

Quality of Groundwater Resources in Chikhwawa, Lower Shire Valley, Malawi

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Abstract Groundwater resources in some parts of the lower section of the Shire River valley, Malawi, are not potable for rural domestic water supply due to high salinity. Knowledge of spatial variation of water quality is essential in locating and sustaining usable water supplies. In this study, a comprehensive assessment of the quality of groundwater from the area has been conducted to establish a spatial variation of major ions and general groundwater quality. World Health Organisation (WHO) guidelines for sodium (200 mg/l), chloride (250 mg/l), sulphate (250 mg/l), magnesium (30 mg/l) and calcium (75 mg/l) in drinking water were exceeded by 42%, 29%, 15%, 70% and 53% for all groundwater samples, respectively. The concentrations of analysed solutes are very wide in range, suggesting that the hydrochemistry is controlled by several intermixed processes such as saline water mixing and water–rock interaction. Based on the interpretation of the cumulative probability curve for TDS content, groundwater samples are grouped into three groups, as follows: (1) Group 1 waters (51%) that

are relatively poor in Cl^- , representing fresh groundwater affected mainly by weathering reactions; (2) Group 2 waters (45%) relatively enriched in Cl^- , indicating considerable effects of rock–water interaction and mixing with saline water; (3) Group 3 waters (4%) enriched in Cl^- , representing the saline groundwater resources. High total hardness (TH) and total dissolved solids (TDS) (in several places) render the groundwater, in large sections of the study area, unsuitable for domestic and irrigation purposes. Results reported in this study provide baseline data towards the utility of groundwater resources in the area.

Keywords Groundwater quality · Salinity · Lower Shire · Malawi

Introduction

Groundwater constitutes the largest readily available freshwater reserve on earth. It plays an essential role in the domestic water supply system for small towns and rural regions, where it represents a relatively clean, reliable and cost effective resource (Bovolo et al. 2009). Globally, about 25% to 40% of the drinking water is derived from groundwater (Morris et al. 2003). Groundwater resources are also of great importance for agricultural development, especially in arid and semi arid areas where surface waters are scarce or absent. In most cases, aquifers are intensively exploited to meet the continually increasing agricultural and domestic needs. However, some of the aquifers are not of adequate usable quality due to natural factors or anthropogenic pressures (Epule et al. 2011). Nevertheless, many groundwater supply schemes in developing countries are implemented without necessary attention to quality issues. Groundwater supply schemes consist typically of a large number of hand

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pumped boreholes, providing untreated, unmonitored and often unconnected supplies (Hiscock 2009). Poor quality of water threatens human health and plant growth (Olajire and Imeokparia 2001), thereby adversely affecting economic development and social prosperity (Milovanovic 2007). It is therefore crucial to establish the current status of groundwater quality and thus its appropriateness for the two major uses of drinking and irrigation.

In the lower section of the Shire River valley, Malawi, exploitation of groundwater resources is of great developmental interest because of the region's potential for irrigated agriculture (Davis 1969; Lockwood Survey Cooperation 1970; Bradford 1973; Bath 1980). Agriculture is a dominant sector in the economic development of Malawi, as it is the source of sustenance for the majority of the population and contributes significantly to the country's economy. However, the occurrence of groundwater with high salinity, represented by elevated content of total dissolved solids (TDS), Cl^- , Na^{2+} , Mg^{2+} and SO_4^{2-} , is a major groundwater quality problem (Davis 1969; Lockwood Survey Cooperation 1970; Bradford 1973; Bath 1980; Monjerezi et al. 2011a, 2011b). The hydrogeochemistry of groundwater resources in the lower section of Shire River valley has been fairly studied, mainly because exploitation of fertile soils of the valley floor depends on availability of groundwater with suitable quality. Davis (1969) suggested a link between fault systems and the localised occurrence of saline groundwater. Bradford (1973) and Bath (1980) classified various aquifers as to their relative productivity and quality. Monjerezi et al. (2011a) applied Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) to a major ion dataset and proposed the major hydrogeochemical processes governing the spatial variation in groundwater chemistry. A later study (Monjerezi et al. 2011b) used isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) to show evidence of mixing of fresh and saline groundwater sources and effect of evaporation for groundwater resources from shallow water table located close to the Shire River. On the basis of Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, they concluded that saline groundwater showed an evaporite dissolution signature. However, these studies did not cover the suitability of the groundwater quality for irrigation and domestic purposes and how this suitability varies spatially. Therefore, there is no established link between the hydrogeochemical processes and groundwater quality and hence its intended uses.

In this context, this paper highlights the spatial variation in quality and major ion content of groundwater in the lower section of the Shire River valley (Chikhwawa district) and evaluates the suitability of the groundwater for irrigation and drinking purposes for sustainable agriculture and basic human needs, respectively. For this purpose, we have collected data from a regional hydrogeochemical survey (Monjerezi et al. 2011a) and calculated key indicators of groundwater quality for irrigation and domestic purposes. Several

researchers have proposed different methods of analysing water quality data for these purposes (Al-Bassam and Al-Rumikhani 2003; Alobaidy et al. 2010). In this paper, Water Quality Index (WQI), total hardness (TH), Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), and salinity hazard (EC), regarded as the most effective ways to communicate water quality (Sinha and Srivastava 1994; Yidana et al. 2008) have been used. In addition, a cumulative probability diagram (CPD) of total dissolved solids (TDS), was used to determine threshold values of a natural background population and distinguish it from an anomalous population of high salinity (Lepeltier 1969; Sinclair 1974, 1991). The CPD was an effective tool for discerning intermixed processes and also for classifying waters based on the dominant process controlling water quality. The results should provide helpful information to local policymakers managing the important fresh groundwater resources and allocation of usable supplies in the lower Shire River valley. In addition, the approach used in this study should render service to others exploring similar groundwater studies.

Materials and Methods

Study Area

Malawi is situated in South East Africa (Fig. 1) and lies within the western branch of the East African Rift system. The study area (Chikhwawa district) is situated in the lower Shire valley, in the southernmost part of the Malawi section of the rift. The Shire River, the biggest river in Malawi, runs through the valley accounting for the outflow from Lake Malawi to Zambezi River. The valley flow flanking the River Shire is of low slope and relief, ranging from 50 m to 76 m above sea level (Hutcheson 1971).

Situated within the East African Rift System (EARS), the area is intensely faulted and the major geology units of the lower Shire Valley are presented in Fig. 1 (Habgood 1963; Bloomfield 1966; Carter and Bennet 1973; Morel 1989; Castaing 1991; Chapola and Kaphwiyo 1992). A basement of Precambrian to lower Palaeozoic Mozambique belt high-grade charnockitic granulites and biotite-hornblende gneisses (semi-pelitic), referred to as the Malawi Basement Complex underlies the area. On the western bank of the Shire River, Karoo sedimentary rocks overlay the basement rocks. Cretaceous Lupata sandstones, in turn, overlay the Karoo sedimentary rocks. The climax of Karoo faulting was the eruption of volcanic basalts and dolerites during the early Jurassic period. Also present are hydrothermal fault rocks, associated with the Karoo boundary faults. The valley floor is a piedmont plain consisting of a large amount of unconsolidated sediments (Habgood 1963; Carter and Bennet 1973).

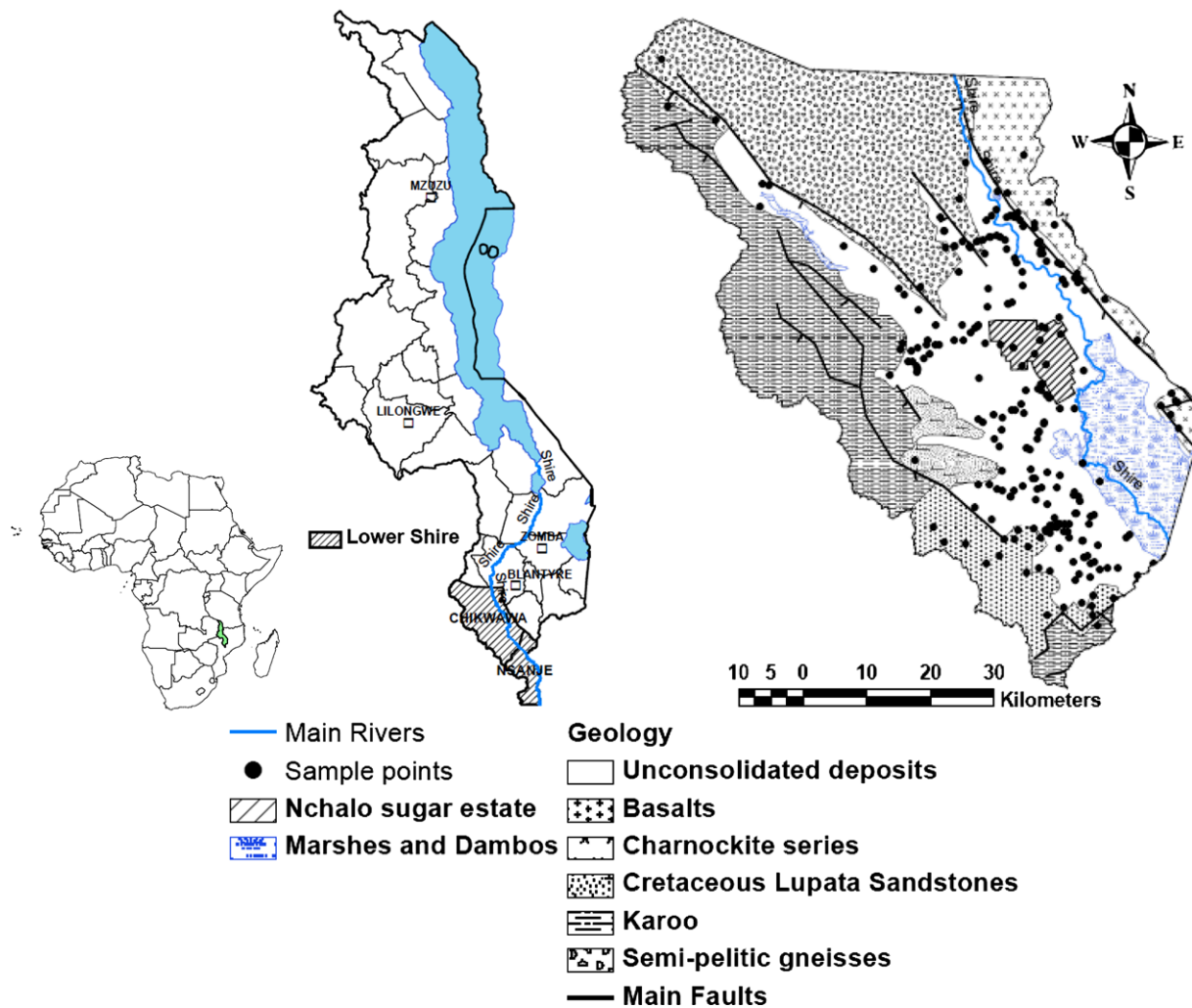


Fig. 1 Map of the study area showing location, geology (modified after Habgood 1963) and sample locations. *Inset* shows location of the study area in Malawi (Africa)

The hydrogeology of the area has been reported upon by Bradford (1973). The main aquifer units, in order of increasing importance as groundwater resources, are (1) the weathered and/or fractured basement rocks, (2) Karoo and Cretaceous sedimentary rocks, (3) weathered basalts and (4) the unconsolidated alluvial deposits. In general, piezometric contours indicate a regime of groundwater flow towards the central axis of the valley i.e. towards Shire River (Bradford 1973).

Hydrochemical Dataset and Data Analysis

The groundwater samples considered in this study were collected and analysed as part of a project addressing the occurrence and evolution of saline groundwater resources in the area (Monjerezi et al. 2011a). Water samples were collected in triplicate from randomly located shallow boreholes and hand dug open wells (Fig. 1) used for rural water supply,

during sampling campaigns conducted in 2008 and 2009, using standard sampling procedures (American Public Health Association (APHA) 2005; ISO 5667-11:1993). The shallow boreholes were drilled typically to depths between 20 m and 67 m, whilst the wells are ≤ 10 m deep. Most of the samples were collected in the valley bottom as this is where human settlements are present and therefore where most boreholes are located. Most of the areas are difficult to access during the rainy season and therefore the data considered in this study are from the dry season. Two sets of groundwater samples were collected at each sampling point, filtered and stored in new pre-cleaned polyethylene bottles. One set of the samples was acidified with HNO_3 (to $\text{pH} < 2$) and analysed for major cations, whereas the other set was stored unacidified and analysed for major anions. All samples were analysed for physical characteristics and main chemical components using standard methods. Temperature, pH (ISO 10523-1:1994) and electrical conductivity (EC) (ISO

7888:1985) were measured in the field, whilst the rest of the parameters (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} and total dissolved solids (TDS)) were determined in a laboratory using the procedures in APHA (2005). The concentrations of Na^+ , K^+ , Ca^{2+} and Mg^{2+} were determined using flame atomic absorption spectroscopy (Buck Scientific Model 200A) whereas $\text{HCO}_3^- + \text{CO}_3^{2-}$ and Cl^- were determined using acid and silver nitrate titrations, respectively (APHA 2005). The concentration of sulphates was determined turbidimetrically (barium sulphate; APHA 2005) and TDS were determined gravimetrically by evaporation (APHA 2005). Charge-balance error was computed, taking the relationship between the total cations (Na^+ , Ca^{2+} , Mg^{2+} and K^+) and the total anions (HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-}) for each set of complete analysis of water samples. Only samples which fall within $\pm 10\%$ were used in this paper. The dataset also had an overall good correlation between total cations and total anions (meq/l) ($y = 0.98x$; $R^2 = 0.98$). The geochemical modelling program PHREEQC v2.16 (Parkhurst and Appelo 1999), implemented with MINTEQA4 database (Allison et al. 1991) was used to calculate saturation indices (SI) with respect to the main mineral phases and theoretical partial pressure of CO_2 ($p\text{CO}_2$).

We calculated key indicators of groundwater quality in order to provide an assessment of suitability of groundwater resources for domestic and irrigation purposes. We used a Water Quality Index (WQI) and total hardness (TH) to assess suitability for domestic uses, whereas for irrigation purposes, we utilised values of sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and EC (salinity hazard). The TH of the groundwater was calculated using the formula given below (Hem 1991; Sawyer et al. 2003):

$$\text{TH (as CaCO}_3\text{) mg/l} = (\text{Ca}^{2+} + \text{Mg}^{2+}) \text{meq/l} \times 50 \quad (1)$$

WQI is a rating that reflects the composite influence of different water quality parameters (Sahu and Sikdar 2008). The WQI therefore provides a comprehensive picture of the overall quality of groundwater for most domestic uses and various calculations of WQI have been widely used in water quality studies (see e.g. Horton 1965; Harkins 1974; Tiwari and Mishra 1985; Mishra and Patel 2001; Naik and Purohit 2001; Stigter et al. 2006; Avannavar and Shrihari 2008; Yidana and Yidana 2010; Vasanthavigar et al. 2010; Gibrilla et al. 2011; Şen 2011). In this study, TDS (as a measure of salinity) and the major ions were used to calculate WQI for the sampled locations as follows:

$$\text{WQI} = 100 \sum_{i=1}^n W_i \frac{C_i}{S_i} \quad (2)$$

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \quad (3)$$

where w_i and W_i are the weight and relative weight of the i th parameter, respectively. C_i and S_i denote the concentration (in each sample) and the WHO drinking water guideline for the i th parameter, respectively (see Srinivasamoorthy et al. 2008).

To calculate the WQI, each of the chemical parameters was assigned a weight (w_i) based on their perceived effects on primary health (see Srinivasamoorthy et al. 2008). The highest weight of five was assigned to TDS and chloride, whilst sodium and sulphate were assigned a weight of 4 each. Calcium, magnesium and pH were assigned a weight of 3 each. Computed WQI values were classified into five categories as excellent water ($\text{WQI} < 50$), good water ($50 < \text{WQI} < 100$), poor water ($100 < \text{WQI} < 200$), very poor water ($200 < \text{WQI} < 300$) and water unsuitable for drinking ($\text{WQI} > 300$) (see e.g. Sahu and Sikdar 2008; Yidana and Yidana 2010; Vasanthavigar et al. 2010).

The quality of water used for irrigation is vital for crop yield, maintenance of soil productivity and protection of the environment. Among the major chemical constituents of groundwater, the concentrations of Na^+ , $\text{HCO}_3^- + \text{CO}_3^{2-}$ and the total concentration of soluble salts (expressed as EC) are essential in assessing its suitability for irrigation (Richards 1954; Al-Bassam and Al-Rumikhani 2003). The use of waters of moderate ($750 \mu\text{S/cm}$ to $2250 \mu\text{S/cm}$) to high (above $2250 \mu\text{S/cm}$) content may result in saline soil conditions. On the other hand, high Na^+ content in irrigation water results in accumulation of exchangeable sodium in the soil because Na^+ replaces adsorbed Ca^{2+} and Mg^{2+} leading to the development of alkali soils. Alkali soils are characterized by crust formation, water-logging, reduced soil aeration, reduced infiltration rate and reduced soil permeability (Kelly 1951). The adsorption of sodium by the soil is simply related to a sodium adsorption ratio (SAR). The SAR is consequently used as an index of the alkali (or sodium) hazard of the water and is defined by the equation (Richards 1954)

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{\frac{\text{Ca}^{2+} + \text{Mg}^{2+}}{2}}} \quad (4)$$

where Na^+ , Ca^{2+} and Mg^{2+} represents concentrations in milliequivalents per litre (meq/l).

For irrigation waters containing bicarbonate concentrations in excess of the sum of calcium and magnesium (in meq/l), calcium and magnesium precipitate as carbonates upon concentration of the soil solution (Richards 1954). This results in an increase in the proportion of sodium ions in the soil solution, leading to sodification of the soil profile (Prasad et al. 2001). Residual sodium carbonate (RSC) is usually calculated to assess the suitability of groundwater with respect to high bicarbonate and carbonate content and is defined by the equation (Eaton 1950)

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (5)$$

where all constituents are in meq/l.

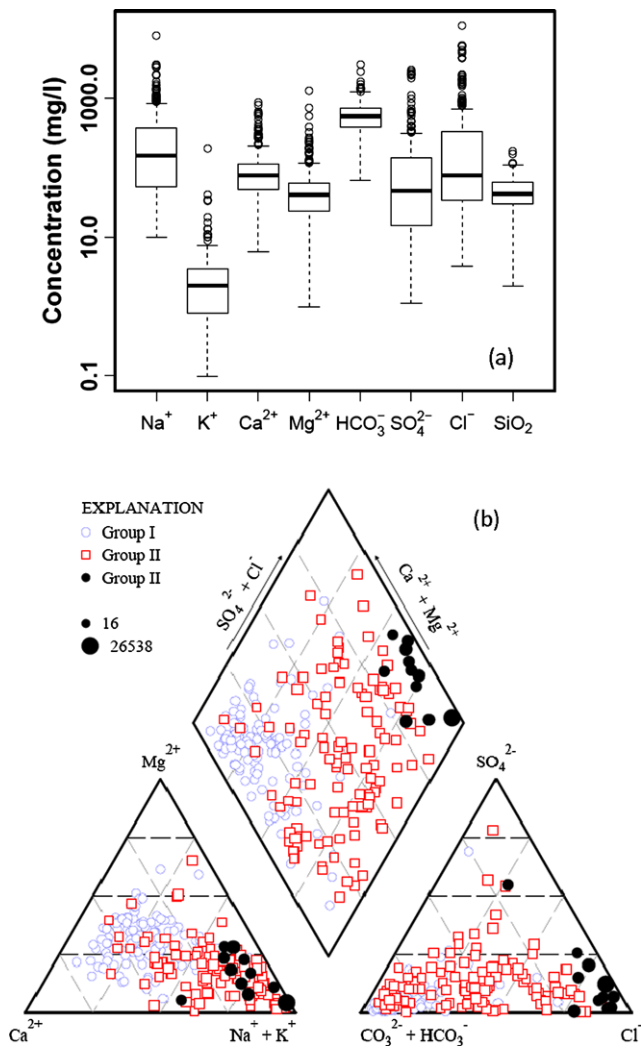


Fig. 2 (a) Box and Whisker plots showing the variation of major ion concentrations in the studied groundwater samples. (b) Piper diagram showing major ion composition of the groundwater samples, classified into three groups based on cumulative probability distribution (CPD) of TDS (Fig. 5a)

Results

Distribution of Major Solutes

The distribution of concentrations of the analysed solutes is shown as box plots in Fig. 2a. Electrical conductivity (EC) varied considerably from 35 $\mu\text{S}/\text{cm}$ to 36000 $\mu\text{S}/\text{cm}$, and correspondingly TDS ranged from 16 mg/l to 26539 mg/l. The ranges of Na^+ and Cl^- ions were from 10 mg/l to 8320 mg/l (mean: 367 mg/l), and 3.8 mg/l to 11767 mg/l (mean: 457 mg/l), respectively. The concentration of SO_4^{2-} also varied widely from 1.1 mg/l to 2600 mg/l (mean: 159 mg/l). The ranges of Ca^{2+} and Mg^{2+} ions were from 6 mg/l to 876 mg/l (mean: 109 mg/l), and 1.0 mg/l to 1302 mg/l (mean: 63 mg/l), respectively. The concentration of HCO_3^- also widely varied from 65 mg/l to 3110 mg/l

(mean: 602 mg/l). Such wide ranges of solute concentrations suggest that multiple sources and/or complex hydrochemical processes act in unison to generate the chemical composition of groundwater (Park et al. 2005; Mondal and Singh 2011). pH values from 5.0 to 9.0 were found, with an average pH of 6.45.

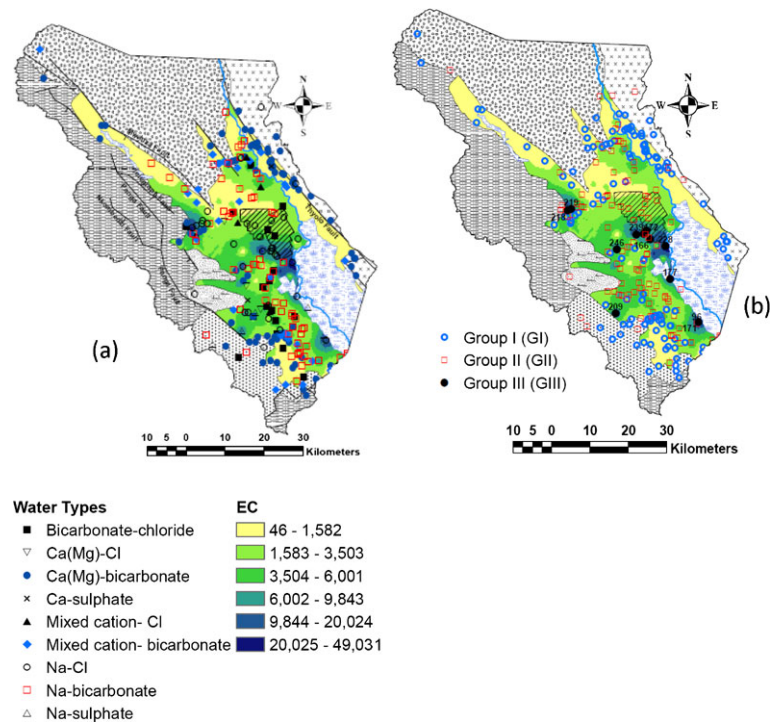
Overall, salinity does not show a significant pattern with depth of boreholes (Monjerezi et al. 2011a), but spatial variation is apparent in Fig. 3. Spatially, highly mineralised groundwater is to be found close to Shire River and in distinct areas associated with the Karoo and Cretaceous formations on the western bank of the Shire River (Figs. 3 and 4). The areas with the Karoo basalt outcrop and their derived sediment and those with the Basement Complex provide groundwater with low mineralisation. Na^+ and Cl^- show similar spatial pattern as salinity. High SO_4^{2-} areas are also coincident with those of high salinity, but these are not necessarily also areas of high Cl^- (Fig. 4).

Hydrochemical facies

The proportions of major solutes in natural water provide the basis for naming the water type. The concentrations of major ions measured in the studied water samples are presented in the Piper trilinear plot (Fig. 2b). This figure shows highly variable major ion chemistry for the study area. Approximately 70% of all samples were of bicarbonate type, of which nearly 40% were sodium bicarbonate (EC in the range 230 $\mu\text{S}/\text{cm}$ to 8500 $\mu\text{S}/\text{cm}$) and nearly half of them were Ca-(Mg)- HCO_3^- (EC in the range 39 $\mu\text{S}/\text{cm}$ to 3220 $\mu\text{S}/\text{cm}$) and the rest were mixed cation- HCO_3^- type. Samples with a Na-Cl composition accounted for 13% of all samples (EC in the range 1590–36000 $\mu\text{S}/\text{cm}$), approximately 10% of all samples had equal bicarbonate and chloride and only 6 samples were of the sulphate type. Figure 3a shows the distribution of water types superimposed over distribution of salinity. Na-Cl groundwater type is associated with high salinity areas, whereas relatively less saline groundwater in the proximity of the areas of high salinity is characterised by Na-mixed anion or Na-Ca (Mg)-Cl and Na- HCO_3^- , indicating possible interaction between saline and fresh groundwater. Ca-(Mg)-bicarbonate and mixed-bicarbonate groundwater is associated with the areas of low salinity. Ca-(Mg)-bicarbonate and mixed-bicarbonate waters occur in areas surrounding the valley on the eastern bank and parts of the west bank of Shire River. Towards the valley centre sodium bicarbonate to sodium chloride (and sulphate) waters predominate (Fig. 3a; Monjerezi et al. 2011a).

TDS and the major ions generally exhibited log-normal density distributions, with an anomalous population as a ‘tail’ on the distribution suggesting that groundwater chemistry is controlled by several intermixing processes. This indicates that some of the samples with high salinity (and

Fig. 3 Spatial distribution of water types (a) and groups (b) with respect to salinity distribution. The geological units and other features are as explained in Fig. 1



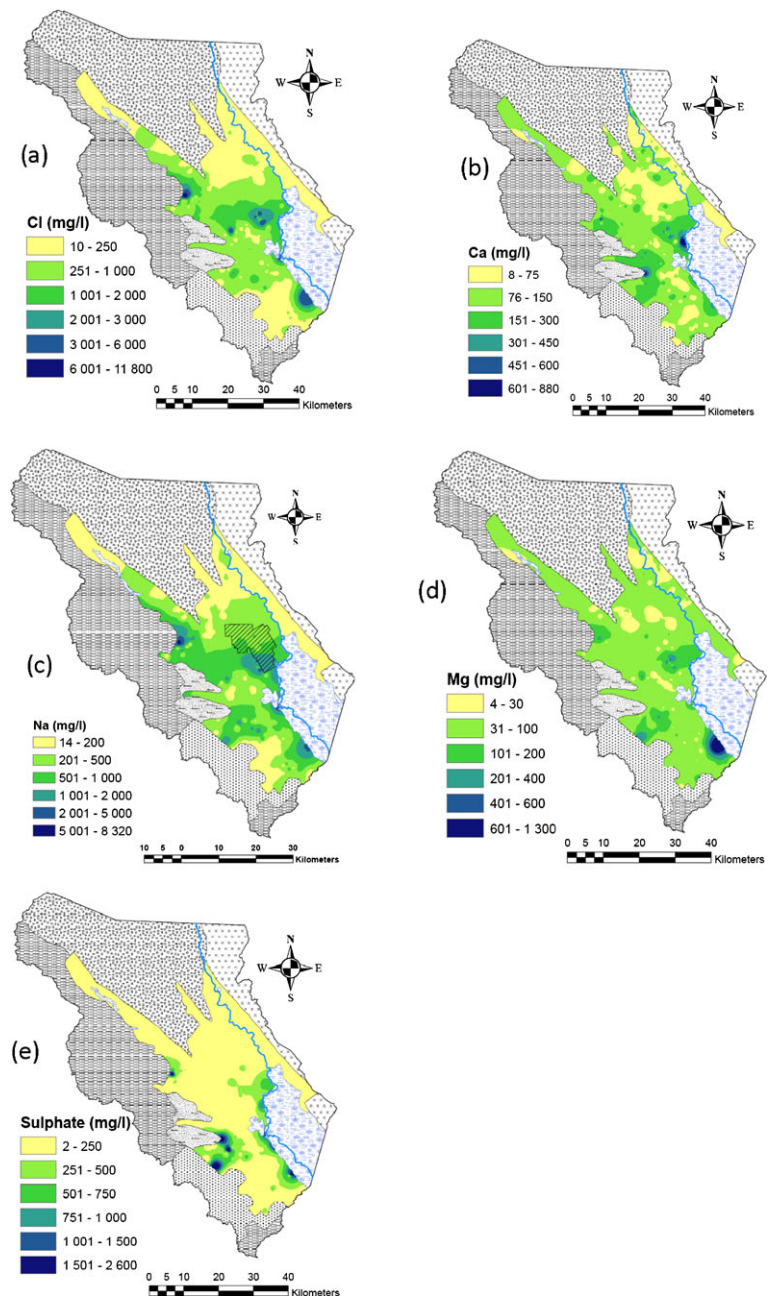
high major ion content) can be attributed to an anomalous population whose chemistry was locally affected by saline groundwater mixing and others (cf. Park et al. 2005; Panno et al. 2006; Mondal and Singh 2011). In particular, a cumulative probability distribution of TDS was examined in order to group the samples on the basis of salinity. Figure 5a shows that two threshold values can be discerned for the data. An upper threshold of 6838 mg/l and lower threshold of 780 mg/l for TDS (Fig. 5a) were then used to group the data into three major populations. The lower threshold value is also the median TDS of the dataset, whereas the upper threshold is similar to the value calculated by using the common method for calculating thresholds as mean plus two standard deviations ($\mu + 2\sigma$; Reimann et al. 2005; Koh et al. 2009). Group I samples, representing 51% of all samples, are characterised by relatively low salinity (Figs. 5a and 5b) (median TDS = 482 mg/l; average TDS = 462 mg/l), representing fresh groundwater. These samples are characterised by mixed cationic composition (abundance order (meq/l): Ca^{2+} (average: 3.97 meq/l) \approx Mg^{2+} (average: 3.18 meq/l) \approx Na^+ (average: 3.77 meq/l) \gg K^+) and anionic composition dominated by bicarbonates (abundance order (meq/l): $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$). Thus most of the samples in Group I can be characterised as mixed cation- HCO_3^- type (Fig. 2b). These are mainly distributed in the bedrock outcropping areas on the east bank and parts of the west bank of Shire River (Fig. 3b). Group 2 samples (median TDS = 1468 mg/l; average TDS = 1880 mg/l) comprise 45% of the samples. These samples are characterised by rel-

atively high values of HCO_3^- (average = 12.37 meq/l and contain higher levels of Na^+ (average = 19.67 meq/l), Cl^- (average = 13.24 meq/l) and SO_4^{2-} (average = 4.57 meq/l) than samples in Group I, indicating an influence of saline water from the anomalous group. However, there are no substantial increases in Ca^{2+} (average = 5.89 meq/l) and Mg^{2+} (average = 5.57 meq/l) in comparison with Group I samples (Fig. 5b). Group 3 samples represent the remaining 4% of the samples and are characterised by high salinity (Fig. 5), with median TDS of 9252 mg/l (average TDS = 11409 mg/l). The constituents of this group are the samples with anomalously high EC values shown in Fig. 3. In comparison with samples in the other groups, they exhibit elevated concentrations of Na^+ (average = 127 meq/l), Cl^- (average = 152 meq/l), Ca^{2+} (average = 17 meq/l), Mg^{2+} (average = 25 meq/l) and SO_4^{2-} (average = 20 meq/l) (Fig. 5b).

Groundwater Quality

Majority (91%) of the groundwater samples would be classified as brackish ($1000 \text{ mg/l} < \text{TDS} \leq 10000 \text{ mg/l}$) and 5% as saline ($10000 < \text{TDS} \leq 100000 \text{ mg/l}$) (Fig. 6a; Freeze and Cherry 1979). WHO drinking water guidelines (WHO 2004) for sodium (200 mg/l), chloride (250 mg/l), sulphate (250 mg/l), magnesium (30 mg/l) and calcium (75 mg/l) were exceeded in 42%, 29%, 15%, 70% and 53% of all groundwater samples, respectively. As regards TH, most of the groundwater samples are classified in the range of slightly hard to very hard (Fig. 6a), with TH values in the

Fig. 4 Spatial variation of selected major ions in the groundwater resources from the study area. The geological units and other features are as explained in Fig. 1



range of 30.3 mg/l to 5837.1 mg/l (average = 532.3 mg/l). 27% of all the samples exceed the upper limit of 500 mg/l, whereas 96% exceed the desirable limit of 100 mg/l (Freeze and Cherry 1979; WHO 2004). There is a close association between TH and salinity (Fig. 6a). Hardness of water limits its use for both industrial and domestic purposes. Hard water causes scaling of pots, boilers, and irrigation pipes due to deposition of carbonates of mostly calcium and magnesium (Hem 1991). For domestic purposes, hardness of water also causes inhibition of soap action in water and some evidence of its role in heart and circulatory diseases has been reported (Schroeder 1960; Muss 1962).

Salinity (TDS) and the major ions were used to compute WQI in order to provide an overview of the quality of water for domestic purposes (Vasanthavignar et al. 2010; Yidana and Yidana 2010). The wide range of the WQI values (24 to 2702) and their spatial distribution (Fig. 7) is reflective of the occurrence and spatial variation of salinity in the study area. Groundwater with bad quality is mainly associated with the areas of high salinity, due to high levels of mineralisation. On the other hand, groundwater grouped into Group I exhibits good quality (cf. Figs. 3 and 7b). On the basis of the computed WQI values, 12%, 45%, 23%, 7% and 13% of the samples were classified as “excellent”, “good”,

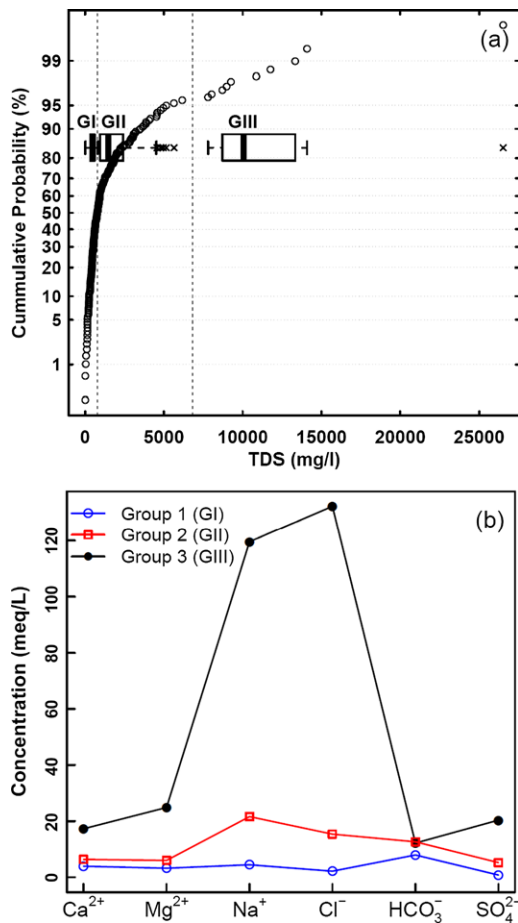


Fig. 5 (a) Cumulative probability diagram of total dissolved solids (TDS). Box plots of TDS for the three groups are also shown on the cumulative probability curve. (b) Average composition (meq/l) of the three groundwater groups

“poor”, “very poor” and “unsuitable” quality, respectively (see e.g. Sahu and Sikdar 2008; Yidana and Yidana 2010; Vasanthavigar et al. 2010).

In order to explore the quality of groundwater for irrigation purposes, computed values of SAR were plotted against those of EC (Fig. 6b). The majority of Group II samples and all samples in Group III exhibit high and very high alkali hazard, respectively (Fig. 6b), whereas samples in Group I show low to medium alkali hazard. If waters used for irrigation are high in Na⁺ (and low in Ca²⁺), the ion-exchange sites may become saturated with Na⁺, which destroys the soil structure, because of dispersion of the clay particles (Appelo and Postma 2005; Janardhana Raju 2007). The computed SAR values for water samples in the studied area of the lower Shire River valley range from 0.39 to 112, with an average value of 6.78. From the calculated values, 77% of the groundwater samples were classified as low (SAR < 10), 15% as medium (10 < SAR < 18), 5% as high (18 < SAR < 26) and 3% as very high (SAR > 26) sodium (alkali) hazard (Richards 1954). In addition, most

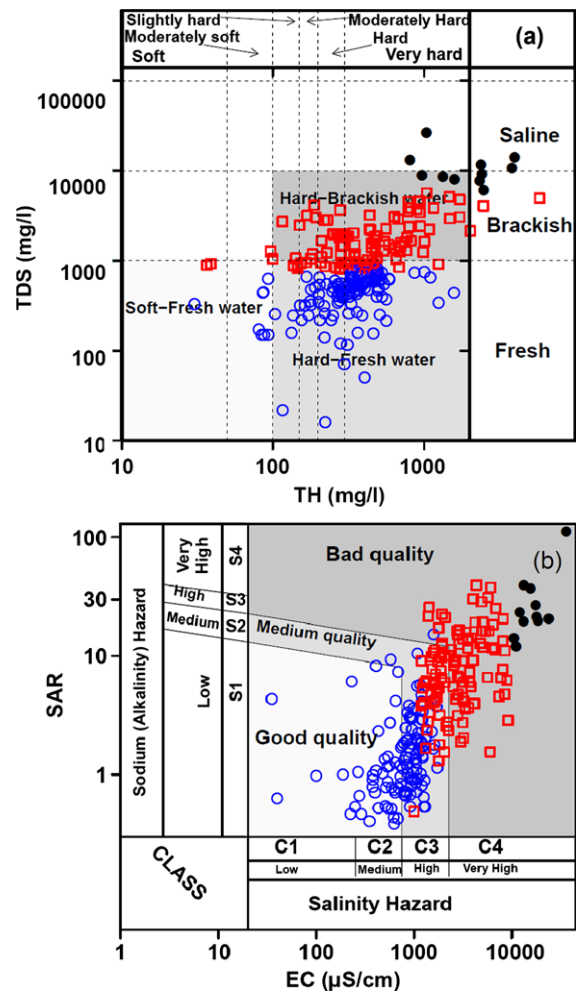
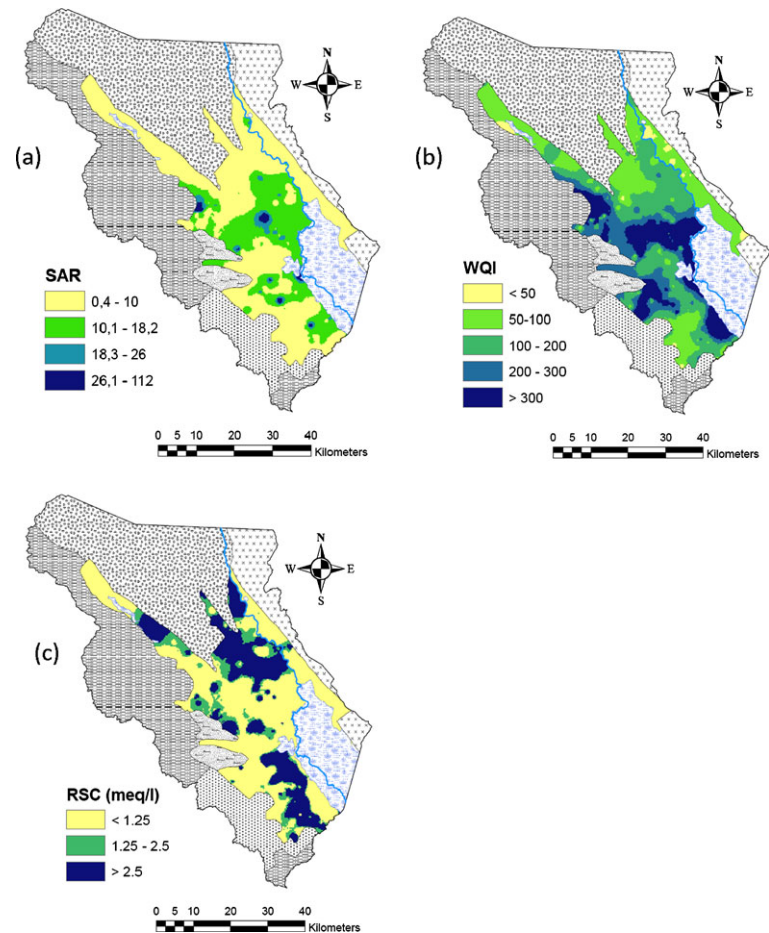


Fig. 6 Classification of groundwater’s suitability for drinking and irrigation purposes. (a) A plot of TDS against Total hardness (TH) expressed in mg/l as CaCO₃ (Classification after Freeze and Cherry 1979); (b) a plot of SAR against EC (adapted after Richards 1954). Water samples are according to their groups (see Fig. 2b for explanation)

samples in Groups II and III are classified in the high to very high salinity hazard classes (Fig. 6b), whereas low and medium salinity hazard classes are comprised of Group I samples. High salinity waters may reduce osmotic potentials of irrigation crops over time (Richards 1954). In terms of the salinity hazard, 3%, 16%, 51% and 30% of the samples were classified into low (EC < 250 μS/cm), medium (250 μS/cm < EC < 750 μS/cm), high (750 μS/cm < EC < 2250 μS/cm) and very high (EC > 2250 μS/cm) zones, respectively (Richards 1954). Overall, Fig. 6b shows a significant number of samples with bad quality water with respect to irrigation purposes and they are characterized by elevated salinity and sodium content (Groups II and III samples).

In addition to the alkali and salinity hazards, values of RSC were also calculated for further assessment of groundwater suitability for irrigation purposes. Classification of the

Fig. 7 Spatial variation of Sodium Absorption Ratio (SAR), Water Quality Index (WQI) and Residual Sodium Carbonate (RSC) calculated for the groundwater resources from the study area. The geological units and other features are as explained in Fig. 1



calculated RSC values indicates that 59% of the groundwater samples have safe RSC values ($RSC < 1.25$), 7% had marginal values ($1.25 < RSC < 2.5$) and 34% were unsuitable ($RSC > 2.5$). Figure 7c shows the spatial distribution of RSC values for the study area. The high RSC values are associated with soda groundwater (characteristic of Group II samples), characterised by low calcium and magnesium content. The lack of overlap in the spatial distribution of the RSC (Fig. 7c) and SAR (Fig. 7a) values means that quality of groundwater from a large area may be deemed unsuitable for irrigation and will have different effects on the soils.

Discussion

The samples with relatively low TDS (mostly in Group I) are located mainly in the Precambrian Basement Complex, Karoo basalts and the unconsolidated sediments derived from these geological formations (Fig. 3b). Although some scatter exists, most of the samples in Group I plot very close to the equivalence line on the plot of concentration of HCO_3^- against total anionic content (Fig. 8d). In addition, these

samples also plot along the equivalence line on a plot of the sum of the major ions, minus their respective chlorides and sulphates against HCO_3^- (Fig. 9a). Furthermore, Na^+ generally increases with HCO_3^- for Group I samples (Fig. 9b) and they have molar Na/Cl ratios of greater than unity (Fig. 10a), indicating a further source of Na^+ (relative to halite dissolution or rainwater), such as silicate weathering and/or cation exchange (of Ca^{2+} (and/or Mg^{2+}) for bound Na^+). The average content of silica in the samples in Group I is 11.25 mg/l and since the effect of cation exchange is minor for the samples in Group I (Fig. 9c), these observations are consistent with dissolution of feldspars and ferromagnesians (Monjerezi et al. 2011a). Plagioclase (e.g. labradorite in the basalts and derived sediment; Habgood 1963) weathering releases Ca^{2+} and Na^+ , although weathering of amphiboles (e.g. sediment derived from the semipelitic gneiss) and pyroxene (e.g. in sediment derived from the charnokites and basalts; Fig. 1) may also contribute to the Ca^{2+} concentration, whilst Mg^{2+} may be derived from the mafic minerals. The samples in Group I constitute the background population in the CPD (Fig. 5a), with relatively low mineralisation. The dissolution of feldspars and ferromagnesians usually leads to low mineralisation (Drever

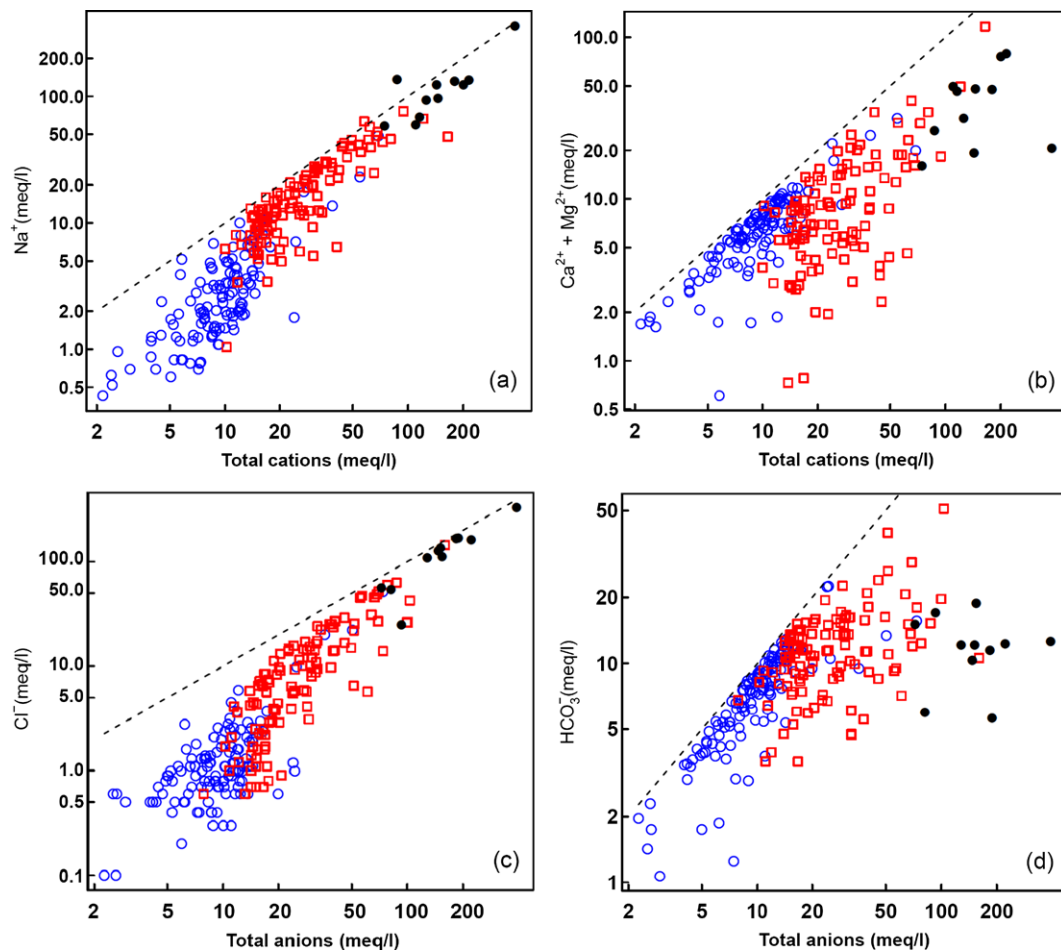


Fig. 8 Bivariate plots showing relationship between (a) Na^+ , (b) $\text{Ca}^{2+} + \text{Mg}^{2+}$, (c) Cl^- and (d) HCO_3^- with total cations/anions (meq/l). The diagonal lines are lines of 1:1 slope. Samples are grouped according to their groups (see Fig. 2b for explanation)

1997; Appelo and Postma 2005; Dongarrà et al. 2009) which is attributable to the “good” water quality associated with Group I samples, as evidenced by computed values of WQI, SAR and RSC (cf. Figs. 3 and 7). However, addition of Ca^{2+} and Mg^{2+} renders the groundwater hard (Fig. 6a).

For Group II samples, there is an increasing trend in Na^+ and HCO_3^- for a significant number of the samples with associated (but incommensurate) decreasing trend in $\text{Ca}^{2+} + \text{Mg}^{2+}$ (Fig. 8). There is also a wide variation in the molar ratio of Na^+/Cl^- for Group II samples (0.27 to 21.48; average 3.30), with some of the samples clustering around a molar ratio of one and others depict high ratios (Fig. 10a). The high molar Na^+/Cl^- ratios indicate that the increase in Na^+ for these Group II samples is also generally not coupled to a matching increase in Cl^- , implying an additional source of Na^+ . Molar Na^+/Cl^- ratios higher than unity may be due to cation exchange (bound Na^+ for Ca^{2+} and Mg^{2+} in solution) or weathering of plagioclase. Cation exchange of aqueous Na^+ with bound Ca^{2+} (and Mg^{2+}) leads to Na^+/Cl^- molar ratios of less than 1. The effect of cation exchange for these samples is illustrated by Fig. 9c, in

which most of the samples plot close to the line of -1 slope. Most of the samples in Group II plot within the fourth quadrant (positive ordinate and negative abscissa) implying that Na^+ and K^+ are enriched relative to Ca^{2+} and Mg^{2+} . Some samples plot within the second quadrant (negative ordinate and positive abscissa), implying that Ca^{2+} (and Mg^{2+}) are enriched relative to Na^+ (Yidana 2010).

Most of the Group II samples that cluster around Na^+/Cl^- molar ratio of unity, also cluster around $\text{HCO}_3^-/\text{Cl}^-$ molar ratio of 1.0 (Figs. 10a and 10b). Generally, these samples also have higher chloride content than those with higher Na^+/Cl^- molar ratios. This suggests that these samples are also affected by mixing with saline groundwater from samples in Group III. The observed hydrogeochemical trends in Group II samples therefore suggest that Ca^{2+} (and Mg^{2+}) ions, from hydrolysis of aluminosilicates and ferromagnesium minerals, are removed from solution by cation exchange with adsorbed Na^+ on the clays and carbonate precipitation to form Na-HCO_3 type of water (e.g. Toran and Saunders 1999; Krothe and Parizek 1979; Chappelle 1983; Foster 1950; Chae et al. 2006; Gascoyne

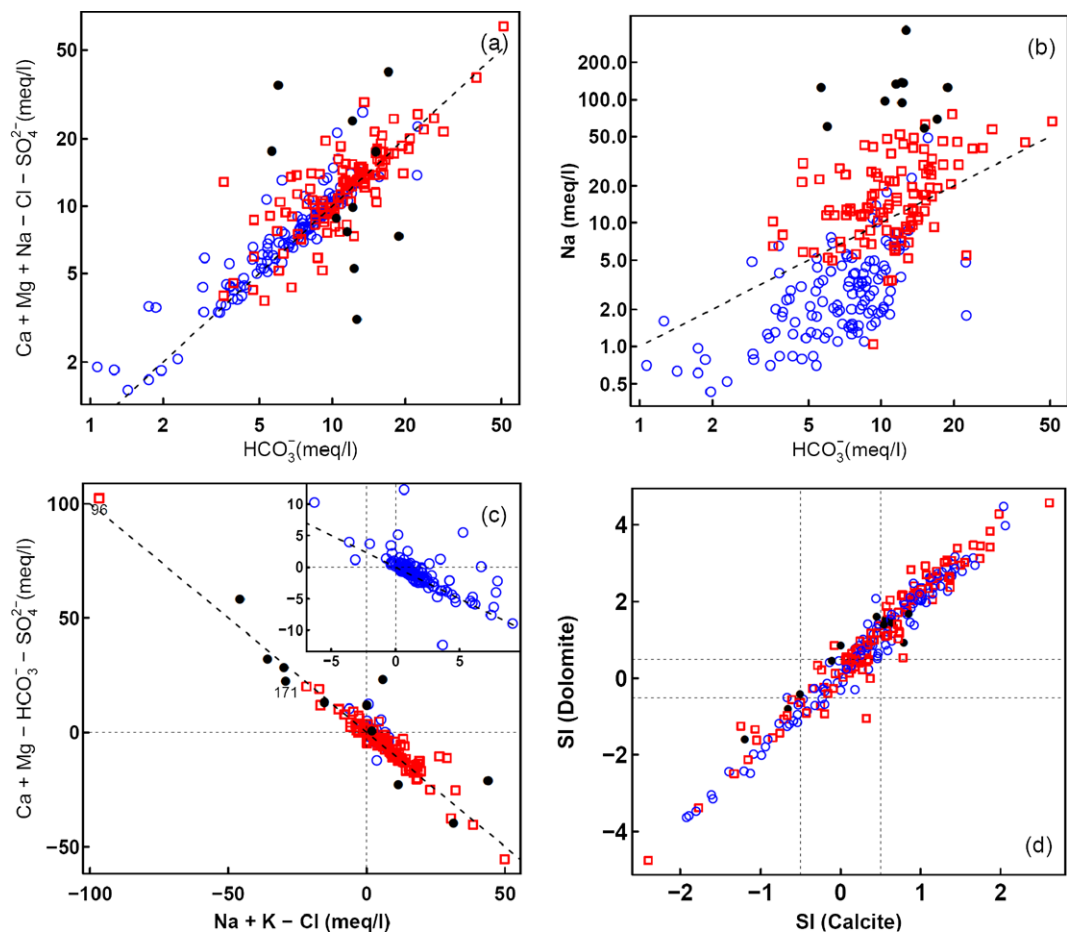


Fig. 9 Bivariate plots showing relationship between (a) $\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} - \text{Cl}^- - \text{SO}_4^{2-}$ (meq/l) and HCO_3^- , (b) Na^+ and HCO_3^- , (c) $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- - \text{SO}_4^{2-}$ (meq/l) and (meq/l) $\text{Na} + \text{K} - \text{Cl}$

to show the effect of cation exchange, and (d) the saturation indices for dolomite and calcite. The diagonal lines are lines of 1:1 slope. Samples are grouped according to their groups (see Fig. 2b for explanation)

and Kamineni 1994; Hanor and McManus 1988; Lee 1985). Clays are present in the area down-gradient of the basalts and in the areas close to the marshes (Lowole 1985; Lockwood Survey Cooperation 1970; Habgood 1963), which may provide exchange sites. Carbonate precipitation is suggested by the fact that most Group II samples are saturated with both calcite and dolomite (Fig. 9d). On the other hand, the increase in chloride, sulphate and further increase in sodium ion concentrations in Group II samples is attributable to mixing with high TDS groundwater from the areas of high salinity (Group III samples), which are in proximity of Group II samples. The samples in Group II constitute an overlap of the background (Group I) and anomalous (Group III) populations in the CPD (Fig. 5a). The high salinity and alkali hazard (Fig. 6b) is attributable to mixing between fresh groundwater and saline groundwater in Group III. On the other hand, the high RSC values are attributable to depletion of Ca^{2+} and Mg^{2+} through cation exchange leading to higher levels of HCO_3^- than the sum of Ca^{2+} and Mg^{2+} . The presence of soda-rich waters with

relatively high salinity renders the groundwater resources a “poor” quality classification (Fig. 7).

Samples in Group III have anomalously high levels of major ions (salinity) and overall show similar composition (Na–Cl type), with the exception of sample 209 (Na– SO_4 type) (Fig. 11). The samples are characterised by high $p\text{CO}_2$ values ($\log P_{\text{CO}_2}$ (atm) range of -1.81 to -0.91) and high sulphate (in addition to high chloride) content (Fig. 5b). The majority of the samples in Group III exhibit molar Na^+/Cl^- ratios close to unity as expected for the dissolution of halite (Fig. 10a), suggesting an original saline groundwater resulting from dissolution of halite, with rock-water interactions modifying the Na^+ content. The influence of evaporation, as a general driver to salinity, is largely precluded by depth of sampled boreholes and distribution of salinity. With the exception of sample 228 (depth = 1 m), all groundwater samples are taken at depths >20 m, which is greater than the depths at which direct evaporation from the water table would be effective. In addition, there is no systematic 1:1 linear relationship between Cl^- ions and SO_4^{2-} as would

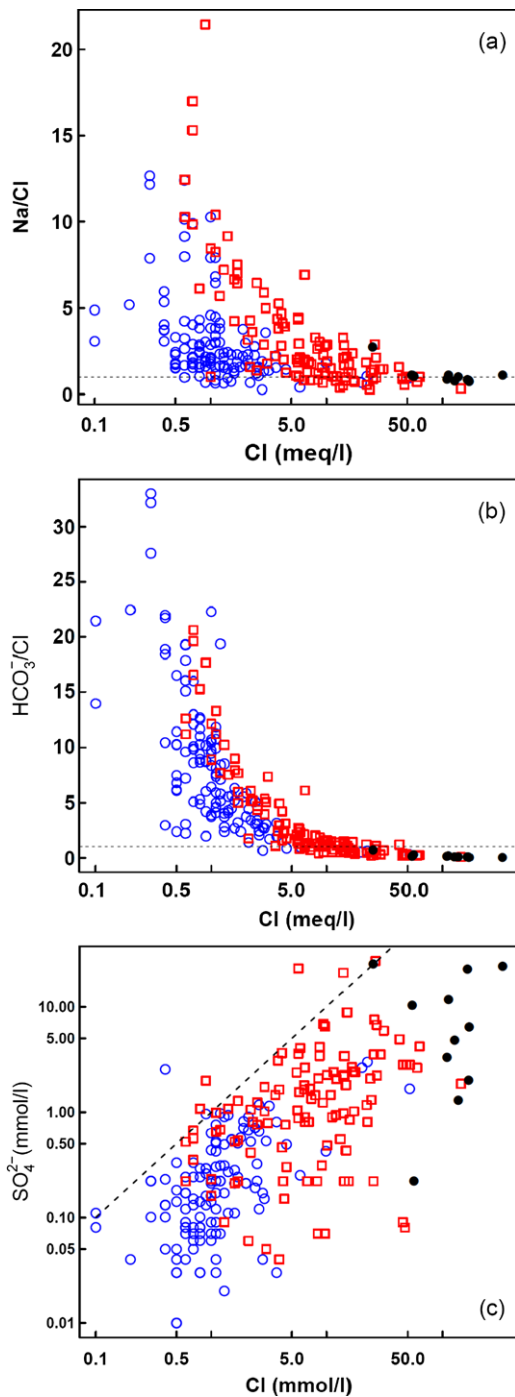


Fig. 10 Variation of (a) molar Na/Cl, (b) molar HCO_3^-/Cl and sulphate with chloride for groundwater from the study area. Water samples are classified according to their groups (see Fig. 2b for explanation)

be expected for evaporation (Fig. 10c). Up-concentration by evaporation would result in ionic ratios unaltered from original groundwater composition, except for precipitation of less soluble salts such as carbonates and gypsum, preventing equivalence between Ca^{2+} , Mg^{2+} , HCO_3^- and SO_4^{2-} with Cl^- from being attained (Eugster and Jones 1979). Gypsum

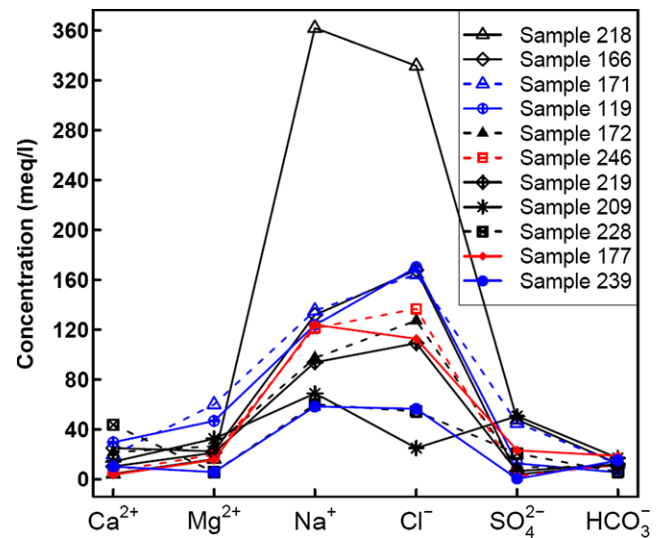


Fig. 11 Chemical composition of groundwater samples with high salinity in the study area (Group 3)

is below saturation in all the samples thus gypsum precipitation is unlikely. Evaporative salt (mainly halite) dissolution is therefore conceived to be a plausible process for the observed elevated major ion content. Dissolution of evaporites containing Cl^- and Na^+ should add these constituents to the water in equivalent amounts (Drever and Smith 1978). In addition, dissolution of other evaporite minerals would cause rise in specific ionic species depending on the composition of the minerals present (e.g. Ca^{2+} , SO_4^{2-} from gypsiferous evaporites), which may not be necessarily in proportion to Cl^- .

The groundwater changes composition within short distances of the areas of highest salinity through processes such as cationic exchange and mixing with fresh groundwater, forming other water types. Both cation exchange of bound sodium for dissolved calcium and magnesium and vice versa is shown in Fig. 9c to affect the composition of Group II and III samples, depending on whether flushing or saline water intrusion occurs. A prime example is given by samples 96 (Mg–Cl type) and 171 (Na–Cl type) which are in proximity of one another (Fig. 3b), with sample 171 having a higher ionic and chloride content (Figs. 3a and 3b) of the two. The effect of cation exchange is illustrated in Fig. 9c, where sample 96 plots within the second quadrant (negative ordinate and positive abscissa), implying enrichment of Ca^{2+} (and Mg^{2+}) relative to Na^+ (and K^+). In this case, the change in groundwater composition from Na–Cl type (sample 171) to Mg–Cl (sample 96) type is similar to the changes during intrusion of a freshwater aquifer by seawater (Appelo and Postma 2005).

The samples in Group III constitute an anomalous (Group III) population in the CPD (Fig. 5a) and they act as point sources of contamination of high salinity on a background population of fresh groundwater. The limited spatial

extent of the saline zones explains the high variation in salinity and major ions. Because of the high salinity and major ion content of these samples, their computed WQI values are classified in the “very poor” to “unsuitable” quality (Fig. 7) and they are also in the very high alkali and salinity hazards (Fig. 6b).

Conclusions

This study reported on the quality of groundwater resources in Chikhwawa district, lower section of Shire River valley, Malawi. Groundwater samples were arranged into three groups based on a cumulative probability diagram for TDS. The first and third group comprised mainly of fresh groundwater, affected by rock–water interactions and saline groundwater, respectively. The second (middle group) comprised groundwater samples with intermediate salinity showing varying extents of contamination with groundwater from the saline zones. The groundwater resources with relatively highly mineralized groundwater occur in several localized places and they show a halite dissolution signature, modified by rock–water interaction. The concentrations of major solutes vary widely, suggesting that the hydrochemistry is controlled by normal water–rock interaction and mixing with the saline groundwater. The presence of highly mineralized groundwater renders groundwater resources in large areas unsuitable for domestic and irrigation purposes. Potential risks of irrigation use of this groundwater include reduced yields for crops with lower tolerance levels as the extremely high RSC, SAR, EC are detrimental to crop growth. However, good quality groundwater is to be found in the Karoo basalts, Precambrian basement complex and their derived sediment found in their vicinity and away from the saline groundwater zones.

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