Integration of Heavy Metal Pollution Indices and Health Risk Assessment of Groundwater in Semi-arid Coastal Aquifers, South Africa

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Integration of heavy metal pollution indices and health risk assessment of groundwater in semi-arid coastal aquifers, South Africa

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Abstract

The metal contaminated groundwater results in serious health issues and hence this study attempts to address metal contamination and its sources by using integrated techniques including indexed and statistical methods and its related health hazards. Groundwater pH varied from 5.3 to 8.3 indicating acidic to alkaline in nature. Heavy metal evaluation index and degree of contamination reveal that all the groundwater samples fall under low pollution and are appropriate for human consumption. According to the pollution index majority of the samples fall in the insignificant pollution zone. Water quality index reveal that 19% and 2% of the groundwater samples belong to the poor and very poor water quality category and are spatially situated on the central, northern and southern parts of the study region. Correlation matrix and principal component analysis reveal that weathering of aquifer matrix and anthropogenic activities are accountable for the release of heavy metals into groundwater. Furthermore, R-mode and Q-mode cluster analysis revealed two clusters which are linked to mixed sources including weathering and anthropogenic activities. Based on the hazard quotient the order of heavy metal impact is: Co>Pb>Cd>Zn>As>Mn>Cu>Cr>Fe>Ni for both children and adult. The hazard index values varied from 0.06 to 8.16 for children and from 0.02 to 2.14 for adult. In this study, it is discovered that 43% and 26% of groundwater samples pose non-carcinogenic health risk in children and adult, respectively. This study highly recommends treatment of contaminated groundwater before consumption in order to protect and maintain the public health.

Keywords: heavy metal pollution, multivariate statistical analysis, pollution indices, water quality index, South Africa

1. Introduction

Groundwater serves as an important water resource supplying the demand for drinking, domestic, agriculture sectors and industries especially in regions of arid and semi-arid countries (Wang et al. 2020; Li et al. 2019a; Ezugwu et al. 2019; Çiner et al. 2020) and it is usually perceived as safe compared with surface water resources due to its natural filtration of contaminants by the soil as water moves into the groundwater (Sener et al. 2017; Wagh et. al 2018; Edokpayi et al. 2018). However, various researchers have reported several cases of

groundwater contamination due to various sources (Li et al. 2021; He and Wu 2019; He et al. 2019). Heavy metal pollution is among the most prominent threat to the quality of groundwater resources owing to its extreme toxicity even at low concentrations (Abou Zakhem and Hafez 2015; Singh and Kamal 2016; Tiwari et al. 2017; Rezaei et al. 2019; Egbueri and Unigwe 2020; Brindha et al. 2020). Heavy metals enter groundwater through natural processes such as weathering and dissolution of rocks and soils, ion exchange processes, volcanism extruded products, decomposition of living matter and atmospheric matter (Prasanna et al. 2012; Rezaei et al. 2019; Çiner et al. 2020; Wang et al. 2021). Mining, industrial, agricultural and disposal of domestic refuse are some of the common anthropogenic activities that influence the concentration of heavy metals in groundwater resources (Rezaei et al. 2017; Wagh et al. 2018; Giri and Singh 2019; Ahamad et al. 2020). However, the accumulation of heavy metals in ecosystem is exacerbated by anthropogenic activities (Ukah et al. 2019) which are classified as essential (copper, chromium, cobalt, iron, manganese and zinc) and non-essential (arsenic, cadmium and lead) (Çiner et al. 2020; Brindha et al. 2020). Some heavy metals are required in small amounts for human body building, however, excess consumption of such heavy metals can be detrimental to health and environment (Haloi and Sarma 2012; Chanpiwat et al. 2014; Li et al. 2014; Boateng et al. 2015; Vetrimurugan et al. 2018; Xiao et al. 2019).

Several numerical and statistical models developed globally are successfully used in water quality assessment. Such methods includes Heavy metal pollution index (HPI), Heavy metal evaluation index (HEI), degree of contamination (C_d), Ecological risk index (ERI), Pollution index of groundwater (PIG), Synthetic pollution index (SPI), and Overall index of pollution (OIP), Correlation analysis (CA), Principal Component Analysis (PCA) and Hierarchical cluster analysis (HCA) (Mohan et al. 1996; Prasad and Bose 2001; Edet and Offiong 2002; Prasanna et al. 2012; Subba Rao 2012; Solangi et al. 2019; Egbueri 2020; Wu et al. 2014, 2020; Li et al. 2015, 2016, 2019b; Ren et al. 2021). About 40% of the groundwater samples in Nigeria ispolluted by heavy metals rendering it inappropriate for human consumption (Egbueri and Unigwe 2020). Another study conducted in southeast Nigeria using HPI, HEI and CI (contamination index) inferred that all of the groundwater samples were excellent for drinking purposes (Ezugwu et al. (2019). A study in Onitsha, Nigeria using the SPI revealed that approximately 91.67% of groundwater samples were not palatable for human consumption (Egbueri 2020). Different techniques such as PIG, ERI and HCA to assess the drinking water quality of groundwater in Ojoto, Nigeria was utilised. According to the PIG

classification, 20% of the groundwater samples were found to be very highly polluted and were found unsuitable for human consumption (Egbueri 2020). The HPI, HEI and C_d results revealed that majority of groundwater samples in central Bangladesh fall under low level of pollution and the C_d provided better insight when compared to the other indices (Bodrud-Doza et al. 2016). The extent of heavy metal contamination on ecology and human health risks in groundwater of Lagos, Nigeria were largely owed to anthropogenic activities (Ukah et al.2019).

Population growth, expansion of agricultural lands, rapid urbanization, industrialization, and climate change are among the factors that lead to water quality problems in South Africa (Vhonani et al. 2019). In Southern Africa approximately, two-thirds of the country's population depend groundwater for their domestic purposes (Nel et al. 2009; Vetrimurugan et al. 2017). According to DWAF (2000), 65% of total water supply in rural areas is derived from groundwater. Direct consumption of groundwater without any form of treatment exposes local residents to various contaminants that may have adverse impact on human health. About 3.6% of deaths per year are linked to water contamination in South Africa (Nel et al. 2009). Arsenic and lead are the major contaminant sources of groundwater in South Africa (Verlicchi and Grillini 2020),

The present study is focused in Maputaland coastal aquifer, South Africa. Rural communities within the area are still without adequate supply of water resources, as a result they solely rely on groundwater resources for their domestic water needs. Previous studies conducted in this area revealed that groundwater is highly contaminated with iron, rendering it unfit for various uses (Demlie et al. 2014). The ecological impact of metals in beach sediments in marine protected areas shows enrichment of metals which are due to the heavy mineral rich coastal dunes and past mining activities (Vetrimurugan et al. 2018). The concentrations of cadmium, zinc, lead, manganese, aluminium and iron exceeded the limits of World Health Organization (WHO) standards for drinking water quality of the Maputaland coastal aquifer (Mthembu et al. 2020). The main objectives of this study is (1) evaluate the extent of heavy metal pollution in groundwater using HPI, HEI and C_d, (2) assess groundwater quality for drinking purposes by adopting PIG, SPI and OIP indices and (3) evaluate potential heavy metal sources in groundwater using multivariate statistical tools such as PCA and HCA. This study will provide knowledge on major pollution sources and assist water management of South Africa in combating further contamination of groundwater resources.

2. Methodology

2.1 Description of study area

The Maputaland coastal plain of northern KwaZulu Natal extends southerly from Mtunzini to the Mozambique border in the North (Fig. 1). It belongs to the uMkhanyakude district municipality with the geographical area covering approximately 4 400km^2. The climate of the study area is humid subtropical with warm summers. The annual rainfall ranges from less than 600mm inland to about 1000mm along the coast (Porat and Botha 2008; Ramsay 1996; Watkeys et al. 1993). Highest rainfall befalls during the summer months (November-March) with the eastern side receiving most of the precipitation. Rainfall received in this area are from tropical and middle latitude weather systems (Weitz and Demlie 2014). Land use activities in the area consists of subsistence agriculture, commercial forestry plantations and eco-tourism. The foremost water supply for drinking, domestic and agricultural activities are from groundwater.

the geology of the Maputaland coastal plain reveal that underlain by unconsolidated to semi-consolidated sediments of Cretaceous to Quaternary age. Alluvial deposits, arenite, sandstone, and siltstone cover the study area (Fig. 1). Deposits of the Zululand Group consists of Makatini, Mzinene and St. Lucia formations. These sediments are overlain by Miocene aged Uloa formation which is in turn overlain by the cross-bedded calcarenites of the Umkhwelane formation (Meyer et al. 2001). Pleistocene aged Port Durnford and Kosi Bay formations are characterised by loosely consolidated sands, silts, clays and lignite beds (Meyer et al. 2001; Demlie et al. 2014; Ndlovu 2015; Ndlovu and Demlie 2016). Overlying the Kosi Bay formation are the redistributed sands of the KwaMbonambi formation. The Holocene aged Sibayi formation is characterised by high coastal dune cordons (Watkeys et al. 1993). The area is covered by sediments that are highly permeable and indorse swift recharge to the aquifers and strongly interact with the wetlands in the region (Mkhwanazi 2010; Weitz and Demlie 2014). Groundwater in this area is encountered within the shallow unconfined aquifer that yields approximately 0.5 to 5.0l/s (Ndlovu and Demlie 2016). The St. Lucia formation is characterised by low permeability and behaves as an aquiclude. Overlying the Uloa formation are sedimentary units characterised by fine grained, less permeable sediments resulting in a leaky aquifer type (Ndlovu and Demlie 2016). The uppermost, youngest sediment of the KwaMbonambi and Sibaya formations are characterised by unconsolidated aeolian and fluvial sands and have high hydraulic conductivity (Kelbe et al. 2016, Ndlovu

and Demlie 2018). Generally, groundwater flows from the west to the Indian Ocean. Highest groundwater level is approximately 25m below ground level.

2.2 Sampling and analysis of groundwater

53 number of groundwater samples were collected from the selected bore wells of the Maputaland coastal aquifer during 2018 (Fig. 1). The wells were purged for approximately 5 minutes to remove stagnant water prior to sample collection. The groundwater samples were collected and stored using a high-density polyethylene (HDPE) bottles after filtering with a membrane filter. membrane filter. The 0.5ml of nitric acid was added to the samples to prevent metal precipitation. The samples were labelled accordingly and stored in the refrigerator at a temperature of 4°C. Groundwater samples were analysed for pH, As, Fe, Mn, Zn, Pb, Ni, Cr, Cu, Cd and Co.

The pH of the groundwater samples were determined with multiprobe meter instrument (Aqua Probe A-700). Heavy metals present in water samples were determined by inductively coupled plasma-mass spectrometry (NexION 2000 ICP-MS) instrument using calibration standards (MERCK) at the University of Zululand hydrogeochemistry laboratory. Throughout the analytical procedures the standards of American Public Health Association (APHA 2005) were followed. Standards and blanks were run to assess the accuracy of the analysis. ArcGIS software v10.5 was employed to plot spatial maps using the IDW (inverse distance weighted) interpolation technique.

2.3 Heavy metal pollution assessment

2.3.1 Heavy metal evaluation index (HEI)

The HEI yields the overall quality and presence of heavy metal in water (Edet and Offiong 2002). It is computed as follows;

$$HEI=\sum_{i=1}^{n}\frac{H_c}{H_{MAC}} \qquad \text{Eq.1}$$

where H_C is the monitored value and H_{MAC} is the maximum admissible concentration (MAC) of the ith parameter taken from SANS (2015).

2.3.2 Degree of contamination C_d

The degree of contamination (C_d) is useful in summarizing the combined effects of various quality parameters regarded as harmful to domestic water (Backman et al. 1997; Edet and Offiong 2002; Prasanna et al. 2012). It is computed by the following equation;

$$C_d = \sum_{i=1}^{n} C_{fi} \quad \text{Eq.2}$$

where

$$Cf_i = \frac{C_{Ai}}{C_{Ni}} - 1 \quad \text{Eq.3}$$

where C_{fi} is the contamination factor for the ith parameter, C_{Ai} is the monitored value and C_{Ni} is the upper permissible concentration of the ith parameter. According to Edet and Offiong (2002), the C_d can be classified into low (C_d<1), medium (C_d=1-3) and high (C_d>3) in order to identify the contaminated areas.

2.4 Assessment of drinking water quality

2.4.1 Pollution index of groundwater (PIG)

PIG was proposed in 2012 by Subba Rao, it is an important tool for monitoring and assessment of drinking water quality. In PIG assessment, five steps are taken into consideration. Firstly, it includes estimating the relative weight (R_w) of all analysed parameters (Table 1) on a scale of 1 to 5, depending on parameters of human health impact. Secondly, it involves computation of the weight parameter (W_p) of each water quality variable to evaluate their relative contributions to overall water quality (Eq.4). Thirdly, it involves estimation of the status of concentration (S_c) which is computed by diving the

concentration (C) of each water quality variable of every sample by its respective water quality standard limit (D_s) as described by SANS (2015) (Eq.5). In the fourth step, the overall quality of groundwater (O_w) is computed by multiplying the W_p by S_c (Eq.6). Finally, the pollution index of groundwater is computed by summing all values of O_w contributed by every water quality variable in each groundwater sample (Eq.7).

$$W_p = \frac{R_w}{\sum R_w} \quad \text{Eq.4}$$

$$S_c = \frac{C}{D_s} \quad \text{Eq.5}$$

$$O_w = W_p * S_c \quad \text{Eq.6}$$

$$PIG = \sum O_w \quad \text{Eq.7}$$

2.4.4 Water quality index (WQI)

The WQI was developed by Horton (1965). It is widely used by various researcher scholars to evaluate drinking water quality. Computing the WQI involves five steps; (i) assignment of weights (wi) to each water quality parameter being analysed, (ii) calculation of relative weights (Wi) of parameters using equation 8, (iii) quality rating calculation (qi) based on equation 9, (iv) determining the sub-index value (SIi) of the analysed parameters based on equation 10, (v) calculation of the WQI based on equation 11.

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \quad \text{Eq.8}$$

$$q_i = \frac{C_i}{S_i} \times 100 \quad \text{Eq.9}$$

$$SI_i = W_i \times q_i \quad \text{Eq.10}$$

230 $$WQI = \sum_{i=1}^{n} SI_i \quad \text{Eq.11}$$

231 where, qi represents the parameter quality rating, Ci represents the chemical parameter
232 concentration (mg/L), and Si represents the drinking water standard prescribed by
233 SANS/WHO. Weight values (wi) ranging from 1 to 5 were ascribed for each parameter
234 according to their relative significance in the overall quality of drinking water and their
235 indebted effects on human health. A maximum weight of 5 was allocated to the most
236 significant parameters while a weight of 1 was assigned to the least significant parameters.
237 Table 2 shows the weights and relative weights assigned while computing WQI.

238 **Health Risk Assessment**

239 Intake of contaminated groundwater by elevated trace metal content is known to pose threat
240 in human health. Evaluation of non-carcinogenic health risks due to trace metal
241 contaminated groundwater particularly in children is crucial. According to guidelines
242 provided by the Unites States Environmental Protection Agency (US EPA (1989), the chronic
243 daily intake (CDI) risks caused by ingestion of a single trace element is computed for adults
244 and children using the equation;

245

246 $$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad \text{Eq. 12}$$

247 where CDI represents chronic daily intake via ingestion pathway (µg/kg/day), C is the
248 concentration of the contaminant in drinking water (µg/L). IR represents the ingestion rate (L/day: 2.2
249 for adults and 1.8 for children). ED signifies the exposure duration (years: 70 and 6 years for adults
250 and children). EF represents the exposure frequency (days/years: 365 for adults and children). BW is
251 the body weight (kg: 70 for adults while 15 kg is for children). AT signifies the average time (days:
252 25 550 and 2 190 days for adults and children) Duggal et al. 2017; Barzegar et al. 2018; Mgbenu and
253 Egbueri 2019; Egbueri et al. 2020; Mthembu et al. 2020). The non-carcinogenic risk of a single trace
254 element is then calculated as the hazard quotient (HQ) using the equation;

255 $$HQ = \frac{CDI}{RfD} \quad \text{Eq. 13}$$

256

where RfD signifies the reference dose of each trace element (µg/kg/day). In this study, the RfD for the different trace metals are given as 0.3 (As), 0.5 (Cd), 40 (Cu), 700 (Fe), 24 (Mn), 1.4 (Pb), 300 (Zn), 0.3 (Co), 3 (Cr), and 20 (Ni) (Duggal et al. 2017; Barzegar et al. 2018; Zhang et al. 2018; Mgbenu and Egbueri 2019; Egbueri et al. 2020; Mthembu et al. 2020). The hazard index (HI) e representing the non-carcinogenic risk of the heavy metal is computed and is obtained by adding the HQs values of each groundwater sample as shown by the following equation;

$$HI = \sum HQ \qquad \text{Eq. 14}$$

HI values less than unity indicates that the non-carcinogenic health risk is within the acceptable limit whereas when the HI values is greater than unity it indicates that they are above the acceptable limit (Egbueri and Mgbenu 2020).

3. RESULTS AND DISCUSSION

3.1 Heavy metal contamination

Table 3 shows the summary of statistical results of physicochemical parameters and its comparative to drinking water standards (WHO 2011; SANS 2015). The groundwater pH varied from 5.3 to 8.3 with an average value of 7.1 resulting the nature of water from acidic to alkaline. The pH of the samples indicated that all the samples were within the standard limits of SANS (2015) but 30% of the samples were found below 6.5 as prescribed by WHO (2011). Groundwater arsenic varied from below detection limit to 3.6 µg/L (mean 0.5 µg/L). Concentrations of cadmium is below the detection limit of 4.6 µg/L (mean 0.9 µg/L) and approximately 23% of the samples exceeds the SANS (2015) and WHO (2011) standard limits. Zinc ranged from 1.9 to 19 964.5 µg/L (mean 499.9 µg/L). 2% of the samples exceeded the SANS (2015) and WHO (2011) standard limits in 2% of the samples. Iron concentrations in groundwater ranged from 2.7 to 1 848.6 µg/L with an average range of 140 µg/L. About 11% of the samples has iron concentrations higher than SANS (2015) and WHO (2011) drinking water standard limits. The high iron concentrations may be owed to the leaching process of iron-rich sediments (Demlie et al. 2014). In this study, lead contents varied from below detection limit to 26 µg/L (mean 6.6 µg/L). Approximately,25% of the samples have lead concentrations exceeding the SANS (2015) and WHO (2011) standard

limits. Hence, the samples were classified as unfit for human consumption. Manganese concentrations ranges from 0.4 to 116 µg/L (mean 19.1). About 2% of the samples has manganese concentrations above the SANS (2015) standard limit. Nickel content in groundwater varied from below detection limit to 9.3 µg/L (mean 2.1 µg/L). Chromium concentrations ranges from below detection limit to 8.4 µg/L with an average value of 3.4 µg/L, respectively. Copper contents ranged from below detection limit to 279.5 µg/L (mean 22.7 µg/L), respectively. Cobalt contents in groundwater varies from below detection limit to 8.4 µg/L with an average value of 1.8 µg/L. It was also observed that arsenic, chromium, copper, cobalt and nickel concentrations are low in groundwater samples and are within the prescribed standard limits of drinking water as prescribed by SANS (2015) and WHO (2011). Furthermore, iron, lead and cadmium were recognised to be dominant heavy metal contaminants in this area. Fig. 2a-d shows the spatial distribution of selected heavy metals in the study area. In this study, high iron concentrations are observed on the north western and south eastern part of the area (Fig. 2a). High manganese are observed in eastern, northern, and south eastern part (Fig. 2b). High lead concentrations are recorded on the south eastern, northern, central and south western part of the area (Fig. 2c). The spatial distribution of cadmium illustrates that high concentrations are recorded on the central, northern and south western part of the area (Fig. 2d). The relationship between groundwater pH and metal load was computed to classify the water samples (Ficklin et al 1992; Caboi et al 1999). Fig. 3 shows that 43% and 57% of the samples are classified as near-neutral high metal and near-neutral extreme metal.

3.2 Heavy metal pollution assessment

3.2.2 Heavy metal evaluation index (HEI)

The values of HEI varied from 0.08 to 10.25 with an average value of 1.83 (Table 4), respectively. The HEI can be classified as low (< 400), medium (400-800) and high pollution (> 800) (Edet and Offiong 2002). In this study, all the groundwater samples were found below the 400 (Table 5; Fig. 4a), respectively. This suggests that the groundwater has low pollution with regards to heavy metals and is safe for human consumption.

3.2.3 Degree of contamination (C_d)

The calculated C_d values varied from -9.92 to 0.25 with an average value of -8.18 (Table 4), respectively. C_d values may further be categorised into (Backman et al. 1997; Edet and Offiong 2002): low (< 1), medium (1-3) and high (> 3). Groundwater samples have C_d values

below one suggesting low contamination by heavy metals (Table 5; Fig. 4a). A similar trend at various sampling locations was observed between the two indices (HEI and C_d) (Fig. 5). Furthermore, the indices were compared with each other and it show strong correlation of HEI and C_d (Paul et al. 2019); Jahanshahi and Zare (2015).

3.3 Drinking water quality assessment

3.3.1 Pollution index of groundwater (PIG)

Computed PIG values are presented in Table 4. In PIG assessment, the relative influence of chemical parameters was considered. When the overall chemical quality of water (O_w) is above 0.1, it contributes 10% of the value of 1.0 of PIG (Subba Rao 2012) confirming the influence of groundwater pollution. PIG values can be classified into five categories as follows; PIG < 1.0 (insignificant pollution), 1.0-1.5 (low pollution), 1.5-2.0 (moderate pollution), 2.0-2.5 (high pollution) and PIG > 2.5 (very high pollution) (Subba Rao 2012; Subba Rao et al. 2018; Egbueri and Unigwe 2019). The PIG values ranged from 0.07 to 1.03 with an average value of 0.25, respectively (Table 3). About98% of the samples has PIG values less than 1.0 (0.23) falling under insignificant pollution zone while 2% of the samples have PIG between 1.0 and 1.5 (1.03) which comes under low pollution zone (Table 6). The spatial distribution of PIG shows that insignificant pollution zone is spread throughout the study area (Fig. 4b). The low pollution zone is predominant observed mainly in the central part (Fig. 4b).

The pH (0.07), As (0.01), Fe (0.03), Mn (0.02), Zn (0.01), Pb (0.07), Ni (0.00), Cr (0.00), Cu (0.00), Cd (0.03) and Co (0.00) show values O_w less than 0.1 in the insignificant pollution zone. These values are therefore regarded as natural contributors of groundwater quality. In the low pollution zone, the Cd (0.16), Fe (0.52), and Pb (0.23) have the O_w values higher than 0.1 (Table 6). Thus, high values in the low pollution zone indicates the influence of anthropogenic sources.

3.3.4 Water quality index (WQI)

The water quality results are shown in Table 2. In the present study, the WQI varied from 7.27 to 89.44 with an average of 25.91 (Table 4). the WQI can be classified into five categories such as; WQI< 25 indicate excellent water quality; 25-50 indicate good water quality; 50-75 indicate poor water quality; 75-100 indicate very poor water quality; and WQI> 100 indicate unsuitable water quality (Rostami et al 2019). In this study region, 70%

of the groundwater samples fall in the excellent water category, 9% of the samples belong to good water, 19% of the samples belong to poor water quality, and 2% of the samples are unsuitable for drinking purposes. Fig. 4b shows the spatial distribution of WQI. It is shown that groundwater samples that fall in the poor and very poor water category are situated in the central, northern and southern part of the study region.

3.4 Multivariate statistical analysis for identification of pollution source

3.4.1 Correlation matrix (CM)

Correlation matrix identifies interrelationship among parameters and their possible sources in groundwater (Table 7). Correlation coefficients r>0.7 is considered as strong, 0.7>r>0.5 as moderate and <0.5 were considered as weak (Egbueri and Mgbenu 2020). The groundwater pH showed a moderate correlation with cadmium (r= 0.57) and cobalt (r= 0.55) (Table 6). Iron showed a strong relationship with HEI and C_d, this suggests that iron has a key role in determining groundwater quality. Lead showed significant correlation with chromium (r= 0.90), cadmium (r= 0.92), cobalt (r= 0.94), HEI (r= 0.84) and C_d (r= 0.84). High concentration of lead and cadmium may be indicative of anthropogenic sources such as agrochemicals (Arslan and Ayyildiz Turan 2015). Chromium has shown strong correlation with cadmium (r= 0.89), cobalt (r= 0.94), HEI (r= 0.71) and C_d (r= 0.71). Furthermore, cadmium show a strong positive correlation with cobalt (r= 0.97HEI (r= 0.86) and C_d (r=0.86). Lead, chromium, cadmium and cobalt shows a significant strong correlation with HEI and C_d. The correlation among heavy metal pollution indices reflected good relation between HEI (r= 0.87) and C_d (r= 0.87). Similarly, HEI is strong correlated with C_d (r=1). This indicates that HEI and C_d can be used to evaluate the risk and contamination of heavy metals in groundwater of this area.

3.4.2 Principal Component Analysis (PCA)

Principal component analysis identifies sources of heavy metals in groundwater. Varimax rotation was used with Kaiser normalization. Component loadings, Eigen values, percentage of variance and cumulative percentages of the identified principal components (PCs) are shown in Table 8. Fig. 6a-c shows the spatial distribution maps of the principal components that were extracted. PCA revealed three principal components that accounted for 70.18% of the total variance. PC1 which explains 37.59% of the total variance has significant positive

loadings of lead, chromium, cadmium and cobalt. The presence of these heavy metals in PC1 revealed the contribution of anthropogenic sources such as the application of agricultural fertilizers and pesticides, leaching or infiltration of domestic wastes and garden refuse from the Mbazwana landfill site (Mthembu et al. 2020). Highest values of PC1 are situated in the northern, central and southern part of the study area, especially in sample BH12, BH15-16, BH26, BH47-53 (Fig. 6a). PC2 accounted for 19.65% of total variance with significant loadings of pH and cobalt, and moderate loading of zinc. This suggests that the groundwater pH is responsible for the release of cobalt and zinc into groundwater. Moderate PC2 values are distributed throughout the study area with highest values seen at the central part of the study area at sample BH21 (Fig. 6b) The presence of zinc is owed to the use of agricultural fertilizers (Razei et al. 2019). PC3 explains 12.9% of the total variance with a negative moderate loading of arsenic, strong positive loading of manganese and moderate loading of nickel. The negative loading of arsenic suggests a different source of origin. The strong and moderate loadings of manganese and nickel may be due to the weathering of manganese and nickel bearing minerals. Landfill leachate may also contribute to the occurrence of manganese in groundwater of this area. For PC3, the distributed loadings were high on the eastern and north western part of the study area for samples BH27-28, BH51-52 (Fig. 6c). For better understanding, three principal components were overlaid into a single map using fuzzy overlay (Fig. 6d). Highest loadings are observed in the northern and central part of the study area with moderate values spread throughout the study area. This indicates that the samples in the northern and central part of the study area are highly influenced with anthropogenic and weathering processes. This also corresponds with the high values of heavy metals observed in these locations (Fig. 2a-d).

3.4.3 Hierarchical cluster analysis (HCA)

The potential sources of pollutants in groundwater of this area was further investigated by carrying out cluster analysis. R-mode cluster analysis was carried out to evaluate the sources of heavy metals in groundwater of this area. R-mode cluster analysis revealed two groups of clusters (Fig. 7). Cluster 1 consists of pH, chromium, cadmium, cobalt, arsenic, nickel and lead. This cluster indicates the influence of both geogenic (weathering of rock minerals) and anthropogenic sources (domestic wastes and agricultural fertilisers) in the study area. Cluster 2 comprises of manganese, copper, iron and zinc and is due to the influences of geogenic and

anthropogenic sources. Q-mode cluster analysis was also used to determine the similarities that exists between sampling points. Two groups of clusters were identified by Q-mode cluster analysis (Fig. 8) Cluster 1 consisted of 46 sampling locations. These sampling locations are BH1-BH14, BH17-BH23, BH25-BH33, BH35-BH41, BH43, BH44, BH46, BH48-BH53. The samples of this cluster are mainly located throughout the entire study area and its characteristics may be linked to the rocks found in this area such as arenite, sandstone, siltstone and alluvium. Furthermore, these sample locations are characterised by elevated average concentrations of iron, zinc, copper and manganese (Fig. 8). These high levels are associated with PC2 and PC3, respectively. This cluster is associated with pollution by mixed sources i.e weathering of soil or rock minerals and anthropogenic sources (agrochemicals). Based on average concentrations, pH, arsenic, nickel and copper were elevated in cluster 1 than in cluster 2. Cluster 2 included 7 sampling locations BH15, BH16, BH24, BH34, BH42, BH45 and BH47. Cluster 2 samples are spatially situated in the southern, central and north western part of the study area. This cluster is characterised by rocks such as arenite, sandstone and alluvium These sampling locations have highest concentrations of zinc, iron, manganese, and lead. These high levels correspond to PC1, PC2, and PC3, respectively. This cluster is also linked to mixed sources i.e. weathering of soil or rock minerals and anthropogenic sources. According to average values, iron, manganese, zinc, lead, chromium, cadmium and cobalt were greater in cluster 2 than those in cluster 1.

3.5 Health risk assessment

Health risk assessment evaluated the potential health risks of ingestion of trace metal contaminated groundwater in children and adult of the study region. Table 9 outlines the statistical summary of for the HQ of the selected heavy metals. The spatial variation of HQ and HI of infants, children, and adults is shown in Fig. 9a, b. The mean values of HQ followed the following decreasing trend: Co>Pb>Cd>Zn>As>Mn>Cu>Cr>Fe>Ni for both children and adult (Table 9; Fig. 9a, b). The average HQ values suggests that Co has shown highest of the total non-carcinogenic health risk in the study region. The HI values for groundwater samples varied from 0.06 to 8.16 for children and from 0.02 to 2.14 for adult, respectively (Fig. 9a, b). HI value for certain elements are is greater suggesting non-carcinogenic health risk for ingestion. Likewise, an HI value below one implies that it is within the acceptable limit. In this study, it was discovered that 43% and 26% of groundwater samples pose non-carcinogenic health risk in children and adult, respectively.

4. Conclusions

The present study address on evaluating extent of heavy metal contamination and their source of origin in groundwater of Maputaland coastal aquifer using indexed and statistical analysis. The following conclusions were made:

- Groundwater is acidic to alkaline in nature. The dominance of heavy metals is in the order; Zn>Fe>Cu>Mn>Pb>Cr>Ni>Co>Cd>As. Of all the heavy metals, lead, cadmium and iron exceeded the WHO and SANS standard limits for drinking water in 25%, 23% and 11% of the samples.

  HEI values of all the groundwater samples fall under low pollution with regards to heavy metals. Similarly, the C_d results revealed all the groundwater samples have low contamination with respect to heavy metals and are suitable for human consumption. The PIG and WQI were used to evaluate the drinking water suitability. Based on PIG results, 98% of the samples fall in the insignificant pollution zone and 2% of the samples fall in the low pollution zone. Moreover, metals such as cadmium, iron and lead had O_w values greater than 0.1 in the low pollution zone suggesting the influence of anthropogenic sources. The WQI revealed that 19% and 2% of the groundwater samples belong to the poor and very poor water quality category and are spatially situated on the central, northern and southern part of the study region.
- Multivariate statistical analysis including that CM and PCA confirms the release of heavy metals into groundwater which is controlled by geogenic (weathering of rocks and minerals) and anthropogenic sources (domestic wastes and agricultural fertilizers).
- From HCA, R-mode cluster analysis showed two clusters. Cluster 1 consisted of pH, chromium, cadmium, cobalt, arsenic, nickel and lead which indicate the influence of geogenic and anthropogenic sources. Cluster 2 comprised of manganese, copper, iron and zinc which is due to geogenic and anthropogenic sources in the study area. Q-mode cluster analysis grouped groundwater samples into two clusters. Samples in cluster 1 have high levels of iron, zinc and copper and correspond to PC2 and PC3. Similarly, samples in cluster 2 have high levels of zinc, iron, and manganese. These samples correspond to PC, PC2 and PC3. Both samples in cluster 1 and cluster 2 are linked to mixed sources including weathering of parent material and anthropogenic sources.

- HQ is in the order: Co>Pb>Cd>Zn>As>Mn>Cu>Cr>Fe>Ni both children and adult. The HI values varied from 0.06 to 8.16 for children and from 0.02 to 2.14 for adult. In this study, it was discovered that 43% of groundwater samples pose non-carcinogenic health risk in children while and 26% of the samples posed health risk in adults.
- This study recommends regular monitoring and treatment of contaminated groundwater prior to consumption by local residents to ensure the public health and to prevent further contamination of the aquifer.

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Figures

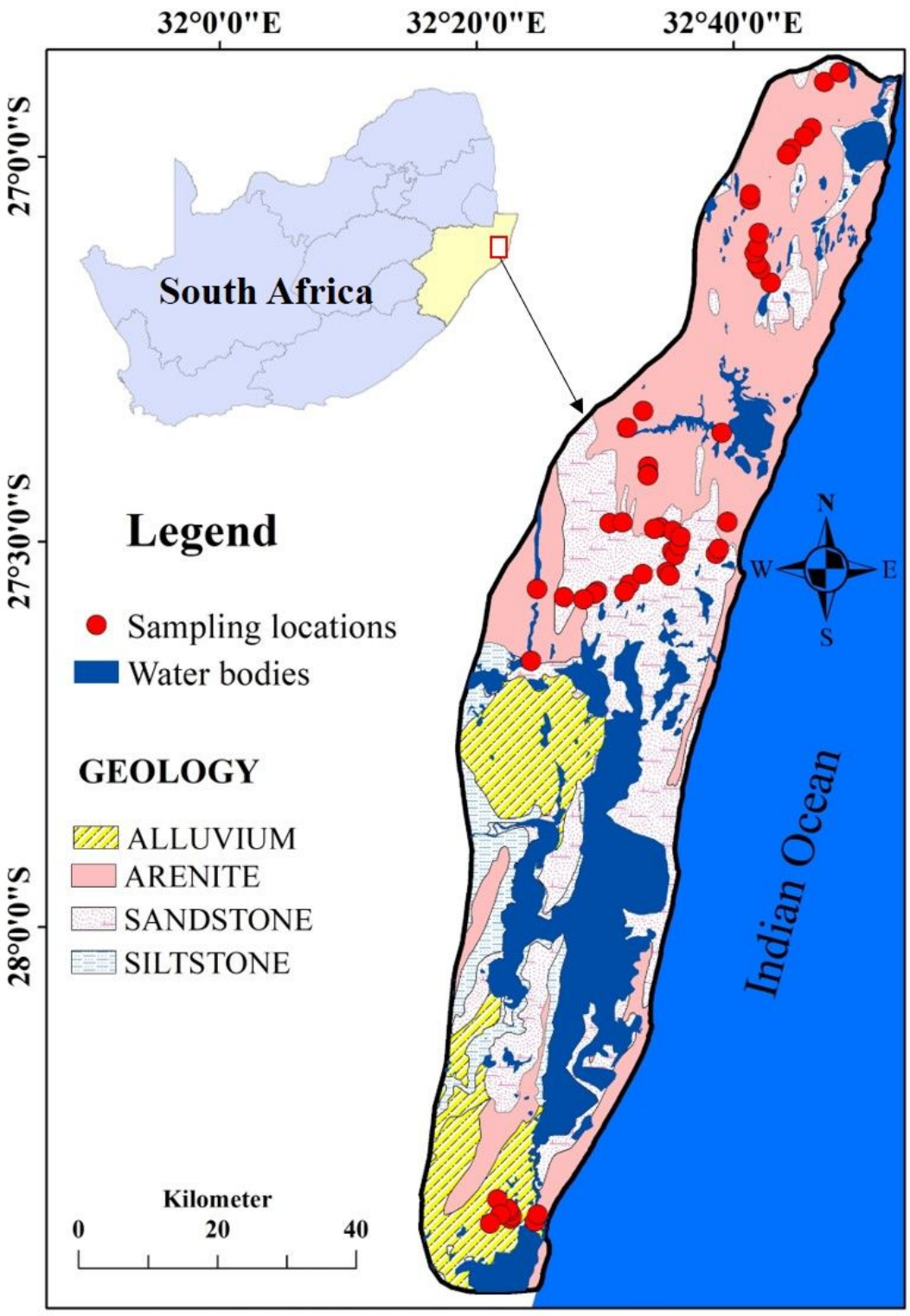

Figure 1

Map showing samping locations and geology of the study area

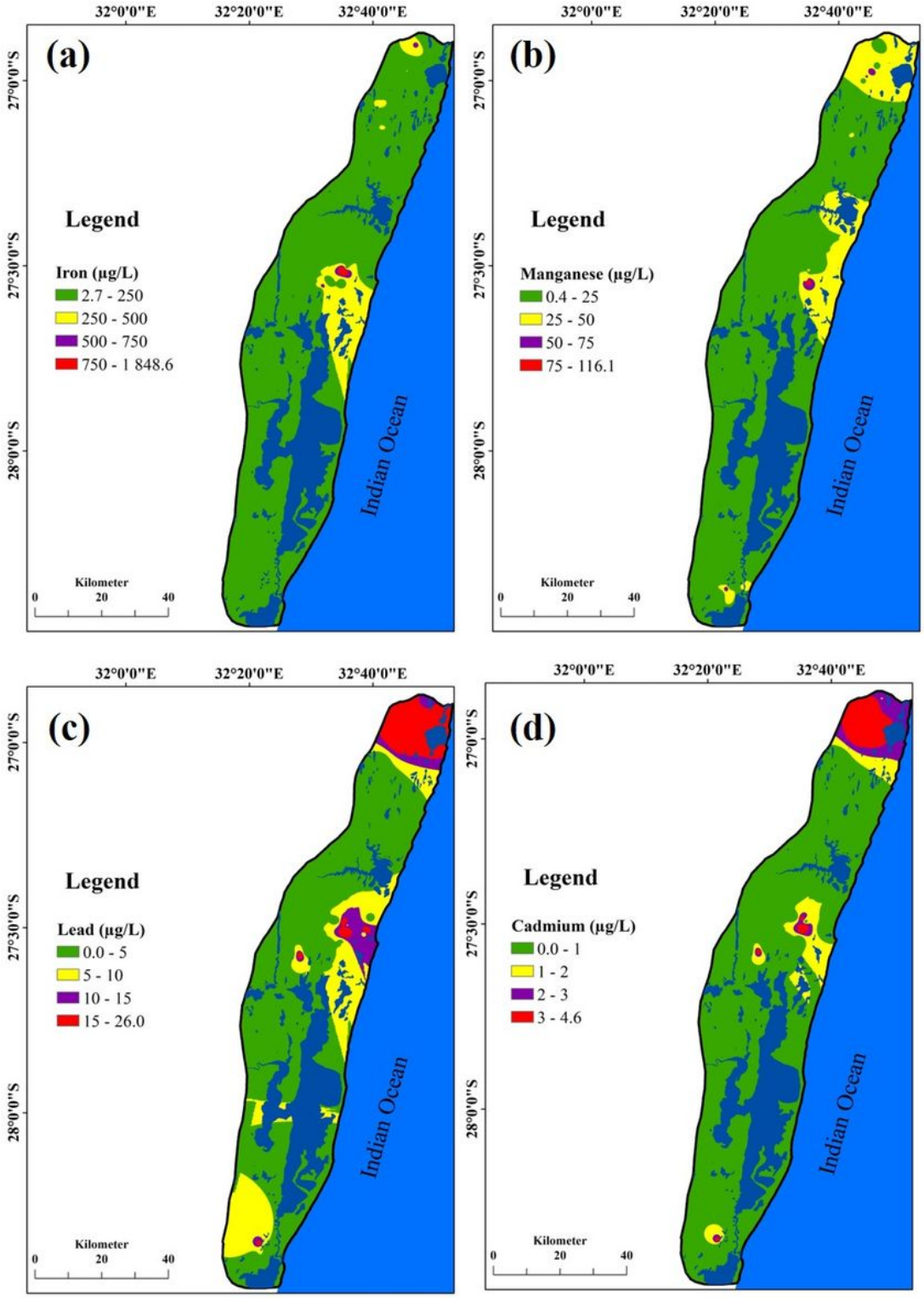

Figure 2

Spatial distribution of heavy metals (a) iron, (b) manganese, (c) lead and (d) cadmium

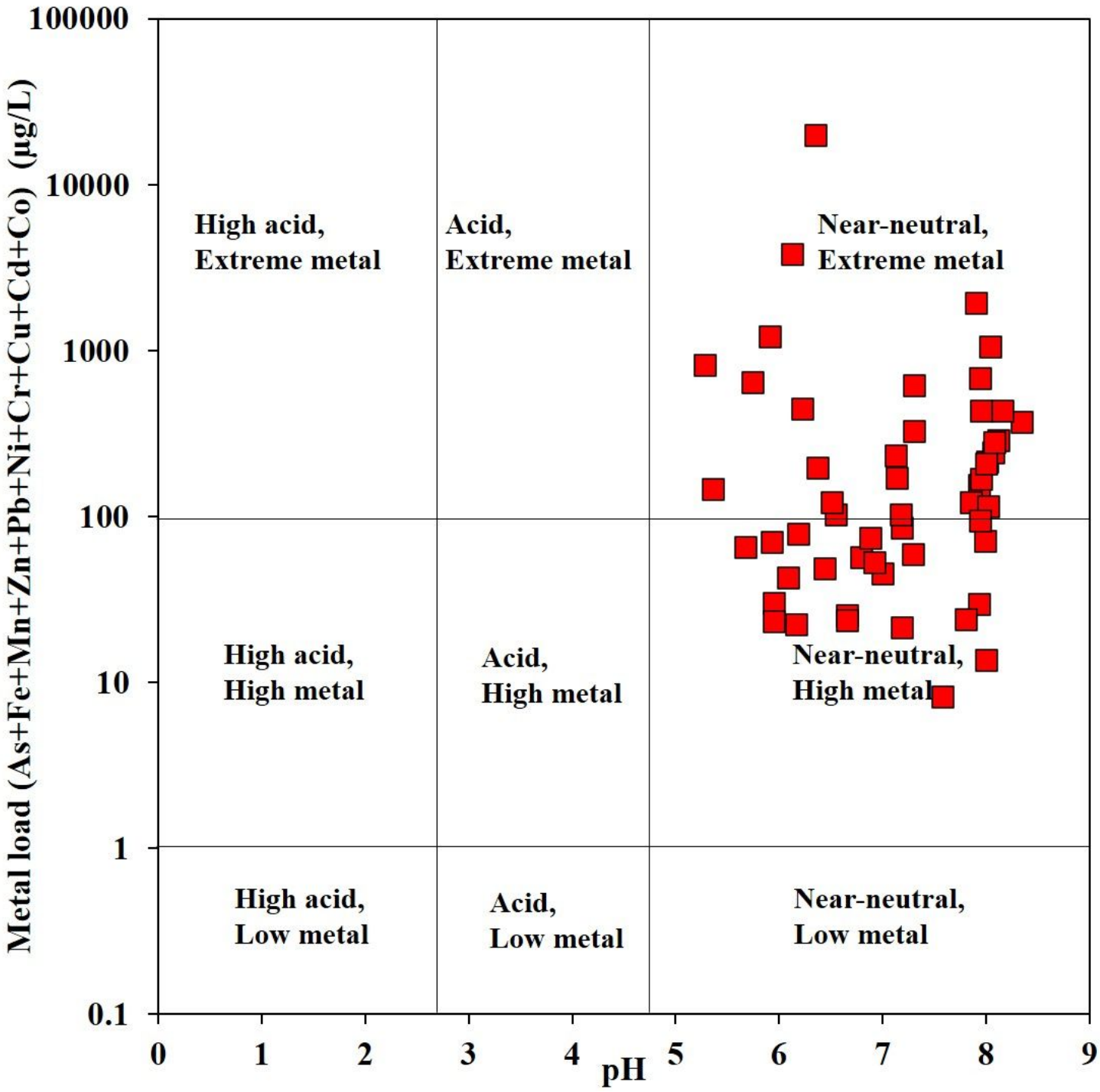

Figure 3

Classification of groundwater samples (pH versus metal load)

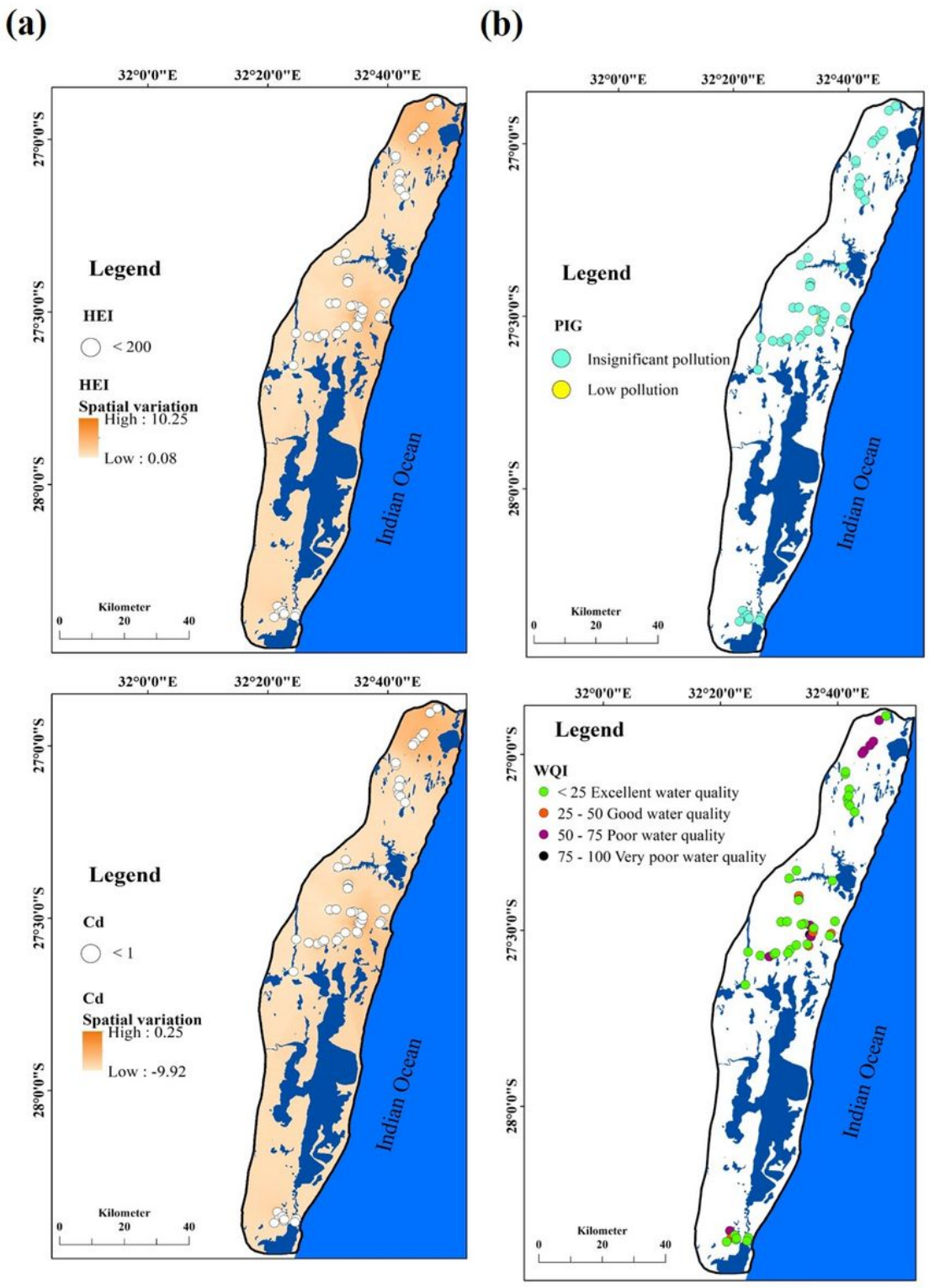

Figure 4

Spatial distribution of (a) heavy metal pollution indices and (b) drinking water quality indices

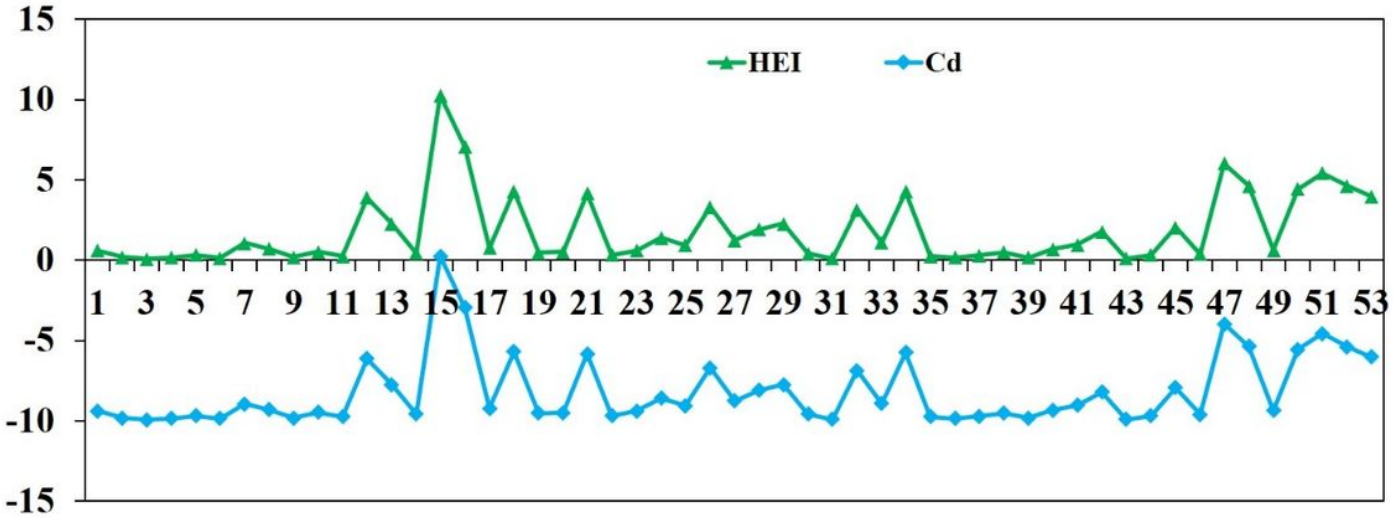

Figure 5

Comparison between pollution evaluation indices

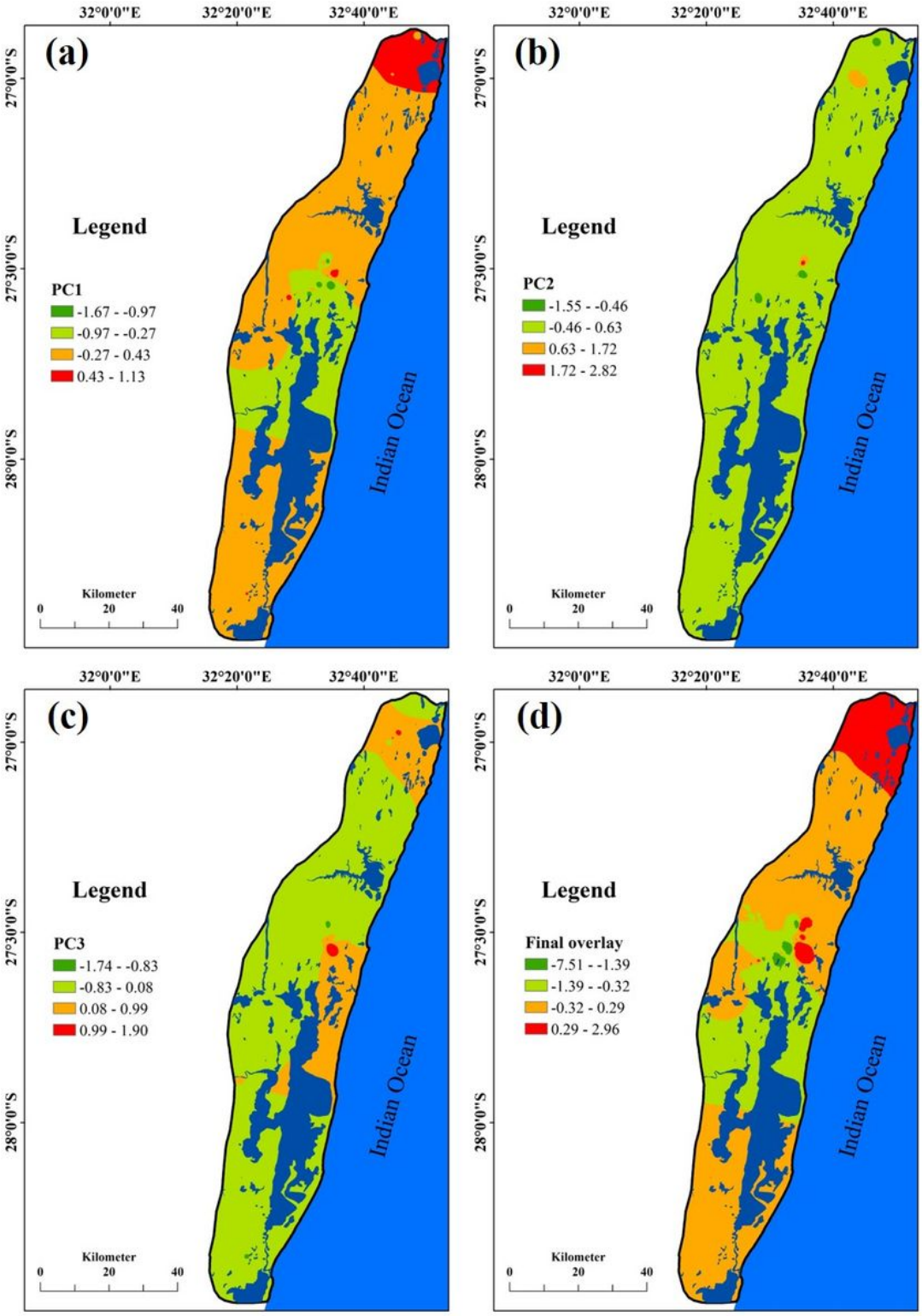

Figure 6

Spatial distribution of principal components in the study area (a) PC1, (b) PC2, (c) PC3, (d) final overlay map of principal components

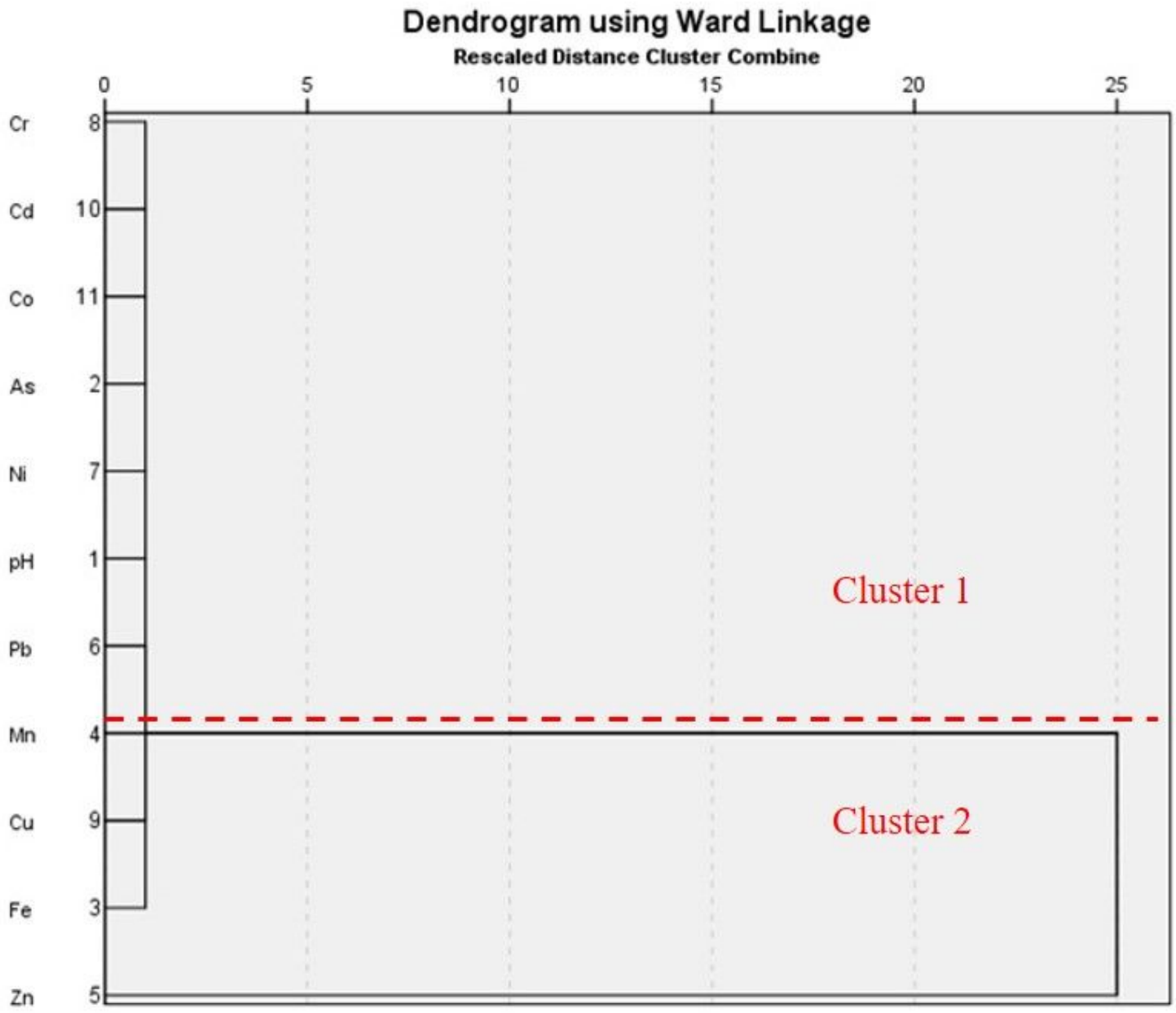

Figure 7

Dendogram grouping of analysed parameters

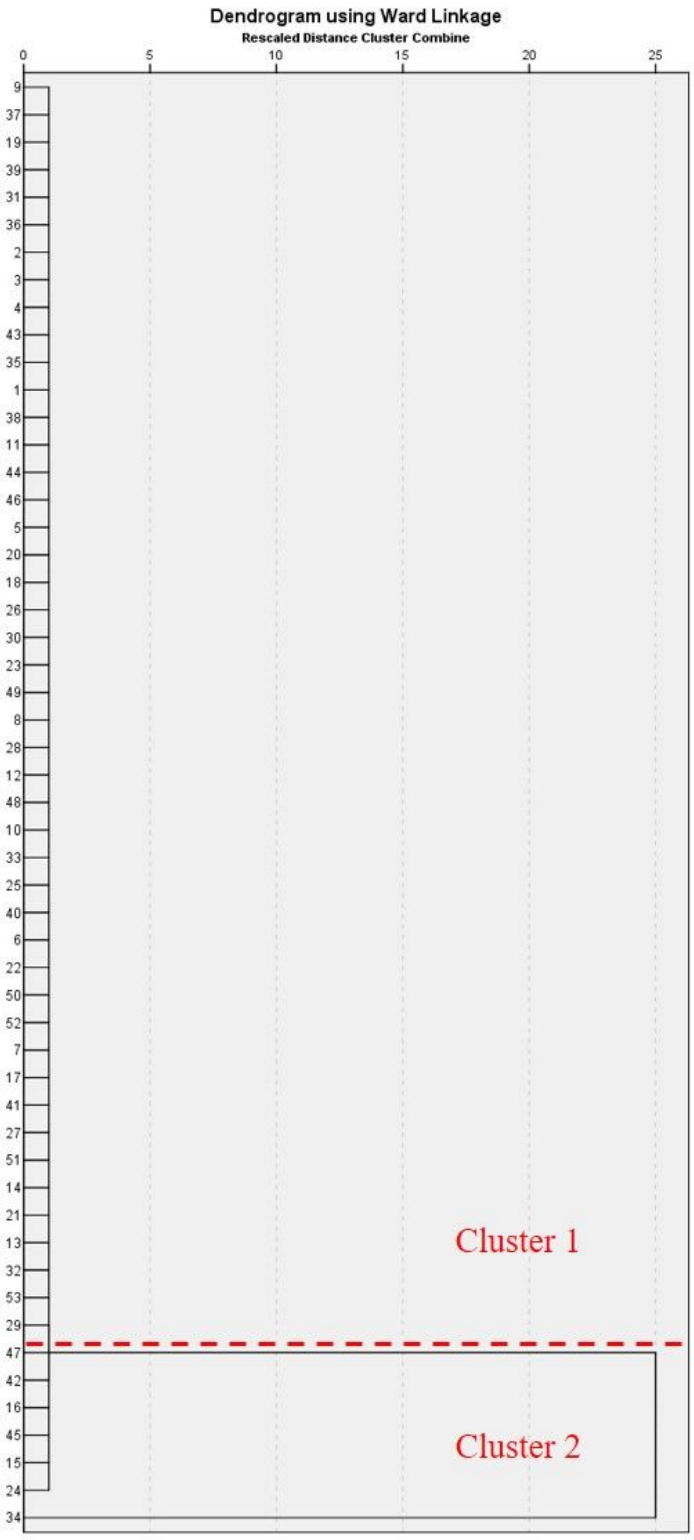

Figure 8

Dendogram grouping groundwater samples with respect to their heavy metal concentrations

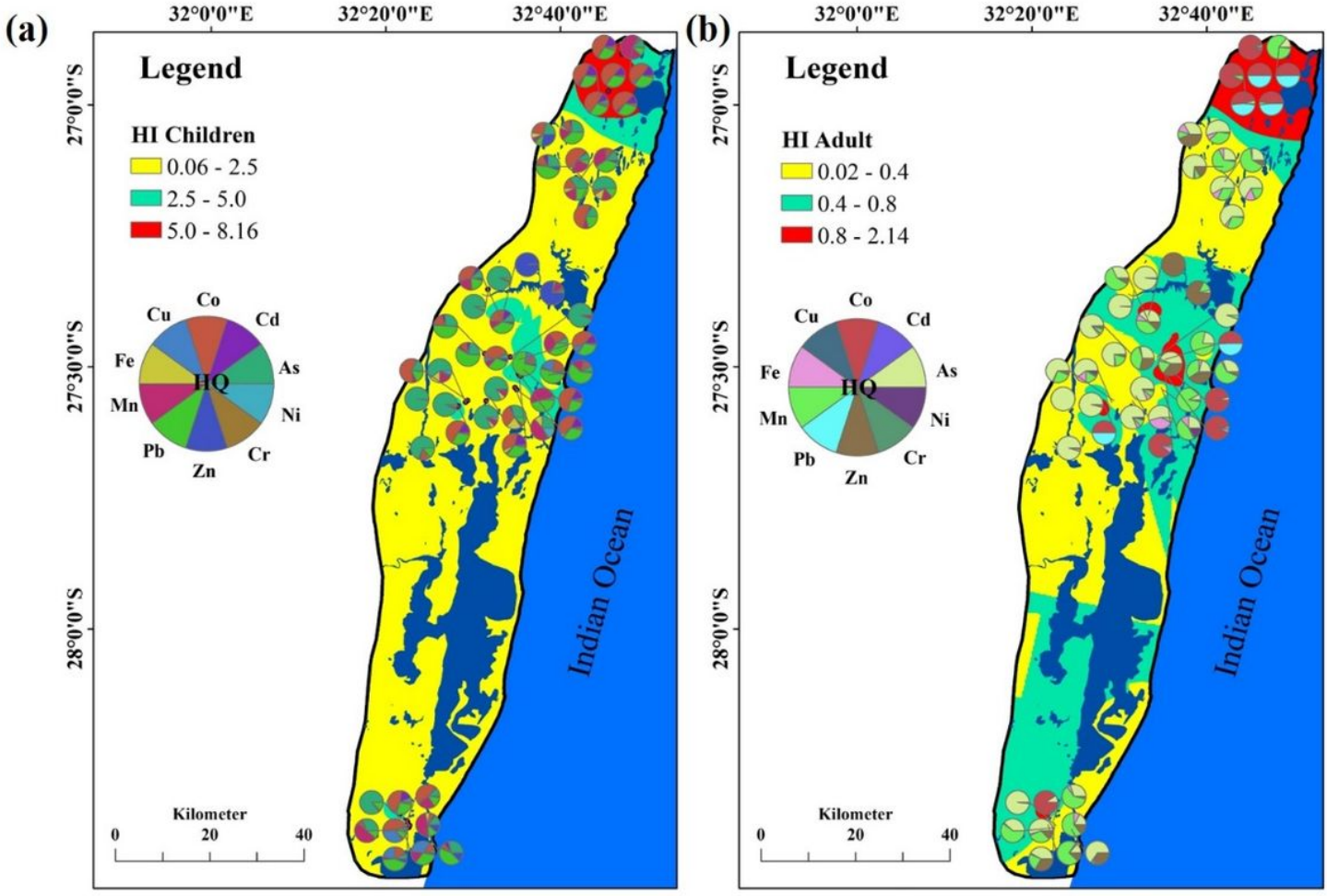

Figure 9

Spatial variation of HQ and HI values in (a) children and (b) adult.