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ARTICLE

Hydrogeological Investigations of Groundwater and Surface Water Interactions in the Berg River Catchment, Western Cape, South Africa

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ABSTRACT

The Berg River Catchment based in the Western Cape Province, South Africa services the greater Cape Town area with water, subsequent to supplying the vast agricultural activities that exist in the middle and the lower reaches. This study thus investigates the hydrogeochemical interactions between surface and groundwater in the Berg River Catchment with the aim of establishing trends and transfer of constituents between the surface and groundwater systems, investigates the role that geology plays in water chemistry as well as identifies the geochemical processes controlling surface and groundwater chemistry in the catchment. This study was carried out using three types of research designs namely i) experimental research design; ii) field research design and meta-analysis research design. Furthermore, the study made use of hydrochemical data ranging from 2003 to 2013 obtained from the National Water Monitoring Database owned and maintained by the Department of Water and Sanitation and data that were sampled in 2016 by authors and analyzed using the ICP-MS Technique Ground Water Chart, Arc-GIS and Geosoft (Oasis Montaj) were further employed to model the data. The results indicated that: i) in the Upper Berg there is not much interaction and transfer of constituents between surface and groundwater; ii) the Middle Berg, however, indicated a degree of interaction with the sharing of constituents between the two water systems and iii) the Lower Berg indicated only NaCl water type also noting that the area situated near the river mouth whereby there is the mixing of river and seawater.

Keywords: Hydrogeology; Groundwater; Surface water; Interactions; Berg River Catchment

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1. Introduction

It is well established that the quality of freshwater resources has been and still is deteriorating at an escalated rate globally affecting the chemical, physical and biological composition of water. As a result, fresh water has thus become a rare commodity that is crucial for the survival of any living organism on Earth [1]. Fresh water is found in groundwater aquifers and surface water resources such as rivers, streams, lakes and dams however, these resources only comprise 0.3% of fresh water that is available for human consumption out of the 71% of water that constitutes the earth [2].

The remaining quantity of water found in oceans and seas requires expensive processes of desalination in order to become potable for human use. According to Khatri, N. et al. [2], the deteriorating quality of fresh water is escalating the already existing problem of water scarcity and in the near future the demand will surpass the supply of fresh water.

The surface and groundwater quality is a function of natural setup and processes as well as anthropogenic activities collectively. According to Khatri, N. et al. [2], human influences towards the quality of water are a result of economic activities such as the application of fertilizers, irrigation, construction sites, mining operations, sewage and industrial discharge, leaching of contaminants from land fill sites and feedlots of livestock farming amongst many others. On the other hand, groundwater quality is influenced by the leaching of organic matter and nutrients from soil, weathering of bedrock minerals, atmospheric processes involving evapotranspiration, deposition of dust and salts by wind or water. All these processes possess a great potential to introduce contaminants in both surface and groundwater systems [2]. Both water systems can further be influenced by physiographical factors such as topography, land cover, climate, stream geomorphology, as well as the positioning of surface water features relative to subsurface water flow paths in catchments [3].

As a result, effective water quality management requires a thorough understanding of how and why chemical composition varies across the catchment. Understanding these many forces playing a role in water quality is thus essential for the development of effective water quality management strategies as per Section 9 of the South African National Water Act, 36 of 1998. According to Lintern, A. [1], immense studies linking anthropogenic activities and water quality have been conducted in the Berg River Catchment (referred to as BRC hereto). However, there have been fewer studies on the natural setting particularly geology and soil types influencing the chemistry of water in the BRC. This research thus aims to lessen this gap by discussing the hydrogeochemical interactions between surface and groundwater with respect to geologic settings and soils in the BRC. This study intends to be of good use to water users, catchment managers and researchers to develop water quality management strategies and models.

2. Study area

2.1 Location of study area

The Berg River Catchment is found in the Western Cape Province broadening about 270 km from Jonkershoek and Franschhoek mountains flowing in a north westerly direction where it discharges into the Atlantic Ocean at Laaiplek [4,5] (**Figure 1**). From the head waters, the river flows north and joins with the Franschhoek River in the Franschhoek valley where it is further merged by two more tributaries: the Wemmershoek River to the east and the Banhoek River to the west [4].

Furthermore, the Berg River flows through Paarl and Wellington where it is joined by the Krom River tributary from the eastern direction [6]. In the north of Wellington, the Berg River is connected to several other tributaries namely: Klein Berg River, Kompanjies River and the Twenty Four Rivers [4,5]. Further southwards it is joined by the Boontjies River where it begins to flow westwards between the Obiekwa and Voëlvlei mountains into the Berg River Valley and joins the Berg River to the west of Saron [6,7]. The Berg River then flows over the Misverstand Weir in which upstream of the weir, the river is joined by the tributaries that drain the areas north of

Porterville and Moorreesburg [4]. The river then flows in a north-westward direction and drains into the Atlantic Ocean at Velddrift [4,5,7].

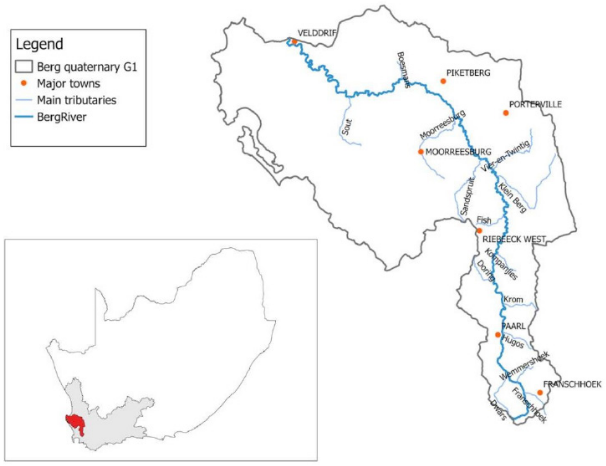

Figure 1. Location of the Berg River Catchment (BRC).

2.2 Land-use activities

The land use in the BRC can be divided into four types namely: i) agriculture which comprises about +60% of the catchment; ii) natural which takes a further +36% of the catchment; iii) urban settlements which take up about +2.5% and iv) forestry which is about, 1% [8]. Furthermore, the agricultural land is further divided into two sectors namely i) dry land farming activities which comprise about 53% as well as ii) irrigated land which takes up +7%. The catchment, however, has recently experienced high a volume of population increase which results in urbanization in the Paarl, Tulbagh and Wellington areas [8].

2.3 Topography, rainfall and flow regimes of the catchment

The topography of the BRC varies greatly from the head waters to the mouth of the river, thus resulting in the great variability of the flow. According to Clark, B. et al. [9], the upper reaches of the Berg River are hydraulically very steep with an average bed slope of 0.67% down to Paarl. From Paarl, the river profile flattens, with an average bed slope to the estuary of 0.045%. According to Madlala T.E. [3], the topography ranges between minimum, mean, and maximum elevations of 213 m, 238 m, and 1500 m above sea level respectively. The highest elevation is found at the head waters with mountainous terrain and flattens towards the river mouth into the Atlantic Ocean. It is worth note taking however that the BRC is mostly flat in terrain.

The catchment receives the most rainfall in winter due to its Mediterranean climate, though the precipitation distribution varies greatly in the extent of the catchment [9]. According to research by Clark, B. et al. [9], the BRC receives the Mean Annual Precipitation (MAP) that is usually above 1500 mm in the southern parts of the catchment but decreases steadily to less than 500 mm further northwards towards the mouth of the river. The MAP then drops further to below 300 mm at the river mouth in Veldrift [10]. There are significant seasonal variations in monthly evaporations which fall typically between 40 mm and 50 mm in winter and 230-250 mm in the summer months [10]. Furthermore, the Mean Annual Evaporation (MAE) in the southern and western regions of the catchment ranges from 1400 mm to over 1600 mm in the northeast [4]. The topography of the BRC varies greatly from the head waters to the mouth of the river, thus resulting in the great variability of the flow.

2.4 Geology and soils

The geology of the BRC comprises four groups namely: a) the Table Mountain Group (TMG), b) the Malmesbury Group (MG), c) the Cape Granite Suite (CGS) and d) the Klipheuwel Group (KP). The catchment is however dominated by TMG and MG therefore the CGS and KG form a relatively small component of the total geology of the BRC [9]. The upper reaches of the BRC consist of a combination of CGS and TMG in areas between Franschhoek and Paarl. According to research by the Council for Geoscience [11] (Geology Map of South Africa), the lithology includes the medium to fine grained granite and granodiorite with subordinate syenite, gabbro, diorite and quartz porphyry. The TMG nonetheless dominates the uppermost reaches of the catchment. There are two geologic formations making up the

TMG in the BRC namely: a) Nardow Formation and b) Peninsula Formation [3]. The Narrow Formation is made up of white coarse-fine-grained, thick-bedded pebbly quartz arenites, thin-bedded feldspathic and ferruginous sandstone, subordinate shale and siltstone.

Furthermore, the Peninsula Formation is made up of pebbly quartz arenites, diamictite, minor conglomerate, mudrock, siltstone and shale. As Madlala, T.E. [3] further summarized the abovementioned, the author noted that the two formations comprise primarily of chemically inert granite, quartzitic sandstones, relatively mineralized siltstones, shale, and mudstones. Madlala, T.E. [3] further highlighted that the dominant formation in the upper reaches is the Peninsula Formation. A layer of alluvium in the valleys covers these formations and constitutes the primary aquifer material in the catchment [3,9].

The MG is the most dominating group of rocks in the middle-lower areas of the catchment such as Darling, Moorreesburg, Piketburg, and Porterville as well as the areas towards the river mouth [9]. According to Kisters, A. [12], the rocks of the MG are largely marine sediments, shales and greywackes that were deposited in a near-shore to deep-water environment. Structurally, the rocks of the Malmesbury Group are folded and also consist of faults [12]. The faults stretch up to numerous kilometer-wide fault zones and are generally thought to disconnect three structurally and lithologically distinct formations comprising the southwestern Tygerberg, central Swartland and northeastern Boland terranes.

The Swartland Formation is the dominant domain compared to Boland Formation within the Malmesbury Group separated by Wellington fault. Therefore, Boland Formation is found east of Swartland in areas such as Piketberg, Porterville and Tulbagh and comprises units such as greenstone, dolomite, chert, quartz-serecite and graphite schist [11,12]. Swartland Formation on the other hand is found in areas such as Moorreesburg, Malmesbury, Hopefield and the areas in the lower reaches towards the river mouth and consists of quartz-serecite, chlorite, schist and phyllite [11].

There have been numerous claims that groundwater quality in the Berg River Catchment is generally quite poor in the middle-lower reaches of the catchment owing to the geologic setting of the MG [8,13]. Clark, B. et al. [9] added that groundwater quality is controlled by, amongst other factors, lithology, residence time and rainfall. Aquifers consisting of rocks of the MG generally yield poor quality groundwater with a NaCl character and an EC fluctuating between 100 and 1000 mS/m.

3. Methodology

This study was carried out using three types of research designs namely i) Experimental research design; ii) Field research design and iii) Meta-analysis research design. The primary data were obtained from published scientific journals and books, and governmental institutions. The data were analyzed and incorporated into the literature to explain the geology, hydrology and geohydrology of the area. The surface and groundwater data from 2003 to 2013 were obtained from the National Water Monitoring Database owned by the Department of Water and Sanitation in South Africa (**Figure 2**). The 2016 data was sampled by the authors is depicted in **Figure 3**.

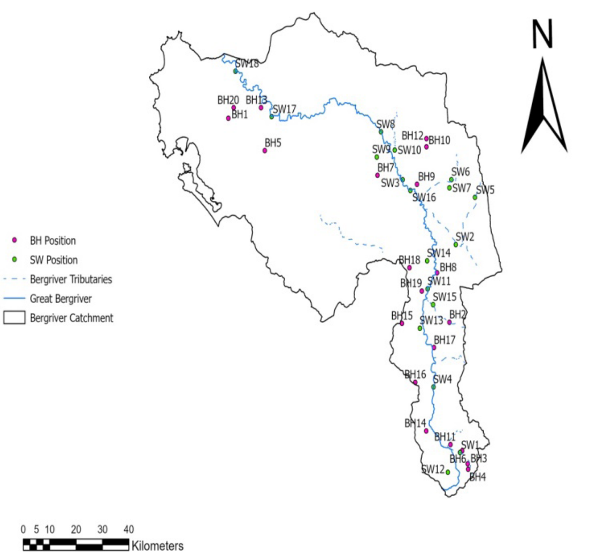

Figure 2. Department of water and sanitation surface and groundwater localities.

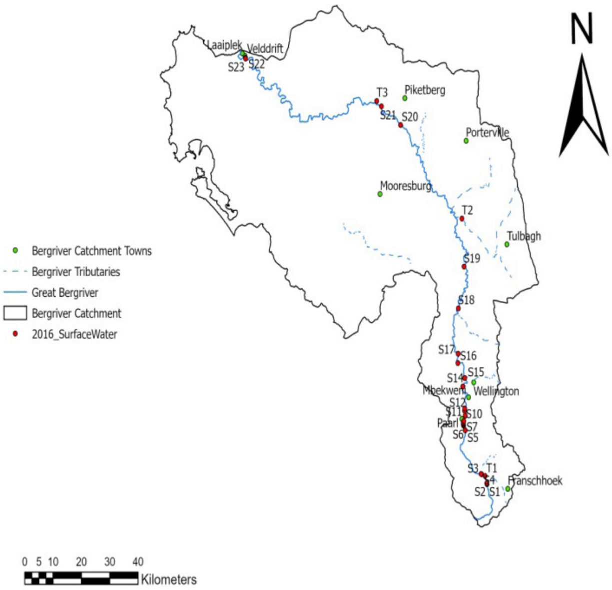

Figure 3. 2016 surface water samples locality collected by authors.

The surface water samples were collected in 2016 during the dry season. The samples were collected from the head waters (Berg River Dam) to the mouth of the river (Laaiplek) by means of grab sample technique. The samples were collected from 23 different locations in the river extent using plastic bottles of 125 mL. Each bottle was labeled by a unique identity (numbers i.e. S1, S2 etc.). To ensure accuracy and avoid cross contamination of the samples, the bucket used to collect water samples was first rinsed with deionized water and secondly rinsed with the water from the river before taking the actual sample. When both the bucket and the bottles were rinsed with deionized water, they were further rinsed again with sample water prior to final sample collection and bottling. This procedure was performed at each sample location to avoid contamination of samples.

Physical parameters (TDS, salinity, pH, EC and temperature) were immediately analyzed in-situ using M99720 Combo Water Meter in order to get the original nature of the sample. The water meter was also rinsed with deionized water prior to taking physical parameter readings from sample water. Thereafter, the samples were stored in cooler boxes whereby the chemical parameters were analyzed in 24-72 hours at the Stellenbosch University (ICP-MS and XRF Laboratory) for the analysis of chemical parameters (nitrates, calcium, magnesium, sodium, potassium, chloride, sulphates and bicarbonates).

3.1 Analysis method for cations (Ca^{++}, Mg^{++}, Na^{+}, K^{+}) using Perkin Elmer ICP-OES Optima 5300 DV

This method describes multi-elemental determinations by ICP-OES using a simultaneous optical system with axial and radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. Samples were nebulized and the resulting aerosol was transported to the plasma torch. Element-specific emission spectra were produced by radio-frequency inductively coupled plasma. The spectra were dispersed by an echelle polychromator, and the intensities of the emission lines were monitored by segmented-array charge-coupled detectors. Simultaneous background correction was performed for each element. The position selected for the background-intensity measurement, on either or both sides of the analytical line, was determined by the complexity of the spectrum adjacent to the analyte line.

3.2 Analysis method for Anions (Cl, SO_4 and HCO_3) using thermo fischer scientific gallery plus discreet analyser

The Gallery Plus Discrete Analyser is designed to selectively analyse chloride, nitrate and sulphate in water samples based on photometric principles where colour-forming complexing reagents were added to a sample to produce a unique coloured solution for each analyte to be determined. Each unique colour was measured at a specific wavelength where colour intensity (absorbance) was directly proportional to the concentration of the analyte.

3.3 Surface water hydrochemical analysis

The samples collected in 2016 were analysed using Waters 717 autosampler, conductivity detector and Waters 2410 pump, controlled with Waters Empower software. An IC Pak A column was used with a Lithium Borate/Gluconate eluent, conductivity 240 µS consisting of 20 mL Lithium Borate Gluconate concentrate (34 g Boric acid, 23.5 mL d-Gluconic acid, 8.6 g Lithium hydroxide monohydrate, 250 mL Glycerin, filled up to 1 litre with Milli-Q water), 10 mL n-Butanol, 120 mL Acetonitrile filled up to 1 litre with Milli-Q water. A 5 µL sample was injected for analysis at a flow rate of 1.2 mL/min.

3.4 Mapping and modeling

Mapping and modelling were done by the use of GW Chart, ArcView and Oasis Montaj (Geosoft) Software packages. GW-Chart is a software program used for creating specialized graphs in groundwater studies. The program can create several types of graphs such as piper diagrams and hydrographs which were created for this study to provide more understanding of the sample results. To create the piper diagrams, raw data from the laboratory which is usually expressed in milligrams per litre "mg/L" units were organized into the Excel spreadsheet and then added onto the GW Chart to create piper plots.

ArcView comprises one of several ArcGIS software that are used for mapping. This software was used in this study for the creation of maps that were used to indicate the direction of water flow, sampling points (location), correlation, trends as well as vulnerable areas that are more prone to contamination. The maps were created using an Excel spreadsheet and base maps by means of shapefiles which were obtained from the Department of Rural Development. The Excel spreadsheet contains the correct sampling location (XY coordinates), sample identity and sample contents (chemical parameters) with concentration. The base maps consist of the following layers: rivers, provincial layers, towns and catchment layers. Oasis Montaj software was used to grid the Nitrates concentrations in both surface and groundwater data to establish the trends and correlations. The color intensity and scale were used to denote the concentration magnitude of the analytes understudied.

4. Results and discussion

4.1 Groundwater and surface water hydrochemical facies correlation

The data from both surface and ground water were grouped according to their geographical locations as explained below (**Table 1**):

SW1, SW12, BH3, BH4, BH6 and BH11 surface and groundwater hydrochemical correlation

The above sample points are in the G10A+B quaternary catchment in the BRC headwaters where the lithology is mostly dominated by sandstones of the Table Mountain Group. The hydrochmeical facies deduce that all the above-mentioned samples are NaCl type. This suggests that the NaCl in the BRC may have originated from the rocks such as siltstone and sandstone which exists in the upper Berg. It can further be observed that surface water samples have both NaCl and Mixed-CaMgCl while groundwater has three additional water types to those of surface including $CaHCO_3$, Mixed $CaNaHCO_3$ and CaCl. It can thus be said there is little to no interaction and transfer of constituents as the water types found in groundwater are not present in surface water. Furthermore, the Mixed-CaMgCl water type in groundwater is only found in BH3, which further suggests that there may be other factors contributing to the presence of this water type in BH3 as it does not occur in other borehole data (**Figure 4**).

SW4 and BH14 surface and groundwater hydrochemical correlation

SW4 and BH14 are in an area in the G10C quaternary catchment where the underlying geology is predominantly of granitic rocks, most of those belonging to the Cape Granite Suite. Based on the hydrochemical facies, there is very little movement of water from the surface into groundwater, but rather a recharge of surface water by groundwater. The borehole waters in this area recorded only NaCl water type while surface waters reflected both NaCl and Mixed-CaMgCl, meaning, this water type does not originate from groundwater but from other factors.

Table 1. Summary of groundwater and surface hydrochemical facies.

Borehole ID	Hydrochemical facies	Surface point ID	Hydrochemical facie
1. BH1	NaCl	1. SW1	NaCl; Mixed-CaMgCl
2. BH2	NaCl ; Mixed CaMgCl	2. SW2	NaCl
3. BH3	$CaHCO_3$; NaCl; Mixed $CaNaHCO_3$; Mixed CaMgCl	3. SW3	NaCl; Mixed-CaMgCl
4. BH4	$CaHCO_3$; Mixed $CaNaHCO_3$; NaCl	4. SW4	NaCl; Mixed-CaMgCl
5. BH5	NaCl	5. SW5	NaCl; Mixed-CaMgCl; $CaHCO_3$
6. BH6	NaCl; $CaHCO_3$; Mixed $CaNaHCO_3$	6. SW6	NaCl; Mixed-CaMgCl
7. BH7	NaCl	7. SW7	NaCl; Mixed-CaMgCl; $CaHCO_3$
8. BH8	NaCl	8. SW8	NaCl
9. BH9	NaCl	9. SW9	NaCl
10. BH10	NaCl	10. SW10	NaCl
11. BH11	NaCl ; $CaHCO_3$; CaCl	11. SW11	NaCl
12. BH12	NaCl ; $CaHCO_3$	12. SW12	NaCl; Mixed-CaMgCl; $CaHCO_3$
13. BH13	NaCl	13. SW13	NaCl
14. BH14	NaCl	14. SW14	NaCl; Mixed-CaMgCl
15. BH15	NaCl	15. SW15	NaCl
16. BH16	NaCl; Mixed CaMgCl	16. SW16	NaCl
17. BH17	Mixed CaMgCl; NaCl	17. SW17	NaCl
18. BH18	Mixed CaMgCl; NaCl	18. SW18	NaCl
19. BH19	NaCl		
20. BH20	NaCl		

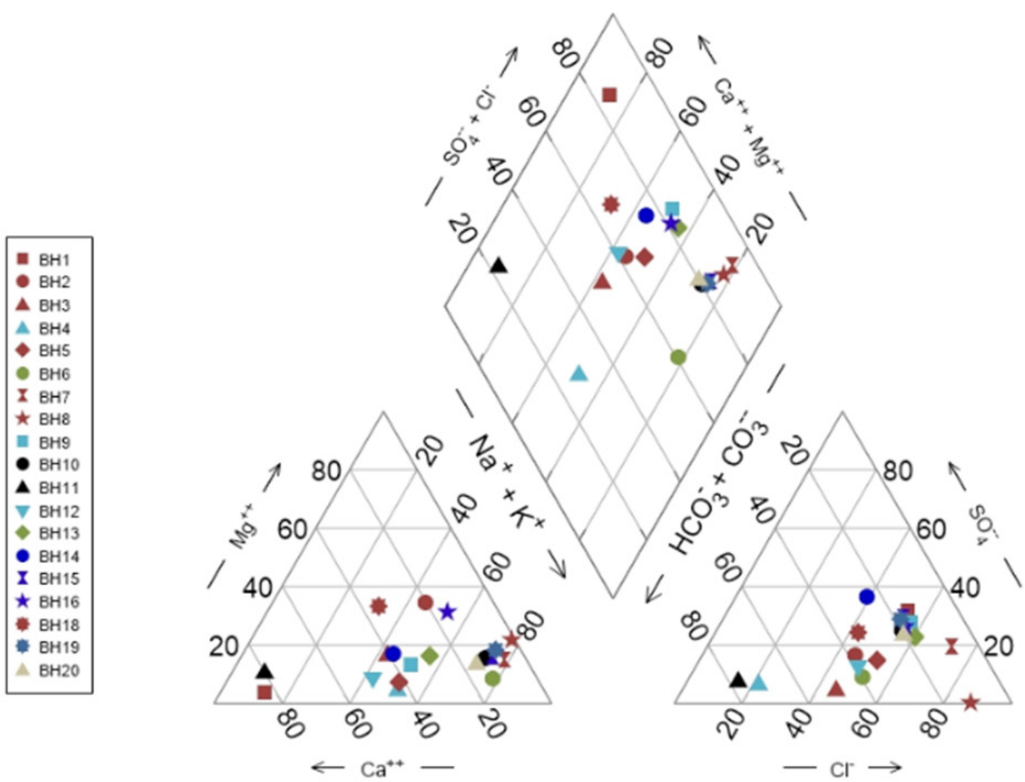

Figure 4. Groundwater chemistry data plot.

SW13, SW15, BH2, BH15 and BH17 surface and groundwater hydrochemical correlation

The correlation of the above-mentioned samples suggested very little interaction of water between the two hydrological components. The groundwater data indicated similarities amongst the boreholes which vary from the surface waters. BH2 and BH17 have both NaCl and Mixed-CaMgCl types; however, BH15, SW13 and SW15 have only NaCl water type (**Figure 5**).

SW11, SW14, BH8, BH18 and BH19 surface and groundwater hydrochemical correlation

The above samples indicated the presence of NaCl and Mixed-CaMgCl water types, therefore it can be said that there is reasonable interaction between the surface and groundwater in this G10F quaternary catchment.

SW8, BH10 and BH12 surface and groundwater hydrochemical correlation

With reference to the hydrochemical facies, it can be said there is little interaction and transfer of constituents amongst the above samples. All sample points have NaCl water type. However, BH12 further shows the presence of $CaHCO_3$ water type.

SW17 and BH5 surface and groundwater hydrochemical correlation

The two sample points above are in the G10L quaternary catchment and both have NaCl water type. It is also worth note-taking that the two sample points are located nearer to the river mouth and therefore, the presence of saline water is inevitable.

SW18, BH1, BH13 and BH20 surface and groundwater hydrochemical correlation

Like those of the G10L quaternary catchment, SW18, BH1, BH13 and BH20 are also located in the G10M quaternary catchment, very close to the river mouth into the Atlantic Ocean and as such the dominant NaCl water type is highly inevitable. All the sample points in the G10M indicated no other water type than NaCl.

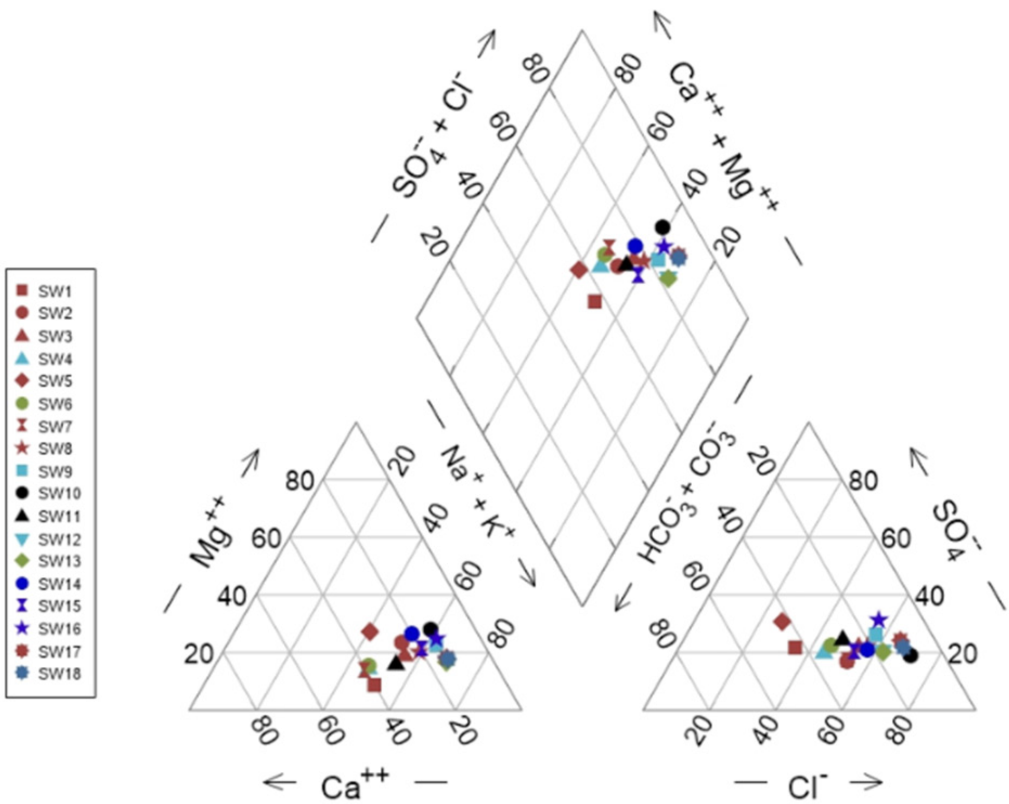

Figure 5. Surface water chemistry data plot.

SW3, SW9, SW10, SW16, BH7 and BH9 surface and groundwater hydrochemical correlation

All the above sample points indicated none other than NaCl water type except for BH3 which reflected both NaCl as well as Mixed-CaMgCl. The presence of Mixed-CaMgCl therefore suggests another factor contributing to its presence as well as no movement of water from surface into groundwater as this water type is not detected in the groundwater.

SW2, SW5, SW6 and SW7 surface and groundwater hydrochemical correlation

These surface water samples could not be correlated with groundwater samples as there were no available groundwater data in the same vicinity (**Table 2**).

4.2 Surface and groundwater nitrates variations in the Berg River Catchment

The data from both surface and groundwater were grouped according to their geographical locations as explained below:

SW1 surface and groundwater nitrate correlation

The SW1 sample recorded nitrate concentrations that exceeded the permissible drinking water standards as stipulated in the SANS 241-1 2015 for more than half the years involved in this research. In most years, however, the values were just below 1.2 mg/L which is negligible. Only on two occasions were the SW1 sample point recorded just above 2 mg/L and 8.6 mg/L in 2008. This indicates that there may have been accidental discharges or releases of excess nitrates into the river by either malfunctioning Wastewater Treatment Works (WWTW) or agricultural activities as the area is highly cultivated with various types of grapes and stone fruits. On the other hand, however, the report by Cullis, J.D.S. et al. [8] rules out the possibility of the Franschoek and Wemmershoek areas being the possible sources of nitrates as they are not listed as part of those which are worst performing in the catchment. The report by the DWAF [6] nonetheless indicated that agricultural practices in the area may be the most possible source of excess nitrates by means of fertilizer application and eventually run-off into the river.

Nonetheless, the boreholes (BH3, BH4, BH6 and BH11) in the same area have not recorded nitrates above 1 mg/L, although the DWAF [6] report indicated the area of Franshoek and Wemmershoek as one of those highly irrigated in the catchment, the boreholes have very low nitrates (**Figures 6 and 7**). This suggests that the river water used for irrigation may be treated prior to irrigation.

BH14 and BH16 surface and groundwater nitrates correlation

The two boreholes showed more than 80% higher nitrate concentrations with BH16 taking the lead. The boreholes are located in the vicinity of Paarl which is industrialized, cultivated and also consists of residential areas. The Berg River around the area of Paarl has been recorded to have slightly bad quality of water due to many activities taking place as well as non-compliant WWTW which discharge into the Berg River [6]. The possible source of the nitrates however points to agricultural activities by means of

Table 2. Correlation of excessive surface water and groundwater nitrate data.

Quaternary catchment—Location	Surface sample ID	Boreholes ID
G10A—Franschhoek	SW1	-
G10C—Paarl	-	BH14 and BH16
G10D—Wellington	SW13 and SW15	-
G10F—Riebeek Kasteel	SW11 and SW14	BH8, BH18 and BH19
G10H—Porterville & Piketberg	SW8	-
G10J—Mooreesburg	SW3, SW9, SW10 and SW16	-
G10M—West Coast	-	BH1 and BH20

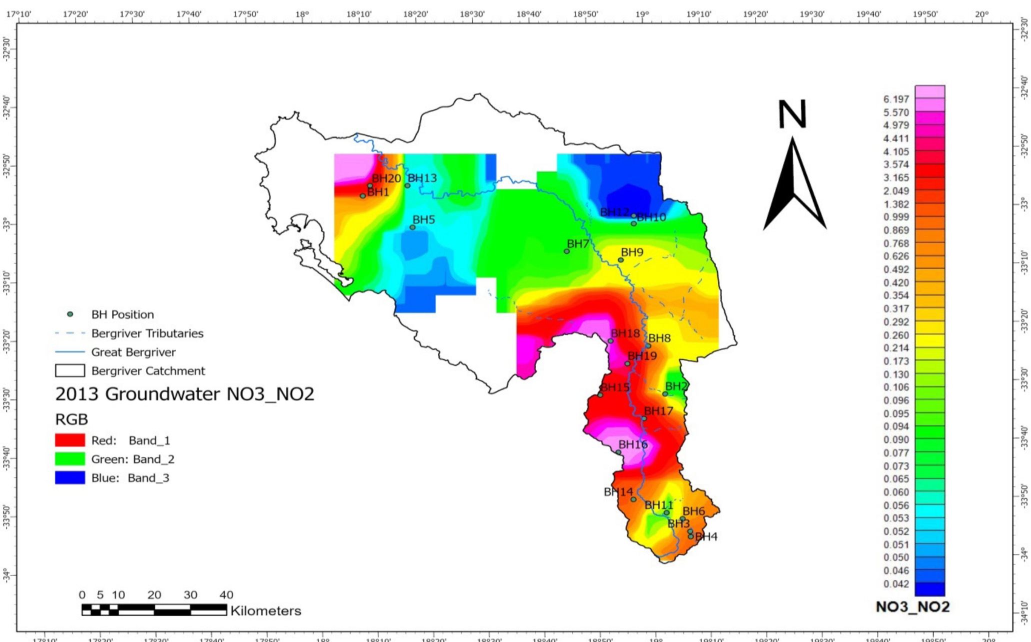

Figure 6. Groundwater NO_3^-+NO_2^-.

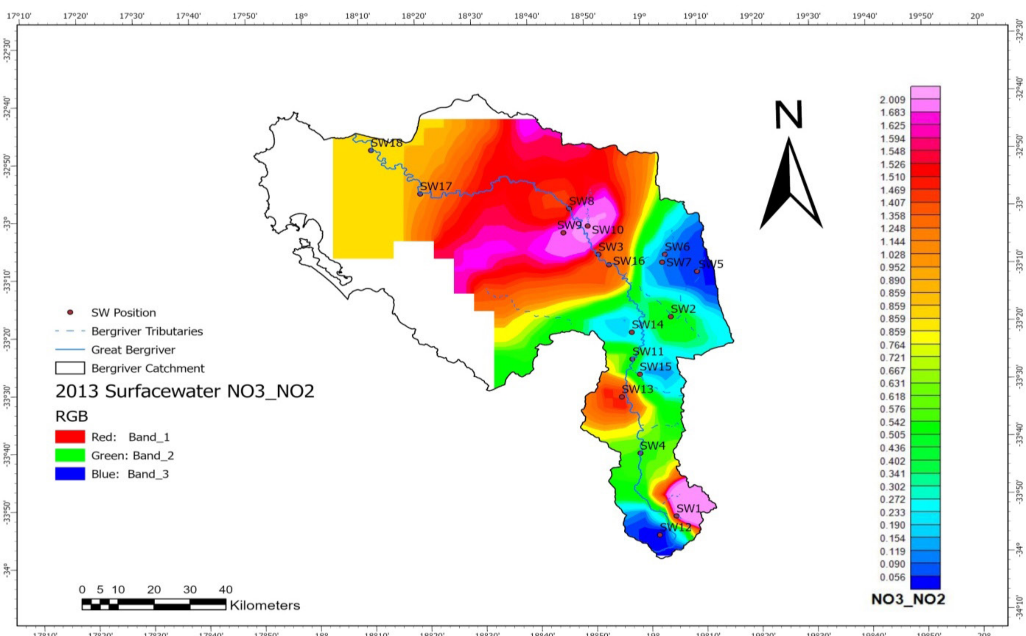

Figure 7. Surface water NO_3^-+NO_2^-.

irrigation and not fertilizer application as the surface water sample point only recorded 1.7 mg/L once in 11 years. The SW4 sample has shown nitrates values less than 1 mg/L in 10 out of 11 years involved in this research. Another possible explanation for the high nitrates in the boreholes can be pointed to the broken sewage infrastructure (pipes in particular) which may leak into the groundwater system.

SW13 and SW15 surface and groundwater nitrates correlation

SW15 had shown nitrates above 1mg/L in only one incident out of the 11 years of sampling. This suggests an accidental discharge by means of damaged sewage infrastructure. On the other hand, SW13 indicated high values of concentrations in 7 out of 11 years. This therefore suggests a constant feeder of nitrates into the river such as an ailing sewage system and damaged sewage infrastructure. SW13 is situated adjacent to an area dominated by informal settlements and has an ailing wastewater infrastructure like most informal settlements in the country. The sewage run-off (overflowing manholes) directly into the Berg River as it passes adjacent to the informal settlement. Although SW13 and SW15 are in the same quaternary catchment, recorded highly variable nitrates suggest a significant dilution and or the presence of marine organisms which consume the parameter at hand. Furthermore, the boreholes (BH2, BH15 and BH17) have shown a record of very low nitrate concentrations contrary to surface data. This may be due to the fact that there are no agricultural activities in the vicinity and further there may be significantly low or no interchange of surface and groundwater.

SW11, SW14, BH8, BH18 and BH19 surface and groundwater nitrates correlation

These sample points showed moderately high nitrate concentrations. The area is also highly cultivated and irrigation with river water is highly practiced. The possible source of nitrates in surface water can be pointed to the application of fertilizers which is transported to the Berg River by run-off. It is also worth noting that the farms in this area are adjacent to the Berg River; as a result, fertilizers are easily leached into the river. In addition, the boreholes in the area have also shown significant concentrations of nitrates with BH18 going up to 16.8 mg/L of nitrates. This notion therefore suggests that there is irrigation with the untreated river water and insignificant dilution in groundwater compared to surface water.

SW8 surface and groundwater nitrates correlation

This sample point only recorded on one occasion values exceeding 1 mg/L of nitrates. This may have been due to an accidental discharge of sewage around the area.

SW3, SW9, SW10 and SW16 surface and groundwater nitrates correlation

SW3 recorded values exceeding the permissible limits only in 2 out of 11 years and SW9 in 3 out of 11 years. Such inconsistencies point to accidental discharges such as overflowing manholes. SW10 and SW16 on the other hand have moderately high nitrate concentrations compared to SW3 and SW9. All the surface samples stated above are situated in an area that is highly cultivated. Therefore, the application of fertilizers is the most possible source of excessive nitrates in the river in the vicinity. In addition, the area is dominated by farmhouses and a small informal settlement of the farm workers. Most of the farmhouses use septic tanks whereas areas like other areas use the oxidation ponds as their sewage system and discharge directly into the Berg River. The sewage discharge from the area's oxidation ponds, however, cannot be pointed as the leading source of excessive nitrates in the river as it has not been listed as one of the worst performing [8].

There is however no corresponding groundwater data which have recorded abnormal nitrate concentrations in the vicinity. BH7 and BH9 in the area have indicated significantly low nitrates throughout 11 years. This further indicates little or no interchange of surface and groundwater as there is no evidence of an exchange of constituents. In addition, the low nitrates in the borehole data may also suggest that irrigation is practised with treated water.

BH1 and BH20 surface and groundwater nitrates correlation

BH1 and BH20 are located on the West Coast known for the cultivation of stone fruits and winter cereals. These two boreholes recorded the highest nitrate concentrations amongst all other boreholes with BH20 recording high values all throughout the 11 years, with 2008 being the highest with the record of 22.11 mg/L. On the contrary, the surface water samples in the area, SW17 and SW18 have shown incredibly low nitrate concentrations all throughout 11 years.

The data from both the DWS surface and 2016 surface water sampled by the authors were grouped according to their geographical locations as explained below (**Figure 8**):

SW1, SW12, T1 & S1-S3 surface water hydrochemical correlation

The 2016 surface data indicated that the data located in the G10A+B quaternary catchment had shown much higher nitrate concentrations compared to the DWS surface data throughout the 11 years of sampling. The SW1 and SW12 from the DWS had been fairly compliant with drinking water standards set out in SANS 241-1 wherein the SW12 had only exceeded the set limits on two occasions in 11 years whereas SW1 exceeded in 7 out of 11 years. Their nitrate values were much lower compared to the 2016 data for S1, S2, S3 and T1. Their nitrates values ranged between 55.1 mg/L and 67.8 g/L which far exceed the WHO nitrates limits of 50 mg/L for drinking. Thus far it is unclear as to how these values arose too much in a span of 3 years from 2013 where they were below 10 mg/L to 2016 where they were above 50 mg/L. According to the land-use data it can be deduced that in the entire catchment of BRC the agricultural activities were reduced between 2006 and 2015 however, urban areas development in the catchment has grown significantly. The urban areas development, however, comes with more sewer system challenges which may be a possible explanation for such a peculiar rise in nitrates.

SW4, SW13, SW15 and S4-17 surface water hydrochemical correlation

According to the geosoft plots, it can be distinguished that amongst the sample points in G10C & G10D (SW4, SW13 and SW15), the sample SW13 illustrated values exceeding the drinking water standards set out in SANS 241-1 while SW4 and SW15 only exceeded once in 11 years. These values however were still not close to the 2016 samples which were between 60.5 mg/L and 92.1 mg/L. Again, there is no possibility of correlating the two as the values are far apart. It is worth noting however that, SW13 and S17 are very close to each other and are adjacent to the informal settlement which had records of continuous sewer overflows from manholes, dilapidated and damaged sewer infrastructure.

Nevertheless, the increase in urban area development is by far the possible explanation for the abnormal nitrate concentrations. In addition, urban developments for residential habitation resulted in the overloading of municipal sewage systems which were already ailing, pipe bursts, overflowing manholes running off in the streets ending up in the river and further by-passing of sewage treatment processes due to ailing infrastructure. The half-treated efflu-

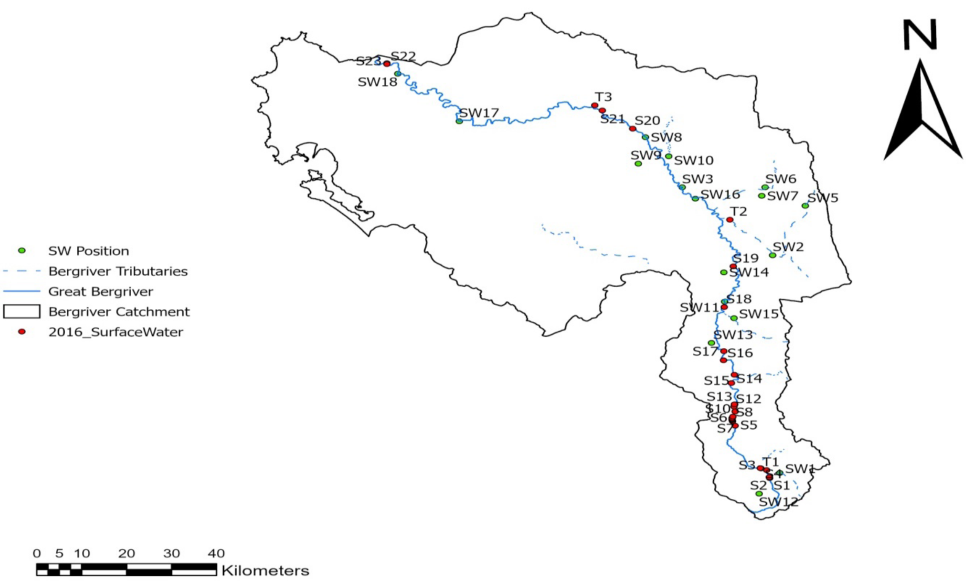

Figure 8. Department of water and sanitation surface sample locations and 2016 sample locations sampled by the authors.

ent is thus discharged into the river.

S18, S19, SW11 and SW14 surface water hydrochemical correlation

The sample points SW14 had moderately high nitrate concentrations. The concentrations however point out to the application of fertilizers since the farms are situated adjacent to the riverbanks and there are no nearby informal settlements. On the other hand, S18 and S19 recorded higher values than other samples from the 2016 surface data wherein S18 had 85.6 mg/L nitrates and S19 had 91.9 mg/L nitrates concentrations. This however, unlike the samples mentioned above are not situated near major towns or informal settlements, as a result, their sources cannot be pointed to anthropogenic influences but rather agriculture through the application of fertilizers. Other parameters were however normal though increasing steadily from S1.

T2, SW3, SW9, SW10 and SW16 surface water hydrochemical correlation

The SW3, SW9, SW10 and SW16 were amongst a group of samples which were among the highest records from the DWS data although they were not any close to the 66.6 mg/L of nitrates recorded in T2. The area where these samples are located is heavily cultivated and there are no nearby major towns and informal settlements with ailing sewer systems. The nitrates are thus the result of fertilizer application which are easily run-off into the river as the farms are adjacent to the riverbanks.

Furthermore, the DWS samples indicated very high NaCl concentrations of more than 3500 mg/L of Cl in some years, with SW9 and SW16 taking the lead. In addition, SW9 and SW16 have also recorded concentrations of Na more than 1000 mg/L in several years wherein the T2 recorded less NaCl with Na^+ concentration of 103.6 mg/L and Cl with 94.3 mg/L.

S20, S21, T3 and SW8 surface water hydrochemical correlation

Both the DWS surface and the authors' data indicate that there are no linkages in this particular area as with the rest of the samples in terms of nitrate concentrations. Nonetheless, this area had shown a steep increase in Na and Cl wherein S20 recorded Na 161.6 mg/L and Cl 162.7 mg/L and S21 had a Na concentration of 201.5 mg/L and Cl 219 mg/L. SW8 however had less than 100 mg/L throughout the 11 years studied. T3 however, recorded NaCl concentrations which are low with Na^+ 61.79 mg/L and Cl 57.8 mg/L.

S22, S23, SW17 and SW18 surface water hydrochemical correlation

S22 and S23 recorded significantly high concentrations in all other parameters excluding nitrates. All these sample points however have similarities in high records of all other parameters except nitrates. Their NaCl is particularly high, and this may be due to the river water mixing with sea water as the sample location is closer to the sea. The nitrates in S22 were undetectable whereas the S23 recorded nitrates just below 30 mg/L which is significantly low compared to other samples from 2016 data. SW17 and SW18 have also significantly low nitrates throughout the 11 years studied except on two occasions the SW17 had nitrates concentrations just above 1 mg/L.

In your results and discussion, you need to include your maps. The maps will help in the understanding of the explanations above. Please work on that.

4.3 Influence of geological features on the water chemistry of the BRC

The Table Mountain Group (TMG) dominates the uppermost reaches of the catchment. The TMG rocks represent a multi-porous medium, consisting of two major components, namely fractures and inter-fracture rock matrix [14]. In general, the fractures act as the more permeable conduits for groundwater movement, while the matrix blocks form the main storage unit or reservoir [15]. However, the TMG rock matrices are very inert and do not contribute much to the mineral content of the groundwater in the aquifers [14]. As a result, the macro-chemical character of the groundwater is determined more by the character of the precipitation than by mineralogy of the rock through which it percolates [16]. Groundwater from the TMG aquifers is generally of the Na-Cl type, reflecting the fact that precipitation generally derives from frontal systems in the Atlantic and Indian Oceans.

The Malmusbury Group (MG) is the most dominating group of rocks in the middle-lower areas of the catchment as well as the areas towards the river mouth [9]. The rocks of the MG are largely marine sediments, shales and greywackes that were deposited in a near-shore to deep-water environment. Structurally, rocks of the Malmesbury Group are folded and consist of many faults [2]. The indication of a degree of interaction between surface and groundwater, is a result of the heavily structured middle and lower parts of the catchment.

4.4 Influence of anthropogenic activities on the water chemistry of the BRC

The NaCl hydrochemical facies in the headwaters suggest disturbances of groundwater quality by activities such as irrigation with saline water which may have enhanced NaCl concentrations as the area is heavily cultivated. In the upper catchment, the underlying geology resembles very little possibility of weathering of salt bearing rocks [9]. As a result, the presence of salt may not be the result of the underlying geology but rather other external factors. Several studies have highlighted that nitrates have for some years become an environmental issue in certain areas of the BRC that have ailing sewage infrastructure. Farmers apply nitrogen-based fertilizers to their crops to enhance plant growth and increase agricultural productivity. When applied excessively or improperly, these nitrates can leach into the soil and, ultimately, groundwater. As a result of the dynamic hydrological system, both surface water and groundwater may be affected by excess nitrates from these activities. Runoff from rainfall or irrigation can wash excess nitrates from agricultural fields into nearby water bodies, such as rivers, lakes, and streams. This runoff contributes to elevated nitrate levels in surface waters of the BRC. Livestock agricultural activities can also contribute to nitrate pollution. Manure from livestock contains nitrogen, and if not managed properly, it also releases nitrates into the environment through leaching and runoff.

4.5 Policies and management implications

To address these issues, sustainable agricultural practices and effective nutrient management are essential to minimize the impact of agricultural activities on nitrate levels in the environment while ensuring food security and economic viability for farmers.

Efficient irrigation practices like drip irrigation, soil moisture monitoring, and rainwater harvesting are crucial for sustainable agriculture as they help conserve water resources, reduce energy costs, and promote healthier crops. Effective soil management practices like nutrient management, compost and organic matter incorporation, soil testing and analysis, and crop rotation are key to maintaining productive and sustainable agriculture while minimizing adverse environmental impacts. Farmers and land managers must adapt these practices to their specific conditions and crop types to achieve optimal results. Effective fertilizer application practices like split application and fertigation, reduce the environmental impact of agriculture and protect both surface water and groundwater quality while maintaining crop productivity.

It is recommended that authorities at the surrounding wastewater treatment works should improve nutrient removal processes and educate, the community about the benefits of these activities. Government authorities should also host regular awareness programs that highlight the impacts of pollution in rivers. In South Africa, the Fertilizers, Farm Feeds, Seeds and Remedies Act 36 of 1947 intends to provide a guide on the manufacturing and use of fertilizers. However, it is recommended that the government needs to enforce such regulations on farmers.

5. Conclusions

Water is a precious and scarce resource that is extremely crucial for life on Earth. In South Africa, water is crucial not only for the socio-economic development but for other forms of ecosystems at large. As a result, it is therefore important to investigate, monitor, record, and rectify water quality degradation and hold accountable those who degrade the water resources.

Therefore, this study investigated the hydrogeochemical interactions between surface and groundwater in the BRC with the aim of establishing trends and transfer of constituents between surface and groundwater systems. The hydrochemical facies indicated that in the upper Berg River Catchment, there is very minimal interaction between surface and groundwater systems. Other water types that were found in the groundwater other than NaCl were barely found in surface water and vice versa. This may be due to the underlying consolidated hard rock formations (granitic rocks) having less geohydrological properties like fractures and voids.

The Middle Berg, however, indicated a degree of interaction with the sharing of constituents between the two water systems. Most of the water types found in borehole data were also found in the surface water. This can be explained with reference to the structural geology of the area in which a northwest-trending strike-slip faults of the Piketberg-Wellington faults occurred which gave rise to more permeability and movement of water. Moreover, the Lower Berg indicated only NaCl water type. It is worth noting that Lower Berg is situated near the river mouth where there is the mixing of river and sea water. This notion therefore further explains the NaCl being the sole water type in the area. In surface water, this may have further been exacerbated by means of sea spray. With reference to groundwater, Lintern, et al. [9] highlighted that there may have been a possibility of seawater intrusion also enhanced by the faulting of rocks originating from the Colenso fault.

With reference to nitrates, the data indicated no interaction and transfer of constituents. The data illustrate that there are 3 boreholes (BH8, BH18 and BH19) which were correlated with the 2 surface samples (SW11 and SW14). The rest of the surface and groundwater samples did not indicate correspondence. It can therefore be deduced that the nitrates in the boreholes came by because of using nitrate rich water from agricultural activities like irrigation.

Overall, the results obtained in this study indicated that:

- The entire catchment geology consists of rocks containing various minerals with varying chemical make-up however, the NaCl exists in the entire geology even though in some areas it is not dominant.
- The geology and soils do not entirely control the water chemistry of the surface water however, in areas which have been affected by geological faults; there was a correlation of water chemistry between the surface and groundwater systems.
- The surface and groundwater interaction and transfer of constituents occurs mostly in the Middle Berg, and Lower Berg of the catchment.
- Nitrates in groundwaters are believed to be a result of agricultural activities as a result of the application of nitrate rich fertilizers, these nitrates can leach into the soil and, ultimately, groundwater.

Author Contributions

The authors confirm their contribution to the paper as follows:

Study conception and design: N. Malaza

Data collection: N. Malaza and S.P Mabokela

Analysis and interpretation of results: M. Malaza and S.P. Mabokela

Draft manuscript preparation: S.P. Mabokela

All authors reviewed the results and approved the final version of the manuscript.

Conflict of Interest

There is no conflict of interest.

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