56.00 | 37.70 | 108.70 | 200.00 | 0.60 | 0.38 | 0.54 | 1.00 | 8.10 | 7.95 | 7.81 | 6.00 | 9.00 |
| 2009 | | 45.62 | 133.77 | 200.00 | | 0.43 | 0.82 | 1.00 | | 8.05 | 7.68 | 6.00 | 9.00 |
| 2010 | | 47.71 | 95.43 | 200.00 | | 0.36 | 0.46 | 1.00 | | 7.71 | 7.69 | 6.00 | 9.00 |
| 2011 | | 53.67 | 84.25 | 200.00 | | 0.43 | 0.41 | 1.00 | | 8.12 | 7.85 | 6.00 | 9.00 |
| 2012 | | 47.00 | 75.85 | 200.00 | | 0.46 | 0.48 | 1.00 | | 8.45 | 7.85 | 6.00 | 9.00 |