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RESEARCH ARTICLE

Spatial interpolation methods and geostatistics for mapping groundwater contamination in a coastal area

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Abstract Mapping groundwater contaminants and identifying the sources are the initial steps in pollution control and mitigation. Due to the availability of different mapping methods and the large number of emerging pollutants, these methods need to be used together in decision making. The present study aims to map the contaminated areas in Richards Bay, South Africa and compare the results of ordinary kriging (OK) and inverse distance weighted (IDW) interpolation techniques. Statistical methods were also used for identifying contamination sources. Na–Cl groundwater type was dominant followed by Ca–Mg–Cl. Data analysis indicate that silicate weathering, ion exchange and fresh water–seawater mixing are the major geochemical processes controlling the presence of major ions in groundwater. Factor analysis also helped to confirm the results. Overlay analysis by OK and IDW gave different results. Areas where groundwater was unsuitable as a drinking source were 419 and 116 km^2 for OK and IDW, respectively. Such diverse results make decision making difficult, if only one method was to be used. Three highly contaminated zones within the study area were more accurately identified by OK. If large areas are identified as being contaminated such as by IDW in this study, the mitigation measures will be expensive. If these areas were underestimated, then even though management measures are taken, it will not be effective for a longer time. Use of multiple techniques like this study will help to avoid taking harsh decisions. Overall, the groundwater quality in this area was poor, and it is essential to identify alternate drinking water source or treat the groundwater before ingestion.

Introduction

Safer and accessible water is essential for human beings to survive. Water intended for any use must comply within the standards proposed for the purpose. Varieties of challenges, both natural and anthropogenic, have appeared as threats to maintain the water quality. Generally, groundwater is considered less contaminated compared to surface water due to its limited contact with the external environment and groundwater undergo natural filtration during percolation through the soil zone. Largest consumer of freshwater is agriculture accounting to 70% followed by industries (20%) and domestic use (10%) (Chiras 2001). Of these sectors, industries take large care in meeting the water standards failing which can cost the investments in machineries. The case may not be the same for wastewater resulting from various processes that is disposed-off by these industries into drains or oceans, except in countries that enforce stringent laws for not complying with the wastewater disposal quality (Brindha and Elango 2012a). Farmers use groundwater for irrigation as it is available throughout the year. But, use of water with enriched salts can also reduce soil fertility and hinder crop yield. In developing countries where treated and tested water is not available through piped networks, surface and groundwater aid as a domestic water source (Brindha et al. 2014, 2016). Indicators that

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determine the water suitability have been classified based on the physical, chemical and biological properties. Depending on the occurrence of water either in the surface or sub-surface, the main indicators vary.

Methods for determining water quality have evolved from simple comparison of water chemistry with the standards to the use of sophisticated models that are data intensive. Water quality index (WQI) developed by Horton (1965) is one of the established and common method used by applying weights to the various ions in water and determining the suitability index. This weighting and analysis method have improved by the inclusion of artificial neural networks, fuzzy theory, etc. Li et al. (2010, 2011, 2016) proposed an entropy-based weight assignment in WQI considering uncertainties associated with the classification which is superior to the traditional WQI. A new coupled groundwater quality assessment model based on rough set attribute reduction and technique for order preference by similarity to ideal solution (TOPSIS) was proposed by Li et al. (2012). Fuzzy approach has been widely used in WQI in recent times (Gorai et al. 2014; Li et al. 2014). Surface interpolation techniques help to predict the concentrations at locations where samples could not be collected. Statistical models have also played their role in narrowing down the pollution sources in many studies (Machiwal and Jha 2015; Venkatramanan et al. 2016). All these methods work in their own way, and the results from each of these methods may not always be similar. Many researches have used these methods in combination to arrive at meaningful interpretations. Inverse distance weighted (IDW) method was more accurate than the kriging (Gaussian, spherical and cokriging) approach in predicting some pollutant levels in groundwater (Gong et al. 2014). Study by Mirzaei and Sakizadeh (2016) compared ordinary kriging (OK), empirical Bayesian kriging and IDW using the WQI approach. OK and IDW predicted similar results of groundwater levels except in shallow water level areas around reservoirs (Buchanan and Triantafilis 2009). Superiority of IDW above kriging was also reported in a landfill site by Spokas et al. (2003). Venkatramanan et al. (2016) have used statistical methods with kriging interpolation to understand the hydrochemical characteristics. Gundogdu and Guney (2007) applied different semivariogram models to analyse depth to water level in an irrigation area.

Mapping areas vulnerable to pollution and its possible health implications is largely adopted by spatial interpolation using the following steps: identification of key parameters of study, applying relative weights for these parameters, assigning sub-weights for variables within the parameter and calculation of an aggregate index. DRASTIC (D is depth to groundwater, R is net recharge due to rainfall, A is aquifer media, S is soil media, T is topography, I is impact of vadose zone, C is hydraulic conductivity of the aquifer) is one of the largely adopted vulnerability mapping model (Aller et al. 1985). Qian et al. (2012) proposed a revised DRASTIC model which can be used in plains where the geomorphological variations are not large.

These spatial interpolation methods give varied results while applied to geographically distinct regions (Stigter et al. 2006; Anane et al. 2013; Brindha and Elango 2015).

Application of multivariate statistical analyses is vast including evaluating hydrochemical characteristics of groundwater (Wu et al. 2014; Chung et al. 2015; Venkatramanan et al. 2015, 2016), identifying the groundwater contamination from landfills (Mouser et al. 2005; Srivastava and Ramanathan 2008), understanding groundwater dynamics of an area (Chen and Feng 2013; Machiwal and Singh 2015), identifying the occurrence of seawater intrusion (Kim et al. 2005; Arslan 2013), differentiating natural/geogenic process from anthropogenic sources (Machiwal and Jha 2015), etc. These models perform differently when applied to datasets from different regions. Hence, the performance of one model over other cannot be considered as universally applicable.

In recent times, use of one method for decision making is not sufficient due to the variety of emerging contamination sources as well as variability in the results from different methods. There is a need to rely on multiple methods and compare the results to arrive at more meaningful decisions. This study compares OK and IDW interpolation methods in mapping potential areas of risk to groundwater contamination. Multivariate statistics are also used to identify the source of chemical contents in water and to compare the results with interpolation methods. Groundwater chemical characteristics of Richards Bay, South Africa (Fig. 1) was used in this study as the published information were scarce for this area, and this research will serve as an insight into the status of water quality in this region. This area is bounded by the coast and has the largest coal export facility in South Africa. Thus, it is vulnerable to contamination from multiple sources. The aim of this study is not to check how well these methods can predict the concentrations of ions in groundwater, but, to compare the reliability of interpolation methods in using them as a tool by decision makers.

Methodology

Description of study area

Coastal city of Richards bay and the nearby town of Empangeni in the Mhlathuze catchment (582 km^2) are located about 180 km north east of Durban, capital of KwaZulu-Natal province in South Africa (Fig. 1). Humid summers and mild winters are experienced with temperature range of 21–29 °C during January–March and 12–23 °C during June–August. The KwaZulu-Natal region is one of the highest rainfall regions in South Africa (Schulze 1982). Annual rainfall in the study area ranges from 850 mm in the west to over 1200 mm along the coast (DWAF 2000). Most of the rainfall occurs from October to March. This area is characterized by flat to
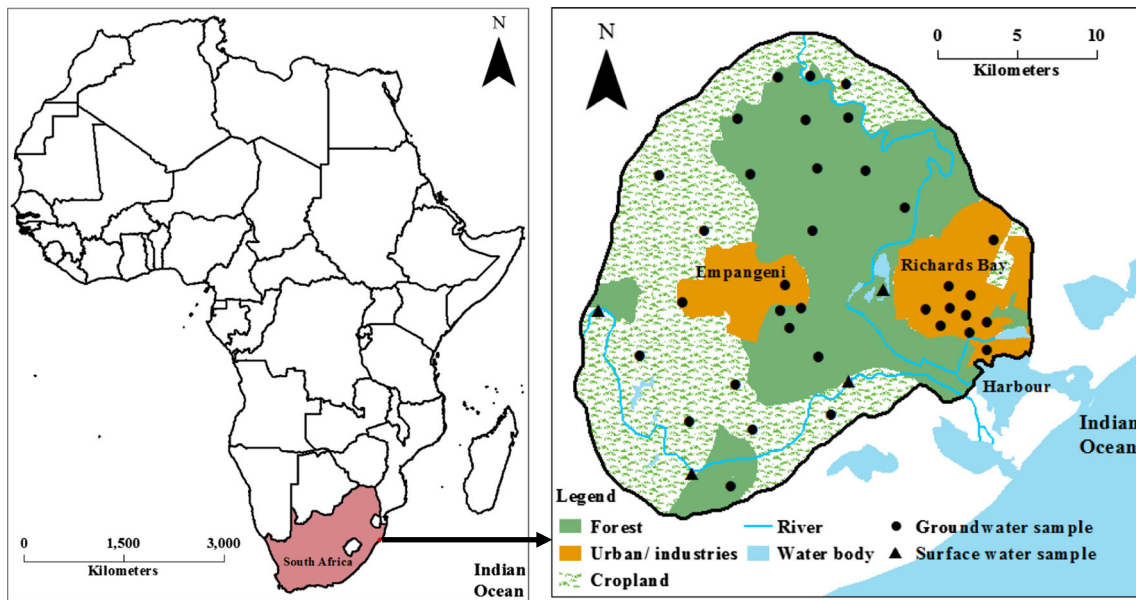
Fig. 1 Study area with land use and monitoring locations

undulating landform with low hills and flat bottomed drainage features. Mhlathuze River, the largest in the region, originates from the Babanago Mountains and flows through Empangeni and Richards Bay and drains into the Indian Ocean. Monthly evaporation from surface water bodies during summer ranges from about 150 to 250 mm and winter evaporation is generally 100 mm/month (Kelbe et al. 2001). The number of industries that function in the Richards Bay area includes aluminium smelters, fertilizer plants and mining of mineral ores. It has the largest coal export facility in South Africa. Agriculture in the region is inland and includes sugarcane, citrus, vegetables, maize, etc. apart from commercial products such as pine and eucalyptus. There is also a landfill site located in the centre of the study area.

Granite of Precambrian age forms the basement in this region (Germishuyse 1999). It is overlaid by sedimentary formations of Triassic. This is followed by the basaltic rocks of Jurassic. Sedimentary formation from Cretaceous to Holocene overlays the basalts. In some places, the Cretaceous sediments directly overlay the granitic basement rocks. Cretaceous sediments are of marine origin with sandstone, mudstone and shale. Marine fossils are also found. Palaeocene period has similar lithological units as Cretaceous. Most of the study area is covered by Pleistocene to Holocene sands. These sands are fine grained, with clay and silt formed by fluvial and aeolian processes. The formation at the ground surface is reasonably permeable and facilitates infiltration of rainwater. Groundwater occurs in these unconsolidated formations in unconfined condition in the upper part and confined condition in the lower part with a think clay layer in between. In this study, only the upper aquifer is considered. Rainfall is the major source of groundwater recharge in this area.

Sampling and analysis

Surface and groundwater samples were collected from Richards Bay and Empangeni areas in September 2015. Care was taken such that the groundwater sampling locations ($N = 35$) were distributed over the area (Fig. 1). Surface water samples include three samples from the river and one sample from a dam that stores water for irrigation use. Electrical conductivity (EC) and pH were measured in the field using portable meters that was pre-calibrated using 84 and 1413 μS/cm conductivity solutions for EC and 4.01, 7 and 10.1 for pH. Calcium, magnesium, sodium, potassium, chloride, sulphate and nitrate were analysed using inductively coupled plasma optical emission spectrometry (ICP-OES). Carbonate and bicarbonate were measured in the field by titration (APHA 1998). Standards and blanks were run frequently for ensuring the accurate determination of the ionic concentration. Analytical precision was determined by calculating the ion balance error that was within ±8%.

Total dissolved solids (TDS) and total hardness (TH) of water was calculated using the formulae proposed by Lloyd and Heathcote (1985) and Sawyer and McCarty (1978), respectively.

$$TDS \ (mg/l) = EC \ (\mu S/cm) \times 0.64 \tag{1}$$

$$TH \ (mg/l) = 2.497 \ Ca^{2+} \ (mg/l) + 4.115 \ Mg^{2+} \ (mg/l) \tag{2}$$

Irrigation water quality was determined from various indices—magnesium hazard (MH) (Szabolcs and Darab 1964), residual sodium carbonate (RSC) (Eaton 1950), sodium

percent (Na%) (Wilcox 1955), sodium adsorption ratio (SAR) (Richards 1954), Kelly's ratio (Kelly 1957) and permeability index (PI) (Doneen 1964).

$$MH = Mg^{2+}/(Ca^{2+} + Mg^{2+}) \times 100 \qquad (3)$$

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \qquad (4)$$

$$Na\% = \frac{(Na^+ + K^+) X 100}{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)} \qquad (5)$$

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (6)$$

$$PI = \frac{\left(Na^+ + \sqrt{HCO_3^-}\right)}{(Ca^{2+} + Mg^{2+} + Na^+)} \times 100 \qquad (7)$$

$$Kelly's\ ratio = \frac{Na^+}{Ca^{2+} + Mg^{2+}} \qquad (8)$$

All concentrations from Eqs. 3–8 are expressed in milliequivalents per litre.

Seawater mixing index

Seawater mixing index (SMI) was developed by Park et al. (2005) to identify seawater intrusion based on magnesium, sodium, chloride and sulphate concentration. This was modified by Mondal and Singh (2011) to understand the salinisation process due to tannery effluents and was called saline water mixing index (SWMI). Thus, this index can be used for studying the seawater intrusion as well as salinisation due to pollution using the following equation (Park et al. 2005).

$$SMI = \left(a \times \frac{C_{Na}}{T_{Na}}\right) + \left(b \times \frac{C_{Mg}}{T_{Mg}}\right) + \left(c \times \frac{C_{Cl}}{T_{Cl}}\right)$$
$$+ \left(d \times \frac{C_{SO_4}}{T_{SO4}}\right) \qquad (9)$$

where a, b, c and d are constants that denote the relative concentration proportion of sodium, magnesium, chloride

and sulphate, respectively, in seawater (i.e. $a = 0.31$, $b = 0.04$, $c = 0.57$ and $d = 0.08$), C is the measured concentration of ions in milligrammes per litre and T is the regional threshold values of the ions estimated from the interpretation of the cumulative probability curves plotted against log concentration of the ions. When applied to areas other than to identify seawater mixing, the values of constants will vary.

Factor analysis

Statistical analysis was performed using IBM SPSS (2013) version 22.0. Correlation matrix was used to identify the positive or negative relationship among ions. Principle component analysis (PCA) was carried out first in which the original variables are transformed into new uncorrelated variables. These variables are called principle components (PC) and are linear combinations of original variables. With minimum loss of original information, PC informs on the most meaningful variable for the whole dataset (Helena et al. 2000). Output from PCA is further simplified in factor analysis through reducing the contribution of less significant variables. This is done by rotating the axis defined by PCA (Shrestha and Kazama 2007). Varimax is the most commonly used rotation in factor analysis and is adopted in this study. The rotation results in smaller number of factors for the same variables as with the larger set of original variables. PCA and factor analysis are expressed as in Eqs. 10 and 11, respectively.

$$z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \ldots + a_{im}x_{mj} \qquad (10)$$

where z is the component score, i and j are the component and sample number, respectively, a is the component loading, x is the measured variable and m is the total number of variables.

$$z_i = a_{f1}f_{1i} + a_{f2}x_{2i} + a_{f3}x_{3i} + \ldots + a_{fm}x_{mi} + e_{fi} \qquad (11)$$

where z is the measured variable, i is the sample number, a is the factor loading, f is the factor score, e the residual term accounting for errors or other source of variation and m is the total number of factors.

Spatial interpolation methods

ArcMap version 10.1 was used to predict values in unsampled locations. The basis of interpolation methods is that it assumes that values that are closer to one another are more alike than those that are farther away. Measured values surrounding an unmeasured location are used for prediction. Most popularly used interpolation methods, i.e. OK and IDW are compared in this study for mapping groundwater contamination zones.

Ordinary kriging

This is a geostatistical method based on statistical models that calculates relationship among the measured points. This multistep model assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain variation in the surface. Computing steps include exploratory statistical analysis of the data, variogram modelling, creating the surface and/or exploring a variance surface (ESRI 2012). Kriging has many types—simple kriging, OK and universal kriging of which OK is the most widely used. Kriging is also based on the application of weights to measured values. Unlike IDW that depends only on the distance between the sample points, kriging depends on the distance and the spatial orientation of the measured points. Weights in kriging are derived from semivariogram models that are of various types—spherical, circular, exponential, Gaussian and linear. Spherical semivariogram model is the most commonly adopted and is used in this study. The semivariogram function is calculated as half the average squared difference between the paired data values given as

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2 \tag{12}$$

where $\gamma(h)$ is the semivariance value at h which is the distance interval, $N(h)$ is the number of sample pairs within h and $z(x_i)$ and $z(x_i + h)$ are the sample values at two points located at distance h (Journel and Huijbregts 1978).

Inverse distance weighted

Predictions by this deterministic method are based on a linear combination of closely located values. Shepard (1968) defines IDW as

$$z = \frac{\sum_{i=1}^{n} w_i z_i}{\sum_{i=1}^{n} w_i} \tag{13}$$

$$w_i = \frac{1}{d_i^{\,p}} \tag{14}$$

where z is the interpolated value, z_i is the known value, n is the total number of known values used in interpolation, d_i is the distance between known and interpolated values and p is the power parameter where weight decreases as distance increases from the interpolated values, hence, the name IDW. Interpolation results are highly influenced by this weighting power (Mueller et al. 2001). Most commonly used and default power in ArcGIS, i.e. inverse of the distance raised to the 2nd power (Gong et al. 2014) is used in this study.

Overlay analysis

To map groundwater contamination zones, overlay analysis was carried out for eight variables. First, these parameters were subjected to spatial interpolation using OK and IDW and then classified as desirable and undesirable areas for drinking purpose by comparing the concentrations with the World Health Organization (WHO) standards. The desirable areas are given a rank of '1' and undesirable areas are ranked '2'. Usually after ranking, relative weights are assigned to the different parameters such as in WQI (Mirzaei and Sakizadeh 2016) and DRASTIC (Brindha and Elango 2015) methods. Brindha and Elango (2012b) have applied equal weightage for all parameters in groundwater suitability mapping based on the argument that even if one parameter exceeds the limit, it is unsuitable for the intended use. This method (Brindha and Elango 2012b) was followed without applying weights to the spatially interpolated layers for overlay analysis. The various spatial layers are overlaid using the 'intersect' tool in ArcMap 10.1. A suitability index is arrived by calculating the sum of ranks. A total index of 8 indicates that all parameters are within limits, 9 indicates that one parameter exceeds the drinking water limits and so on. Highest suitability index of 16 indicates that all the samples have exceeded limits for all parameters.

Result and discussion

Groundwater level ranged from 1 to 46.5 m bgl with an average of 12.2 m bgl. Spatial variation of depth to groundwater level indicates deeper water levels in the industrial areas located near the coast and in agricultural areas inland. Groundwater flows towards the sea (Fig. 2).

Drinking and irrigation water quality

Statistical summary of various ions in groundwater and measured concentrations of surface water are given in Tables 1 and 2. Target water quality proposed by Department of Water Affairs and Forestry (DWAF), South Africa is the range that has no negative effect on human health. It denotes good or ideal water quality rather than being merely acceptable. This also means that concentrations of ions beyond this range can still be suitable for drinking under certain circumstances (DWAF 1996). Seventeen samples were within the target water quality range (<700 μS/cm) for EC, and 16 samples were permissible, i.e. drinking water ranging between 700 and 4500 μS/cm does not cause adverse health effects when consumed for a short time (DWAF 1996). River and dam water were also within the suitable to tolerable range for drinking and irrigation. TDS and TH were grouped based on the classification by Freeze and Cherry (1979) and Sawyer and

Fig. 2 Spatial variation in groundwater level
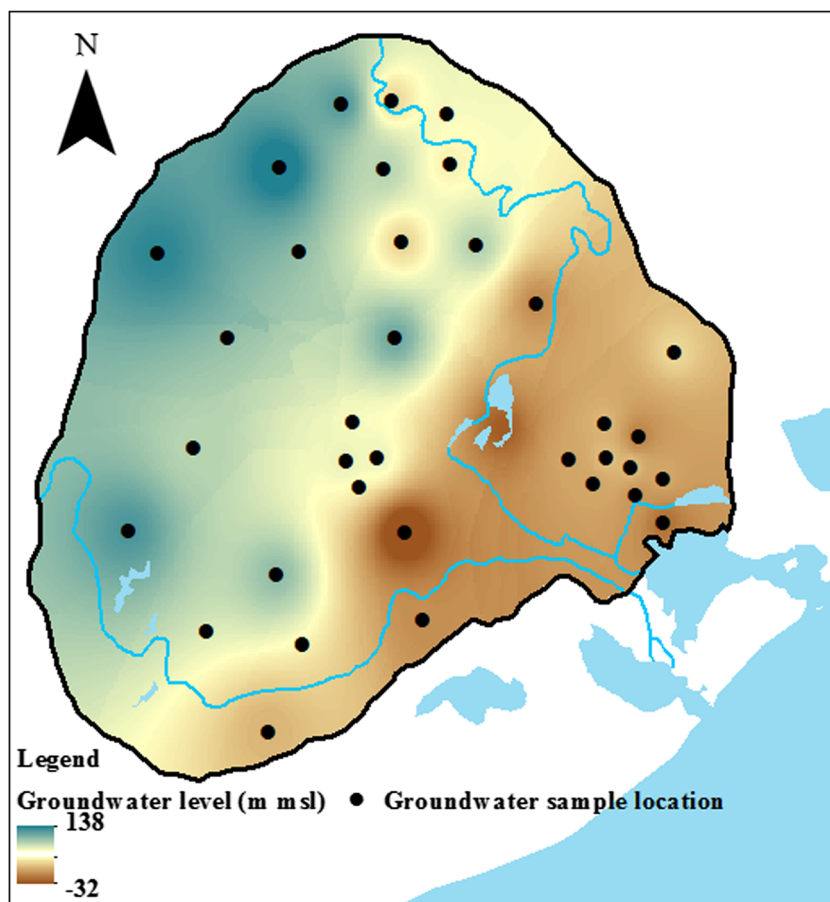
McCarty (1978). Most of the area had hard water ($N = 28$) except for few locations ($N = 7$) based on TH (Fig. 3). TDS indicates that large part of the samples was fresh ($N = 29$) except for few samples being brackish ($N = 5$) and saline ($N = 1$) (Fig. 3). Brackish and saline water is unsuitable for irrigation, and if used for agricultural purpose over a long-term, it may decrease the soil fertility due to increase in salinity.

Water quality requirements in South Africa are much more stringent than the values recommended by WHO. A comparison of these standards for various chemical ions is given in Table 3 along with the natural concentration of these ions in fresh water and seawater. Groundwater exceeded DWAF (1996) limits for pH, calcium, magnesium, sodium, potassium, chloride and sulphate in 3, 31, 17, 26, 14, 54 and 3% of sampling locations, respectively. Similarly, groundwater exceeds the highest desirable limit (WHO 1993) for pH, calcium, magnesium, chloride and sulphate in 20, 14, 9, 17 and 3% of the samples, respectively, and exceeds the maximum permissible limits of WHO (1993) in 14, 3, 3, 6 and 0% samples, respectively. Sodium and potassium do not have highest desirable limit, but, has maximum permissible limits which exceeded in 14 and 23% of the locations. Limits for bicarbonate are not given by DWAF

and WHO. It is suggested that bicarbonate levels less than 200 mg/l is safe for human health through the drinking water pathway (Bhardwaj and Singh 2011). Surface water was within this limit, but, it exceeds in 10 groundwater sampling locations. Surface water is safe based on WHO standards for all ions except for pH (Table 2). DWAF standards also indicate that surface water is suitable for drinking. Mhlathuze River water exceeded the pH range at one location. Dam water exceeded limits for sodium and chloride concentrations.

Water quality evaluation for irrigation is based on many indices (Table 4). MH and Kelly's ratio had unsafe water for irrigation at more than 50% of the area. This shows that hardness is an issue for irrigation. Sodium and EC play an essential role in determining the irrigation suitability. In most locations, water was suitable or permissible for irrigation for sodium-based indices, i.e. RSC, PI, Na% and SAR. Sodium plotted against EC (Fig. 4a) indicates most area has high salinity and low sodium hazard. Two groundwater samples were undesirable for irrigation (C1S1 and C2S1) with high salinity and high sodium. River water had comparatively low salinity as well as low sodium hazard and fit for agricultural use. Dam water had high salinity and low sodium hazard (C3S1) like the nearby groundwater.
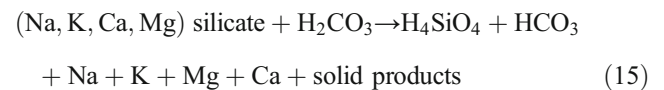
Table 1 Statistical summary of various parameters in groundwater ($N = 35$)

Parameters	Minimum	Maximum	Mean	Median	Standard deviation
pH	4.8	8.9	7.5	7.6	0.9
EC (μS/cm)	140.0	26,260.0	1960.7	745.0	4543.7
Calcium (mg/l)	4.0	217.0	37.2	16.0	47.8
Magnesium (mg/l)	3.0	184.0	26.9	16.0	32.8
Sodium (mg/l)	18.0	5121.0	255.2	60.0	868.1
Potassium (mg/l)	4.0	634.0	51.1	6.0	148.1
Bicarbonate (mg/l)	12.0	1903.0	190.7	105.0	321.1
Chloride (mg/l)	50.0	7657.0	403.8	123.0	1288.7
Sulphate (mg/l)	4.0	374.0	25.5	10.0	62.2
TDS (mg/l)	89.6	16,806.4	1254.9	476.8	2908.0
TH (mg/l)	42.1	1296.9	203.3	118.6	242.8

Geochemical processes

Sodium chloride was the dominant water type followed by Ca–Mg–Cl (Fig. 4b). Order of dominance of cations was Na > K > Ca > Mg, and that of anions was Cl > HCO_3 > SO_4 for groundwater and for surface water were Na > Mg > Ca > K and HCO_3 > Cl > SO_4. General processes controlling salinisation of aquifers are identified as oxidation–reduction, ion exchange, precipitation and dissolution and mineral weathering (Appelo and Postma 1993; Richter and Kreitler 1993; Jones et al. 1999). To narrow down to the processes controlling the groundwater characteristics, Gibbs plot was used. This plot indicated rock–water interaction as the dominant process with few cases of evaporation and precipitation. Rock–water interaction includes many processes and needs further refinement to identify the process that plays a major role in this area. Change in Na–Cl dominant water to Ca–Mg–Cl is suggestive of cation exchange reaction (Kumar et al. 2014). Plot of (Ca + Mg) − (HCO_3 + SO_4) versus Na–Cl determines the gain or loss of Ca and Mg due to carbonates

and gypsum dissolution and gain or loss of Na due to halite dissolution (Bouzourra et al. 2015). A linear relationship with a slope of −1 indicates cation exchange and samples that plot close to 0 are not influenced by ion exchange (Jankowski et al. 1998). Figure 5 indicates that reverse ion exchange with a slope of −0.7 occurs at many cases. Sodium normalized with calcium, magnesium and bicarbonate indicate silicate weathering as the dominant process (Fig. 6). Silicate minerals such as quartz, amphibole and pyroxene are present in the aquifer materials of this area. This is likely to be the source for calcium, magnesium, sodium and potassium as reported by Rajesh et al. (2012) and Brindha et al. (2016) in similar situations. Carbonic acid causing weathering of silicate minerals is denoted as

$$\text{(Na, K, Ca, Mg) silicate} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3$$
$$+ Na + K + Mg + Ca + \text{solid products} \qquad (15)$$

Points below the 1:1 line in the plot between sodium and chloride also indicate silicate weathering (Stallard and Edmond 1983) (Fig. 7). A linear increment of sodium and chloride suggests seawater intrusion (Vetrimurugan et al. 2013), i.e. the samples that plot near the fresh-saline water mixing line. Halite dissolution in samples also plots on the 1:1 line. This denotes interactive process between groundwater and the aquifer clay matrix (Bouzourra et al. 2015). However, there is no likely geological source for halite in this aquifer. Hence, mixing with seawater from the rivers as well as directly from the sea is the likely cause for this relationship (Fig. 7).

Threshold values for SMI were calculated by plotting the cumulative probability percentages of the parameters against the measured concentration of corresponding parameters. The inflexion point for sodium and chloride were at 300 and 550 mg/l (Fig. 8). Two inflexion points were noticed for magnesium and sulphate (Fig. 8). The threshold values represent the natural background levels of ions in groundwater, and the

Table 2 Chemical constituents in surface water

Parameters	Dam	River 1	River 2	River 3
pH	8.05	9.5	8.7	7.23
EC (μS/cm)	1040	225	274	280
Calcium (mg/l)	17	9	6	11
Magnesium (mg/l)	23	9	4	8
Sodium (mg/l)	103	15	25	23
Potassium (mg/l)	6	5	4	5
Bicarbonate (mg/l)	176.9	52	48	52
Chloride (mg/l)	165.6	40	42	57.9
Sulphate (mg/l)	16	2	4	4
TDS (mg/l)	665.6	144	175.36	179.2
TH (mg/l)	136.8	59.4	31.4	60.3

Fig. 3 Groundwater classification based on TH and TDS
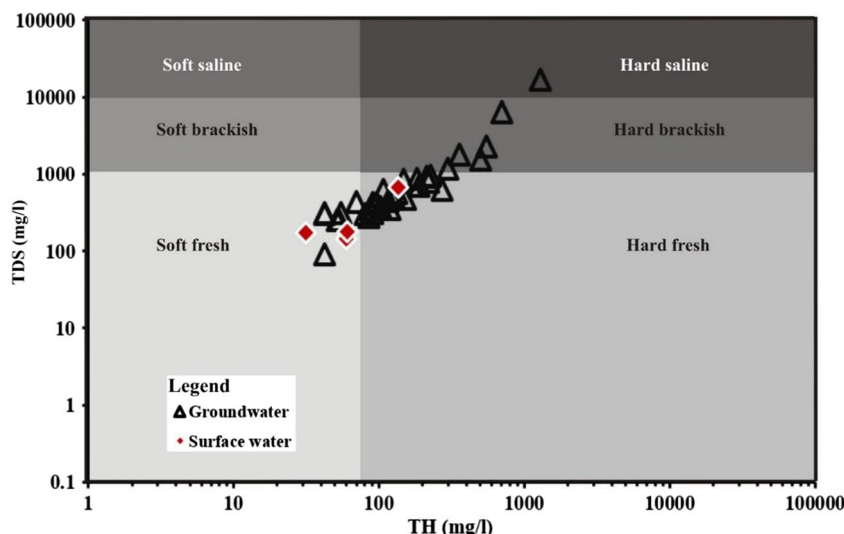
upper and lower limits for magnesium and sulphate were both within the drinking water standards limits (WHO 1993). If the lowest threshold values are considered, all samples will have SMI greater than 1 and will be classified as a record of seawater mixing (Park et al. 2005). In this area, seawater intrusion along with other sources is the cause for contamination. Hence, to differentiate these contamination zones, the upper limits for magnesium and sulphate, i.e. 40 and 65 mg/l, respectively, were chosen. Sodium and chloride, the significant ions representing seawater intrusion, have only one threshold limit that is higher than the maximum permissible limits for drinking. So, using the highest threshold values for magnesium and sulphate is considered suitable. SMI was higher at two locations (Fig. 9), i.e. the landfill and industrial sites. This indicates that seawater intrusion is not a major threat, but it could have contributed to the chemical composition of groundwater to some extent especially for sodium and chloride. Saline intrusion in the Lake Mzingazi (located north of the current study area) was reported by Simmonds (1990).

Statistical analysis

Inter-ion relationship (Table 5) was strong among calcium, magnesium, sodium, potassium, chloride and sulphate. Bicarbonate correlates strongly with potassium and moderately with magnesium (Table 5). To further ascertain and group the sources identified for the presence of ions in groundwater, multivariate statistical analysis was performed for the hydrochemical data. Eigen values above 1 were exhibited by two factors with a cumulative variance of 87% (Table 6). First factor with the highest variance of 77.6% shows positive relation among calcium, magnesium, sodium, chloride and sulphate. Comparing the measured concentrations of ions in this study (Table 1) with the natural concentrations in fresh and seawater (Table 3) indicates that calcium, magnesium and sulphate were in the fresh water range. Measured concentration of sodium and chloride was in the fresh water and seawater range. Rock–water interaction processes

Table 3 Permissible limits of chemical ions in drinking water and composition of ions in fresh and seawater

Parameter	Target water quality[a]	Health effect reported[a]	Highest desirable limit[b]	Maximum desirable limit[b]	Fresh water[a]	Sea water[a]	Sea water[c]
pH	6 to 9	<6 and >9	6.5 to 8.5	6.5 to 9.2	6.5 to 8.5	–	7.5 to 8.4
Calcium	<32	>80	75	200	15	400	411
Magnesium	<30	>70	50	150	4 to 10	1300	1290
Sodium	<100	>400	–	200	Low	11,000	10,800
Potassium	<50	>100	–	12	2 to 5	400	392
Chloride	<100	>600	200	600	Few to several hundreds	19,800	19,400
Sulphate	<200	>200	200	400	5 to several hundreds	Over 900	2701

[a] DWAF (1996)

[b] WHO (1993)

[c] Turekian (1968) except for pH from Chester and Jickells (2012)

Table 4   Irrigation water quality

Parameter	Range	Irrigation suitability	Number of samples		Reference
			Groundwater (N = 35)	Surface water (N = 4)	
MH (meq/l)	<50	Suitable	8	–	Szabolcs and Darab (1964)
	>50	Unsuitable	27	4	
Kelly's ratio	<1	Safe	14	2	Kelly (1957)
	>1	Unsafe	21	2	
PI	Class I	Good	14	1	Doneen (1964)
	Class II	Permissible	15	2	
	Class III	Unsuitable	6	1	
RSC (meq/l)	<1.25	Safe	34	4	Eaton (1950)
	1.25–2.5	Moderate	–	–	
	>2.5	Unsuitable	1	–	
Na%	<20	Excellent	1	–	Wilcox (1955)
	20–40	Good	1	1	
	40–60	Permissible	20	1	
	60–80	Doubtful	11	2	
	>80	Unsuitable	2	–	
SAR	<10	Excellent	33	4	Richards (1954)
	10–18	Good	–	–	
	18–26	Doubtful	1	–	
	>26	Unsuitable	1	–	
Salinity hazard (EC in μS/cm)	<250	C1—Excellent or low	1	1	Freeze and Cherry (1979)
	250–750	C2—Good or medium	17	2	
	750–2250	C3—Permissible or high	12	1	
	>2250	C4—Unsuitable or very high	5	–	

including silicate weathering, reverse ion exchange and mixing of seawater are the major sources of these ions in groundwater. Second factor shows stronger relation for bicarbonate and potassium due to alkaline nature of
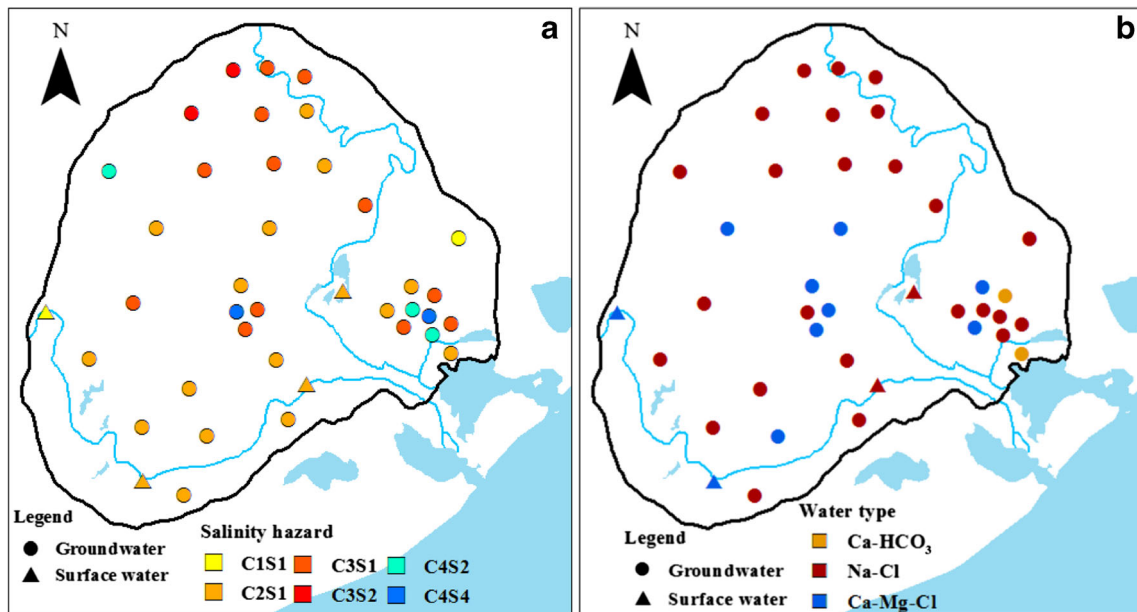

Fig. 4 **a** Sodium and salinity hazard. **b** Water type
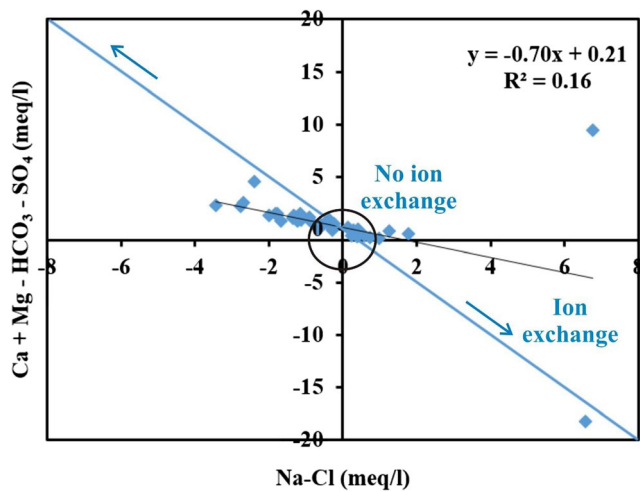
Fig. 5 Ion exchange process in groundwater

Fig. 7 Sodium versus chloride indicating various geochemical processes

groundwater. This is because factor analysis was carried out with groundwater samples collected from the entire region including the landfill and industrial locations. In regions other than the landfill and industries, the relationship is negative indicating the influence of seawater mixing with groundwater (Fig. 10a). Only in landfill and industrial areas, a strong relation between potassium and
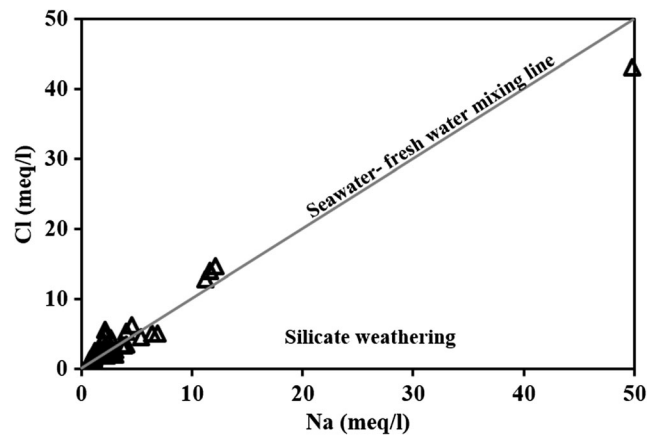
bicarbonate was observed (Fig. 10b) indicting a common source of contamination.

Groundwater contamination mapping

Due to the different permissible limits suggested by different organisations (DWAF and WHO), there are varied number of samples that exceed the limits for the same ion. In such case, it is a challenge to choose the standards to adopt for decision making. Nature of these studies only informs us on the quality of water at the sampled location and not for areas between these locations. Also, one location can be suitable based on most ions but unsuitable for few. Spatial tools assist in the interpolation of values in areas where samples are not collected, and overlay analysis can help to arrive at an integrated groundwater suitability or contamination map.

Accuracy of these methods in groundwater contamination mapping was compared using OK and IDW interpolations. Each parameter was interpolated with these methods and differentiated into desirable and undesirable areas based on WHO (1993) drinking water standards (Figs. 11 and 12). In this study, the internationally recognized WHO standards are used as the main aim is to test the capability of these methods in using them as a management tool that can be adopted to any part of the world. The standards used for differentiating desirable and undesirable zones as per WHO standards for pH, calcium, magnesium, sodium and potassium were 6.5 to 8.5, 75, 50, 200 and 12 mg/l, respectively. Limit adopted for bicarbonate, chloride and sulphate was 200 mg/l. EC represents the total ionic concentration, and it will be double accounted if included in the analysis. Carbonate was not present in groundwater. TDS and TH were calculated from other parameters. To avoid errors, these four parameters were not included in the overlay analysis.
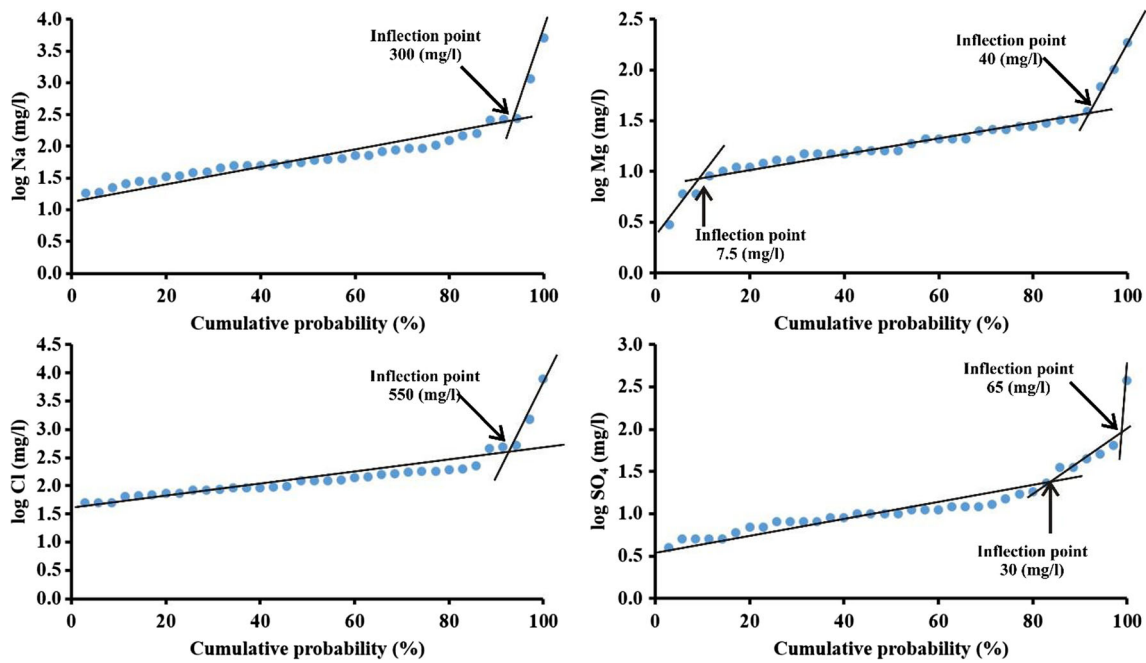

Fig. 6 Weathering of minerals in groundwater

Fig. 8 Cumulative probability distribution of ions for determining the regional threshold values

Comparing the interpolation among these methods indicates similar spatial variation in pH, calcium, magnesium and sulphate. Sodium, potassium and chloride highly differ in their suitable areas and bicarbonate shows

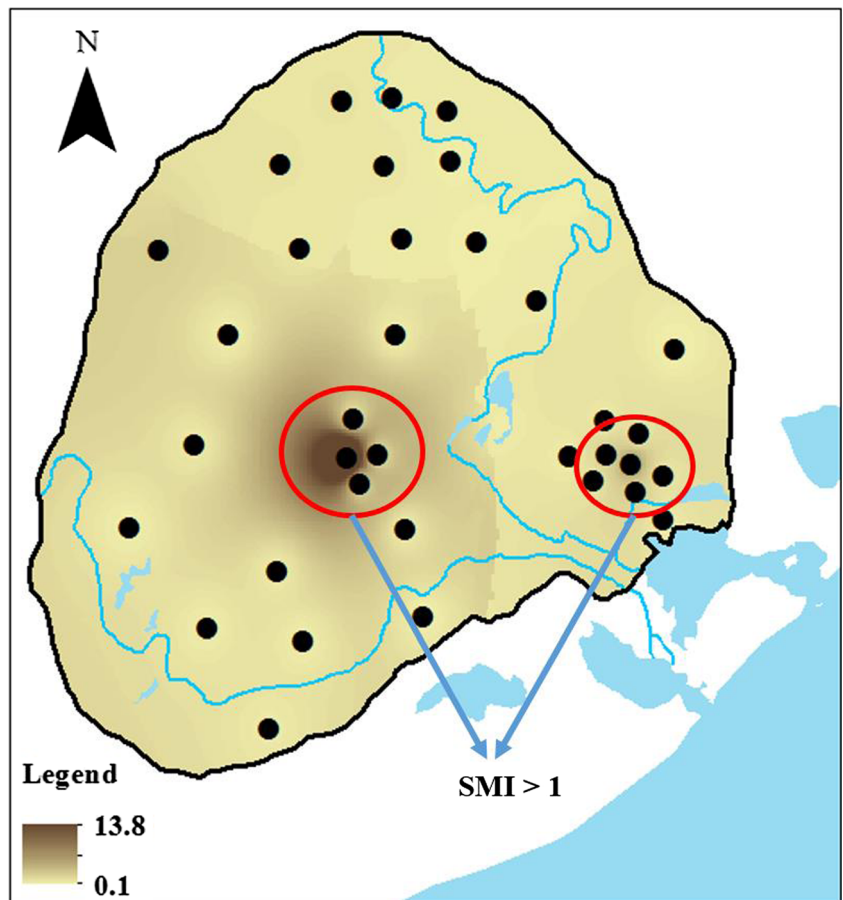**Fig. 9** Spatial distribution in SMI in groundwater

Table 5 Correlation among variables in groundwater

Parameter	pH	TDS	TH	Ca	Mg	Na	K	HCO₃	Cl	SO₄
pH	1									
TDS	−0.02	1								
TH	−0.01	0.93	1							
Ca	−0.02	0.81	0.95	1						
Mg	0.00	0.96	0.96	0.83	1					
Na	−0.02	0.99	0.88	0.74	0.92	1				
K	−0.07	0.89	0.86	0.76	0.88	0.82	1			
HCO₃	0.02	0.53	0.63	0.59	0.62	0.40	0.82	1		
Cl	−0.03	0.99	0.88	0.75	0.92	1.00	0.81	0.37	1	
SO₄	0.02	0.96	0.89	0.78	0.92	0.98	0.75	0.32	0.99	1

moderate variation (Figs. 11 and 12). Area classified as suitable and unsuitable by OK and IDW is given in Table 7. These eight variables were subjected to overlay analysis without assigning any weights (i.e. all parameters are considered equally important). Larger variation in sodium, potassium and chloride by the two interpolation methods is because of two samples, one located in the centre and one near the coast. These two locations have high concentration of most ions than the other samples. IDW exhibits that most of the area is contaminated (70%) compared to OK (28%) (Fig. 13). Three zones within the study area exhibiting high concentration of most ions were correctly mapped by OK than by IDW. Similar results were also reported between these methods by Mirzaei and Sakizadeh (2016). Areas exceeding the limits by one, two or more parameters by OK and IDW are given in Table 8. High discrepancy in the results is found

in areas where groundwater exceeds the limits in 0, 1 and 2 parameters.

OK performs better than IDW for the dataset of this study. Mirzaei and Sakizadeh (2016) indicate that the spatial distribution of wells plays an important role in the interpolation analysis. It is argued by Falivene et al. (2007, 2010) that kriging provides better results than IDW in regularly spaced datasets as the former considers the relative position of the data from the interpolated

Table 6 Factor scores of groundwater samples

Parameter	Factor 1	Factor 2
pH	−0.01	0.50
TDS	*0.93*	0.35
TH	*0.83*	0.51
Ca	*0.71*	0.52
Mg	*0.86*	0.46
Na	*0.97*	0.20
K	0.67	*0.70*
HCO₃	0.19	*0.97*
Cl	*0.98*	0.18
SO₄	*0.99*	0.13
Eigen value	8.53	1.02
% variance	77.55	9.27
Cumulative % variance	77.55	86.83

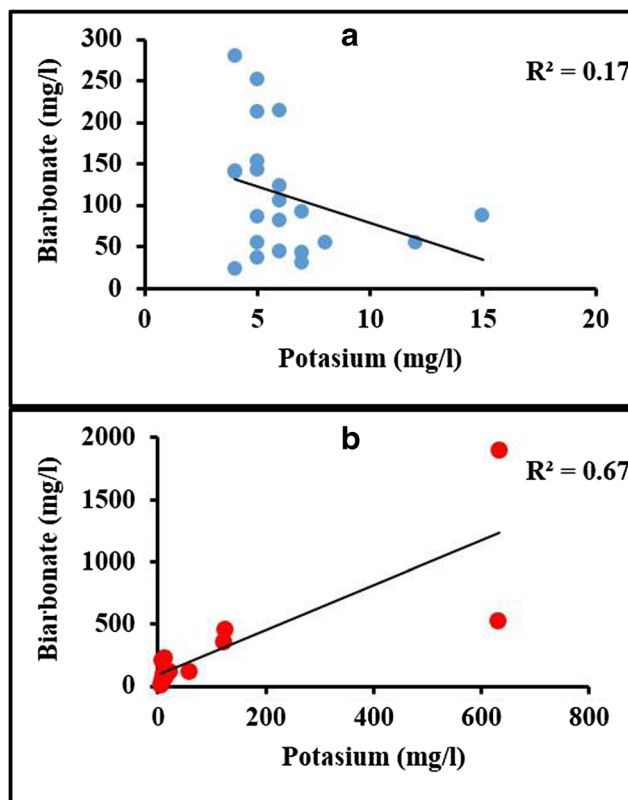Italic values indicate positive correlation

Fig. 10 Relationship between bicarbonate and potassium in groundwater (**a**) except in landfill and industrial areas (**b**) at landfill and industrial areas

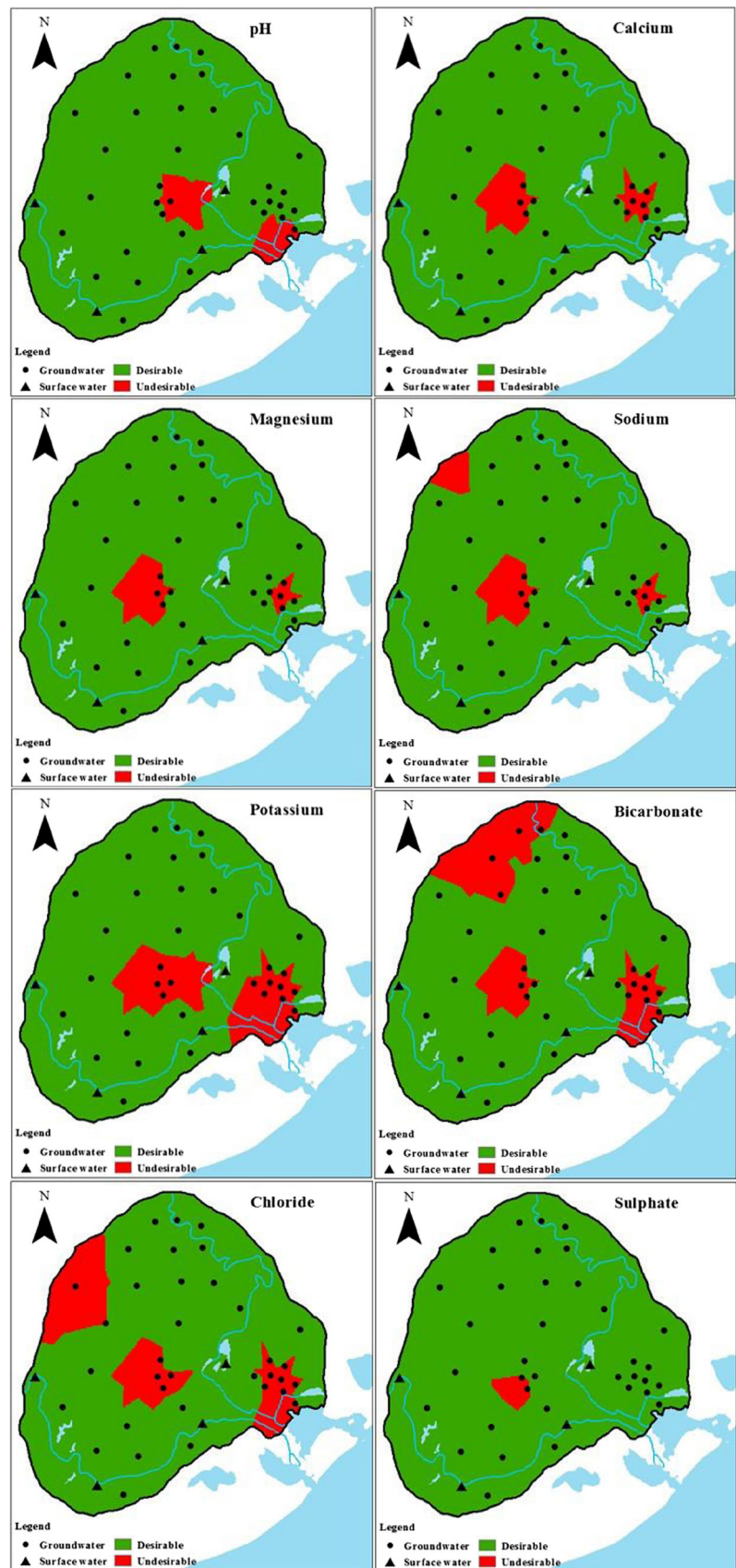**Fig. 11** Spatial interpolation of parameters by OK
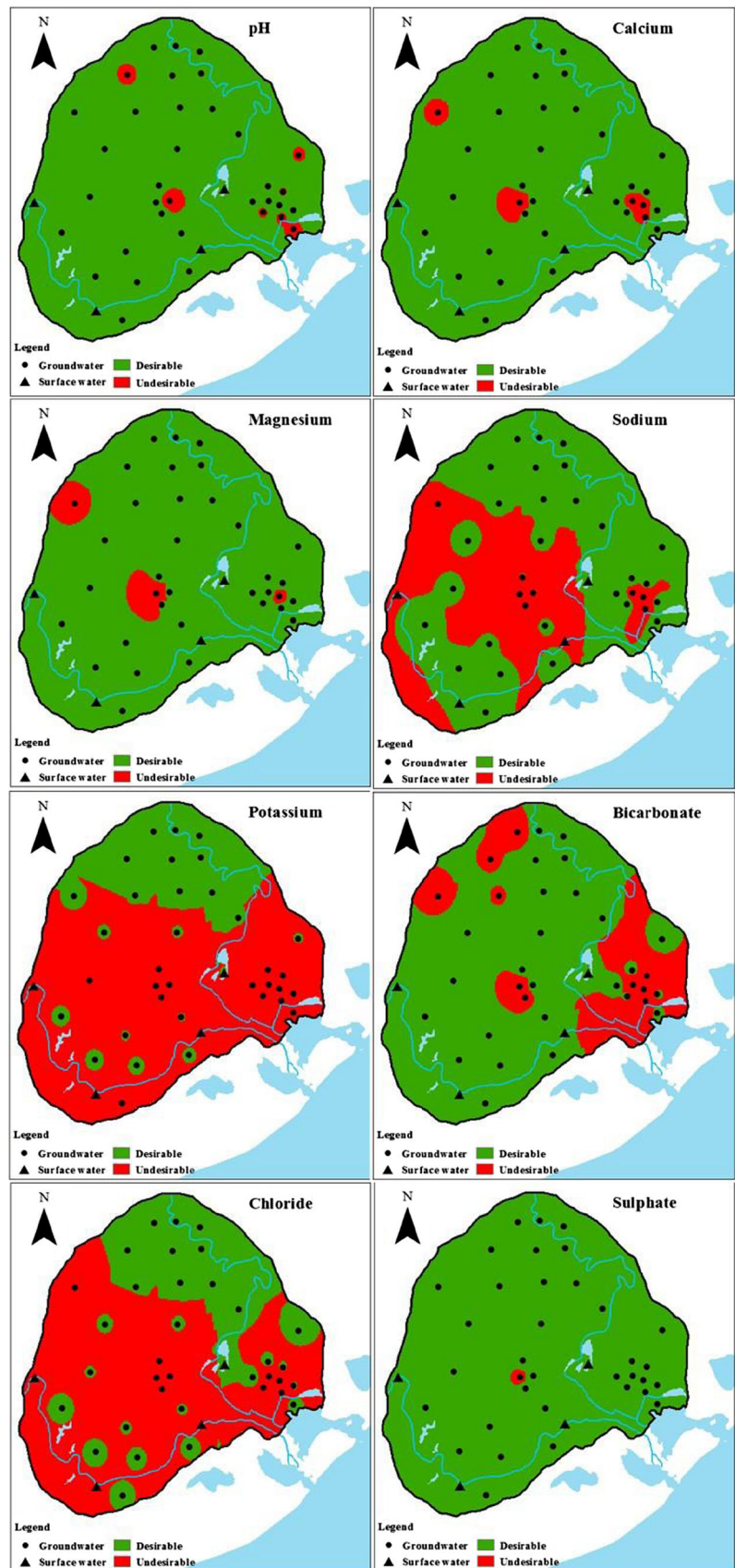
Fig. 12 Spatial interpolation of parameters by IDW

Table 7 Suitable and unsuitable areas for various parameters and interpolation methods

Parameter	OK		IDW	
	Desirable (km²)	Undesirable (km²)	Desirable (km²)	Undesirable (km²)
pH	571.1	12.0	553.3	29.7
Calcium	565.8	17.3	551.3	31.8
Magnesium	556.4	26.7	554.9	28.2
Sodium	354.6	228.4	544.4	38.6
Potassium	156.2	426.9	507.0	76.1
Bicarbonate	453.2	129.8	480.4	102.7
Chloride	195.9	387.1	491.9	91.2
Sulphate	581.4	1.7	575.2	7.9

Table 8 Groundwater contamination areas by OK and IDW

Number of parameters that exceeds quality criteria	OK (km²)	IDW (km²)	Suitability
0	418.9	116.2	Desirable
1	90.2	73.7	Undesirable
2	14.0	103.8	Undesirable
3	15.0	242.6	Undesirable
4	16.4	23.0	Undesirable
5	0.9	13.4	Undesirable
6	18.5	7.9	Undesirable
7	8.8	1.9	Undesirable
8	0.0	0.0	Undesirable

point. Kriging was better than IDW for many studies, and the uncertainty of the interpolation methods associated with the results has been questioned by many researchers (Xie et al. 2011; Gong et al. 2014; Mirzaei and Sakizadeh 2016). Number of wells, their location, distribution, depth, distance between the samples and choice of interpolation techniques influence the decision-making process. Unusual values at one location also can influence the interpolation of results. Hence, using one of the spatial methods alone is not sufficient to determine and delineate the areas of groundwater pollution. It should be used along with several other statistical analyses. From field visits and multiple methods used in this study, three contamination zones were identified in Richards Bay. They are (1) agricultural areas in the north-west, (2) landfill site in the centre and (3) effluent from industrial operations near the harbour/sea in the eastern part of the study area (Fig. 13).

Conclusion

This study demonstrates the use of spatial interpolation and statistical methods in mapping groundwater contamination in Richards Bay, South Africa. Groundwater quality exceeded limits for drinking use for most ions at certain locations. Irrigation water quality was unsuitable in most locations based on MH, Kelly's ratio and Na%. Sodium and chloride were the abundant ions in groundwater because of seawater intrusion. Concentration of calcium, magnesium and sulphate was in the fresh water range. Sodium and chloride were in the fresh water and seawater range. Dominant geochemical processes controlling the presence of these ions in groundwater include silicate weathering, ion exchange and mixing of fresh water with seawater. SMI was higher in two clusters indicating contamination from landfill and industrial sources. Water quality in this area was poor, and management measures are needed especially at the landfill site and industrial areas to prevent percolation of leachate and wastewater.

OK and IDW showed diverse results with contaminated zones at 28 and 70% of the areas, respectively. Highly

Fig. 13 Groundwater contamination maps
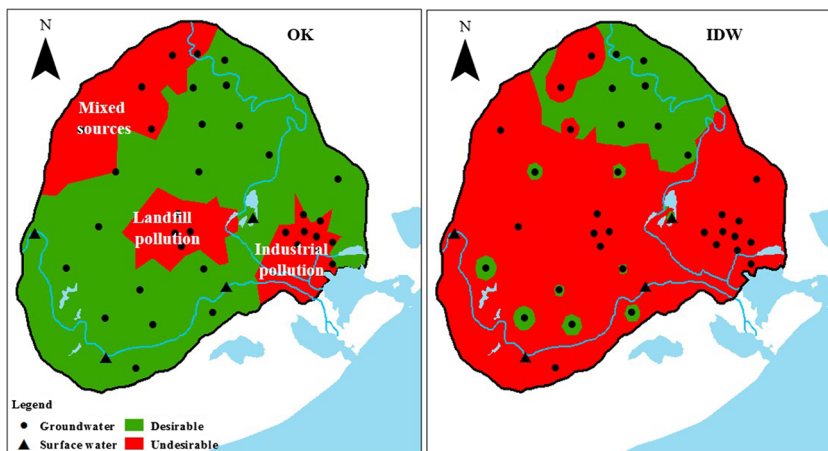
contaminated areas surrounded by less contaminated areas are mapped better by OK. The three contaminated zones by landfill, industries and agriculture were identified precisely by OK while IDW connected all the contaminated zones indicating most of the study area as contaminated. Discrepancy in results predicted by OK and IDW was greater when (1) one or two parameters exceeded the prescribed limits for water quality and (2) when the water quality was within limits for all eight parameters. Less variation in results was observed when four to eight parameters exceed the water quality criteria. Because of the unclear nature of outcome from different interpolation methods, the results and maps obtained by various techniques should be compared with one another along with field information to arrive at more meaningful understanding of the situation. This study sets as an example for such a multi-method analysis.

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