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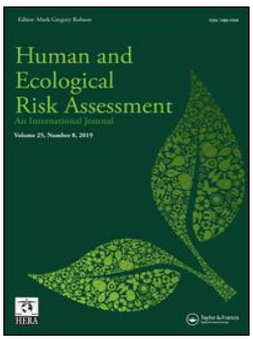
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Assessment of groundwater geochemistry and human health risk of an intensively cropped alluvial plain, NW Italy

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ABSTRACT

Groundwater chemistry data play an essential role to identify the water quality status and assess the exposure to human health. Therefore, in the present research, combined approaches used to assess the geochemistry, sources of ions and human health risk in the groundwater of the Tronzano Vercellese. Moreover, a geographic information system (GIS) technique was applied to identify locations have the most risk to human health. The results of the present study show that the groundwater samples had sequence of $Ca^{2+}>Mg^{2+}>Na^{+}>K^{+}$ in cationic, $HCO_3^{-}>SO_4^{2-}>NO_3^{-}>Cl^{-}>F^{-}$ in anionic and $Zn > Fe > Ba > Ni > Mn > Cu > Cr > As$ in metals abundance. The hydrogeochemical approaches indicate that the major ions chemistry was mainly controlled by the weathering of carbonate and silicate minerals, and ion-exchange reactions. Furthermore, statistical analysis reveals that the non-lithogenic origin was the primary sources of some elements (Mn, Zn, Ba, NO_3^{-} and K^{+}) in the water samples. The hazard quotient (HQ) and hazard index (HI) were estimated to assess the risk to human health using the United States Environmental Protection Agency (USEPA) methods. Estimated HQ and HI values were higher for the child as compared to the adult and suggesting that the elements posed little hazard individually in the case of the child.

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Introduction

A key objective of the European Directives 2000/60/EC and 2006/118/EC is to attain good ecological condition in water bodies. Likewise, in Italy, the legislation for water quality has been introduced a law (319/76) for the first-time emission standards for all discharges into watercourses and public sewers and introduced a law (D.Lgs 152/99) for the water protection plan. The Water Framework Directive (WFD) has been enforced in Italy through D.Lgs 152/06 and its modifications (D.Lgs 4/08), which provide a comprehensive treatment of the whole subject concerning the legislation on

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environmental matters. The Legislative Decree No. 152/06 is committed to the protection of waters against pollution and management of water resources. The Italian Legislative Decree 31/2001 has set 64 significance parameters of water for human consumption for all Italian reasons. Thus, to analysis and reporting of groundwater chemical data of Italian regions are very significant for the current and future groundwater resources management.

Assessment groundwater geochemistry and human health risk due to the consumption of metals in the groundwater is essential for the people of any area in the world. In the recent era, groundwater depletion and contamination are the most serious issue to society due to several factors, such as climate change, rock-water interaction, urbanization, agricultural, seawater intrusion, industrialization etc (Giménez-Forcada et al. 2010; Aeschbach-Hertig and Gleeson 2012; Huang et al. 2013; Kløve et al. 2014; Singh et al. 2015; Wu and Sun 2016; Morán-Ramírez et al. 2016: Vengosh et al. 2016: Sar et al. 2018; Selvakumar et al. 2017; Mukate et al. 2018; Abu-Alnaeem et al. 2018; Enitan-Folami et al. 2019; Qiu and Gui 2019; Subba Rao et al. 2019; Ahamad et al. 2020). Weathering of rocks, seawater intrusion and anthropogenic activities are highly responsible factors for the deterioration of groundwater quality in Italy (Debernardi et al. 2008; Capri et al. 2009; Ghiglieri et al. 2009; Giménez-Forcada et al. 2010; Sappa et al. 2014a, 2014b; Serio et al. 2018; Busico et al. 2018; Tiwari et al. 2019a).

Land use and land cover can affect the groundwater quality of any area (Singh et al. 2010; Morgenstern and Daughney 2012). Kulabako et al. (2007) studied the impact of land use on groundwater quality and observed that the informal settlements as solid waste dumps, animal rearing activities, excreta disposal systems and greywater are key factors for deterioration of groundwater quality at Kampala, Uganda. Aiuppa et al. (2003) stated that the natural and anthropogenic (agricultural and urban wastewaters) factors are responsible for the contamination of the Etna aquifers, Italy. Cidu et al. (2009) assessed the impact of past mining activity on groundwater of SW Sardinia, Italy and found that a high concentration of Pb in drinking water in the area. Pisciotta et al. (2015) reported that the groundwater of several regions of Italy is contaminated with nitrate due to the use of large-scale manure and fertilizers for farming. Furthermore, several researchers have reported that the groundwater of different region of Italy is contaminated with As (Sappa et al. 2014a, 2014b), Hg (Grassi and Netti 2000) and Cr^{VI} (Brunetti et al. 2014; Lelli et al. 2014; Tiwari et al. 2019b).

The risk to human health assessment due to intake of metals contaminated groundwater has recently increased in significance across the globe. In case of Italy, recently some researchers have assessed the human health risk due to groundwater contamination in the urban and industrial sectors (D'Ippoliti et al. 2015; Paladino and Massabò 2017; Tiwari and De Maio 2017; Riva et al. 2018). Furthermore, in agricultural areas of Italy, there is some information available on human health risk due to consumption of nitrate contaminated groundwater resources (Pisciotta et al. 2015; Paladino et al. 2018). However, there are not much data available on risk to human health due to the intake of metals in the groundwater resources of the agricultural areas of Italy. Therefore, the aims of the present research were(i) to assess the concentration of metals and major ions in the groundwater of an agricultural area; (ii) to evaluate the hydrogeochemistry and sources of elements; (iii) to calculate the health risk on adult and child; (iv) to

identify the high-risk zones in the study area using a GIS technique. The outcome of the present research could play the most vital role in taking quick groundwater management decisions by policymakers of the area.

Materials and methods

Study area

Tronzano V.se is situated in the Po River plain in Piedmont region of Italy and has an area around 45 km^2 with an elevation of 182 m. The water consumption for the municipality is around 196.000 m^3 (2015, http://dati.istat.it/Index.aspx?QueryId=20138). Usually, drinking water comes from wells (415 Mm^3) and then from springs (160 Mm^3) and the remaining from lake river and artificial basin (88 Mm^3) in Piedmont region. However, in Tronzano V.se population (3454, census 2019 https://www.tuttitalia.it/piemonte/85-tronzano-vercellese/statistiche/popolazione-eta-sesso-stato-civile-2019/) use wells water for drinking, domestic and irrigation. The study area climate is the continental Mediterranean and from 1994 to 2012, it has mean annual temperature of 12.7 °C with a maximum monthly mean of 26.3 °C in 2003 and a minimum of −0.9 °C in 2006. The mean annual rainfall from 1994 and 2012 is 878 mm with a maximum of 1197 mm in 2010 and a minimum of 511 mm in 2001 (Zhao et al. 2013). The major portion of Tronzano V.se is an agricultural area with approximately 65% of the study area. Around 27% of the area covered by forest, fruit crops and lawn, and 8% by other lands (such as urban areas and water bodies). The municipality of Tronzano V.se has a total of 11 farms (https://www.impresaitalia.info/013/1/aziende-agricole/tronzano-vercellese.aspx) and these farms mainly produce corn and rice. The north part of the municipality has mainly corn production, while the south part of the municipality is producing different types of rice.

The Tronzano V.se has "Fluvioglacial and Fluvial Riss" and "Fluvioglacial and Fluviale Würm" deposits (Figure 1), which formed after the incision of the glacial apparatuses through various occurrences (Bonsignore et al. 1969).

Fluvioglacial and Fluvial Riss: the sediments that give rise to this type of deposit refer to an interval of time that appears to be entirely included in the basal part of the Recent Pleistocene. These deposits are essentially made of clayey-sandy-gravelly materials and at their base, they present paleosols with a characteristic red-orange color (Giraudi 2014; De Luca et al. 2019).

Würm Fluvioglacial and Fluvial: it is sedimentary, alluvial in nature, which, fundamentally, fall into the category of substances characterized by a gravel-sandy granulometry, to which is added the presence of soil with the typical brown color that in some situations was found terraced. There are also some subordinate strips of soil that have a decidedly finer grain size, falling into the silty soils (De Luca et al. 2019).

The Tronzano V.se has two key hydrogeological complexes: gravel complex and multi-layered complex. The gravel complex consists of the alluvial mattress that contains the entire region, which is characterized by the alluvial fluvial and fluvioglacial alluvial successions. The gravel complex, mostly formed by sandy gravel, hosts a free aquifer located a few meters from the countryside and emerging in the area of the fountains. It is locally confined to areas where less permeable sediments form the roof of

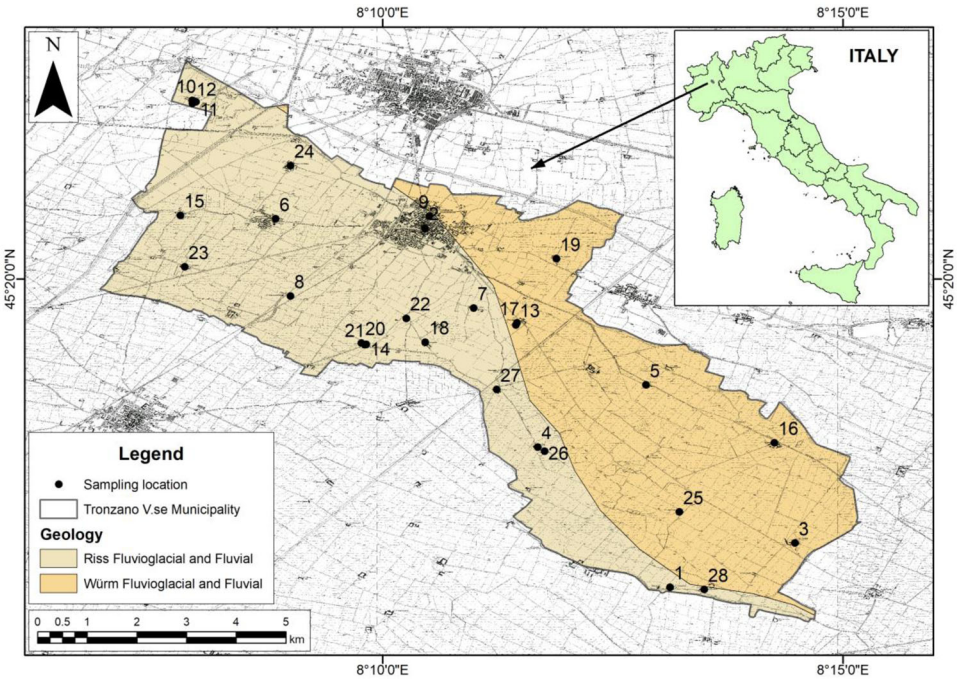


Figure 1. Geology and sampling location map of the Tronzano Vercellese.

gravelly sequences. The permeability value of the gravel complex varied between 10^{-1} and 10^{-3} m/s (Civita et al. 1990). However, the multi-layered complex consists of alternations of the gravel-sandy levels, with finer levels of the type from clay-silt to sandy-clay, with the presence of numerous peaty levels that can be linked to fluvial-lacustrine environments and in some cases marginal marine; these lithologies belong to lands of the Villafranchian age (De Luca et al. 2019). The complex has good permeability due to the grain size of sediments and their porosity, except for silts and clays that exhibit impermeable or semipermeable hydrogeological behaviors (Bove et al. 2004).

Sampling and analysis

Twenty-eight (n = 28) groundwater samples were collected from the 28 wells of the Tronzano V.se area during the month of July 2011 (Figure 1). Most of the wells are actively used for the drinking and irrigation uses in the area. In the study area, the average depth of wells was around 20 meters. Water samples were collected in 500 ml polyethylene bottles (high-density) for major ion analysis and in 250 ml bottles for metals analysis. Before the sampling stage, the wells were subjected to pumping for adequate time to drag the water from the aquifer. Electrical conductivity (EC) and pH values of the groundwater samples were monitored with a Hanna instrument (HI 9828) at the sampling location. In the research laboratory, collected groundwater samples were filtered through Millipore membrane filters paper (pore size 0.45 μm) to separate suspended particles. Bicarbonate concentration was analyzed by acid titration method. To analyses of concentrations of major anions (F^-, Cl^-, SO_4^{2-}, and NO_3^-) an ion

chromatography (Metrohm 883 Basic IC Plus) and for major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) atomic absorption spectrophotometry (AAS-Shimadzu AA6800) were used. Metals (As, Ba, Cr, Cu, Fe, Ni, Mn, and Zn) were analyzed by an inductively coupled plasma mass spectrometry (ICP-MS-Thermo Fisher Scientific X Series II).

Quality control

Proper quality assurance procedures and precautions were taken during the groundwater sampling and analysis to certify reliability and avoid contamination. Milli Q water (throughout the study), properly cleaned glassware and analytical grade reagents were used during the analysis processes. Moreover, reagent blank determinations were used to correct the instruments readings and the instruments were recalibrated after 15 samples. Certified Merck reference materials were used during the analysis of water samples. Furthermore, during the analysis of major cations using AAS, the RSD (relative standard deviation) value was obtained $<10\%$ for the entire samples. Moreover, the RSD value was obtained below 5% during the analysis of metals using ICP-MS. Anionic and cationic charge balance was found to be $<5\%$ during the study.

Hydrogeochemical and statistical

In the current research, significant hydrogeochemical approaches (Gibbs diagram, Piper diagram, saturation index (SI), Schoeller diagram, box diagram, scatter plots and ion exchange reactions) were used to evaluate the groundwater geochemistry of the area. Moreover, multivariate statistical analysis was applied to estimate the source of elements present in the groundwater.

Pollution index

Heavy metal pollution index (HPI) is a technique that rates the cumulative effect of individual heavy metal on the overall quality of water and is valuable in receiving a composite influence of all the metals on total pollution (Giri and Singh 2014). Prasad and Bose (2001) considered unit weightage (W_i) to compute the HPI. This value is inversely proportional to the recommended standard (S_i) of the corresponding parameter proposed by Reddy (1995). The critical pollution index of HPI value for drinking water as given by Prasad and Bose (2001) is 100.

For the present study, the concentration limits [i.e., highest permissive value for drinking water (S_i) and maximum desirable value (I_i)] for each parameter were obtained from the World Health Organization (WHO 2017) drinking water specifications. The S_i refers to the maximum acceptable concentration in drinking water in the absence of any alternate water source. Moreover, the I_i specifies the standard limits for the same parameters in drinking water. The HPI values of the groundwater water samples were computed as per Eq. (1), which was provided by Mohan et al. (1996). In the present study, the HPI value has calculated for each sampling location. The specimen calculation for the HPI using the mean value of metals is presented in Supplementary Table 1.

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_i \; Q_i}{\sum_{i=1}^{n} W_i} \tag{1}$$

where, Q_i is the sub-index of the ith parameter. W_i is the unit weightage of ith parameter, and n is the number of parameters considered.

The sub-index (Q_i) of the parameter is calculated by Eq. (2)

$$Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100 \tag{2}$$

where M_i is the monitored value of the heavy metal of the ith parameter, I_i is the ideal value (maximum desirable value for drinking water) of the ith parameter and S_i is the standard value (highest permissive value for drinking water) of the ith parameter. The sign (−) indicates the numerical difference between the two values, ignoring the algebraic sign.

Health risk assessment

Ingestion is the most significant source of exposure of humans to metals for drinking water (USEPA (US Environmental Protection Agency) 2004; De Miguel et al. 2007; Wu et al. 2009; Giri and Singh 2015). The dose received through ingestion was determined using Eq. (3) from the US Environmental Protection Agency (USEPA (US Environmental Protection Agency) 1989). In the present study, the average daily dose (ADD) value has calculated for each sampling location. The specimen calculation for the ADD using the mean value of metals is presented in Supplementary Table 1.

$$\mathrm{ADD} = (C_w \times IR \times \mathrm{EF} \times \mathrm{ED})/(\mathrm{BW} \times \mathrm{AT}) \tag{3}$$

where, ADD represents the average daily dose (µg/kg/day), C_w is the concentration of metals in water (µg/L), IR is the ingestion rate (L/day), EF is the exposure frequency (days/year), ED is the exposure duration (years), BW is the body weight (kg), and AT is the averaging time (days). In the present study, EF of 350 days and ED of 6 and 30 years for child and adult respectively were used for the calculations. The AT was calculated by multiplying ED by 365 days. The IR of 1 L/day and body weight of 15 kg was used for the child. However, bodyweight of 70 kg and water consumption of 2 L/day was used for the calculations for the adult (USEPA (US Environmental Protection Agency) 1989, 2004).

In the present study, non-cancer health risk, reflected by the hazard quotient (HQ) was calculated.

$$\mathrm{HQ} = \mathrm{ADD}/\mathrm{R_fD} \tag{4}$$

where, R_fD is the reference dose according to the USEPA risk-based concentration table (USEPA IRIS (US Environmental Protection Agency's Integrated Risk Information System) 2011)

For the risk assessment of multiple metals in the drinking water, a hazard index (HI) was employed by summing all the calculated HQ values of metals as described in Eq. (5). HI $>$ 1 indicated the potential for an adverse effect on human health and the necessity for further study (USEPA (US Environmental Protection Agency) 1989, 2004).

$$HI = \sum_{i=1}^{n} HQ_i \quad (5)$$

where, HQ_i is the hazard quotient of an individual metal, HI is the hazard index for all the eight metals studied in the present study and n is 08.

Geographic information system (GIS)

GIS is a valuable software for storing, handling and demonstrating spatial environmental data, including water (Clarke 1995; Nas and Berktay 2010; Tiwari et al. 2019b). In water quality mapping and water resources management, the role of GIS is constantly on the rise (Tsihrintzis et al. 1996). In the present study, the average distance between sampling points was 4.5 km. The inverse distance weighted (IDW) interpolation technique of ArcGIS 10.7 software was used for the spatial distribution analysis of the analyzed and calculated indices of the groundwater samples.

Result and discussion

Groundwater chemistry

The analyzed groundwater samples had pH from 6.9 to 8.6 and indicate near neutral to slightly alkaline in nature. Groundwater samples had electrical conductivity (EC) from 190 to 442 µS cm^{-1} and had the highest 335 mg/L total dissolved solids (TDS) value in the study area (Table 1). In the case of major ion chemistry, HCO_3^- (54%), Ca^{2+} (16%), SO_4^{2-} (10.5%), NO_3^- (8%), and Mg^{2+} (5%) were dominant dissolved ions and the major contributor to the TDS in the groundwater of the area. However, Cl^- (4%) and Na^+ (2%) were a minor contribution to the TDS. Potassium and fluoride contributed very little toward the TDS solute load.

Calcium and magnesium were the dominant ions and majorly contributed to the total cation equivalent concentrations (TZ^+) as compared to the sodium and potassium ion in the study area (Figure 2a). However, bicarbonate and sulfate were dominant ions and majorly contributed to the total anion equivalent concentrations (TZ^-). Nitrate and chloride were fewer dominant ions and contributor to TZ^- (Figure 2b). Moreover, fluoride ion was a very little contributor to TZ^-. In the study area groundwater, $Ca^{2+}>Mg^{2+}> Na^+>K^+$ and $HCO_3^->SO_4^{2-}>NO_3^->Cl^->F^-$ sequence was found in the cationic and anionic abundance, respectively.

Hydrogeochemical facies and water type

The Piper (1944) trilinear diagram help to assess the geochemical relationship among different dissolved ions and evaluate the dominant water type. Around 86% groundwater samples plot in the Ca^{2+} dominance zone, 10% in the Mg^+ dominance zone and 100% in the HCO_3^- dominance zone, respectively. The Piper diagram shows that the groundwater samples 1 to 4 (inside a blue color box) had high dominance of bicarbonate (HCO_3^-) and samples 13, 23, 25 and 28 (inside a yellow color box) had high dominance of Mg in the area. The diamond-shaped diagram demonstrates that the study area groundwater had Ca-Mg-HCO_3 type water (Figure 3). Moreover, the Schoeller

Table 1. Summary statistics of the analytical data of the groundwater samples and compared with the WHO drinking water guidelines.

Parameters	Minimum	Maximum	Mean	Std. deviation	WHO, 2017
pH	6.9	8.6	7.7	0.5	6.5–8.5
EC	190	442	296.9	49.9	–
TDS	186.1	355	273.4	42.7	600
F^-	0.0	0.1	0.04	0.01	1.5
Cl^-	1.3	18.4	9.9	4.7	250
HCO_3^-	109	195.1	147.9	26	–
SO_4^{2-}	3.5	53.3	28.7	11.4	250
NO_3^-	1.2	36.1	22.6	9.9	50
TH	4.7	72.8	51.3	19	100
Ca^{2+}	27.9	62.3	42.8	10.3	–
Mg^{2+}	8.3	33.5	14.6	5.1	–
Na^+	3.1	8.4	5.1	1.4	200
K^+	1.0	4.0	1.6	0.7	–
As	0.1	1.3	0.4	0.4	10
Ba	8.9	29.5	16.5	4.0	1300
Cr	0.1	9.1	2.6	2.2	50
Cu	0.5	30.0	3.9	5.7	2000
Fe	0.1	134.2	16.8	28.8	300
Mn	0.1	63.8	4.0	11.9	100
Ni	0.1	47.6	14.1	12.9	70
Zn	1.9	2547	200.8	502.1	4000

Unit: mg/L, except pH, EC ($\mu S\ cm^{-1}$), and metals (μg/L)

diagram (1965) used to understand the chemical composition of different groundwater samples. The Schoeller diagram is graphically characterized major ions of numerous water samples, which is significant to easily identify the chemical composition/water type of any area. Schoeller diagrams show four significant chemical composition of the groundwater, such as HCO_3-Ca, HCO_3-Ca-Mg, Ca- HCO_3 and HCO_3-Mg-Ca in the study area (Supplementary Fig. 1). In this study, 39.3% of groundwater samples was HCO_3-Ca type, 25% of HCO_3-Ca-Mg type, 21.4% of Ca-HCO_3 type and 14.3% of HCO_3-Mg-Ca type, respectively (Figure 5). The Piper and Schoeller diagram suggested that the weathering of minerals was the main sources of these ions in water.

Zones	Characteristics of water
1	Alkaline earth (Ca + Mg) exceed alkalies (Na + K)
2	Alkalies exceed alkaline earth
3	Weak acids (CO_3+ HCO_3) exceed strong acids (SO_4+ Cl)
4	Strong acids exceed weak acid
5	Carbonate hardness (secondary alkalinity) exceeds 50%
6	Non-carbonate hardness (secondary salinity) exceeds 50%
7	Non-carbonate alkali (primary salinity) exceeds 50%
8	Carbonate alkali (primary alkalinity) exceeds 50%
9	No one cation-anion pair exceeds 50%

Mechanisms controlling groundwater chemistry

Gibbs diagrams (Gibbs 1970) are usually applied to calculate the efficient sources of dissolved ions in water, such as evaporation, weathering of rocks and precipitation occurrence. The Gibbs diagrams represent the $Cl^- + NO_3^-/(Cl^- + NO_3^- + HCO_3^-)$ and $Na^+ + K^+/(Na^+ + K^+ + Ca^{2+})$ ratio as a function of TDS values. The plot of proper

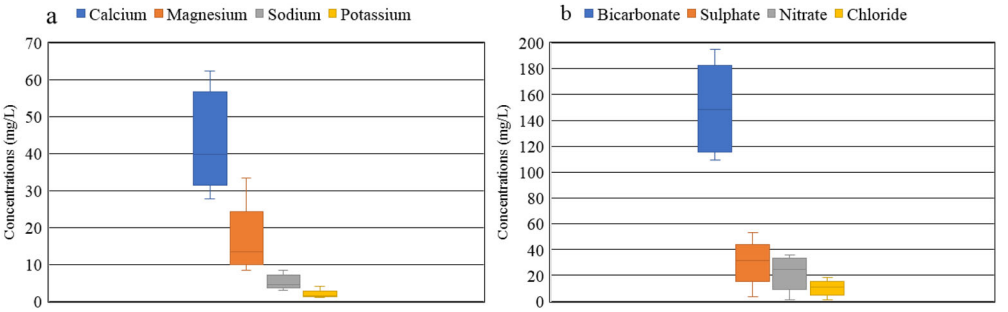
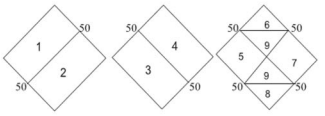


Figure 2. (a, b) Box diagram of major cations and major anions.



Zones	Characteristics of water
1	Alkaline earth (Ca+Mg) exceed alkalies (Na+K)
2	Alkalies exceed alkaline earth
3	Weak acids (CO_3+ HCO_3) exceed strong acids (SO_4+ Cl)
4	Strong acids exceed weak acid
5	Carbonate hardness (secondary alkalinity) exceeds 50%
6	Non-carbonate hardness (secondary salinity) exceeds 50%
7	Non-carbonate alkali (primary salinity) exceeds 50%
8	Carbonate alkali (primary alkalinity) exceeds 50%
9	No one cation-anion pair exceeds 50%

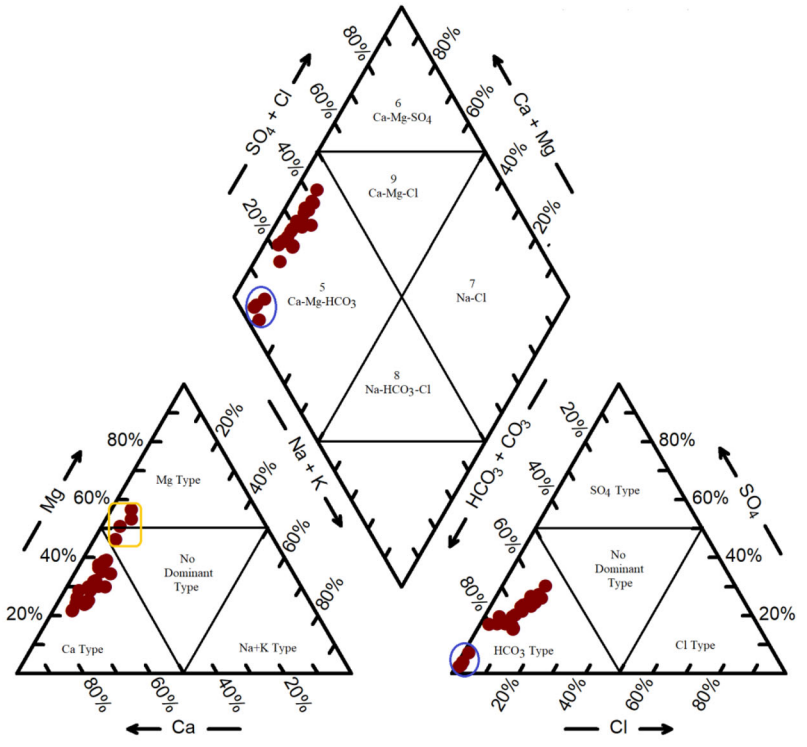


Figure 3. Piper's trilinear diagram showing the relationship between dissolved ions and water type.

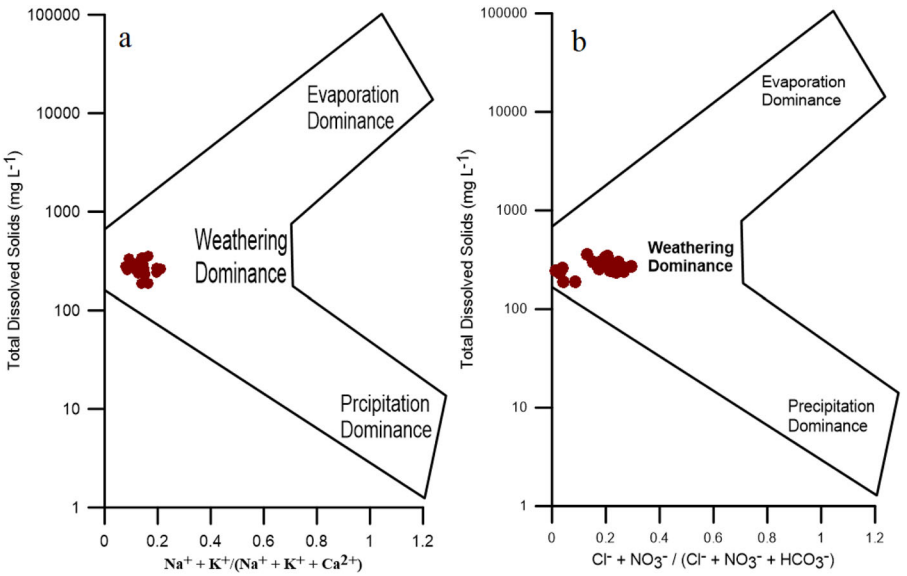


Figure 4. Gibbs diagram representing the ratio of (a) $Na^+ + K^+/(Na^+ + K^+ + Ca^{2+})$ and (b) $Cl^- + NO_3^-/(Cl^- + NO_3^- + HCO_3^-)$ as a function of TDS.

geochemical data on Gibbs diagrams indicates that the weathering of rocks was controlling the chemistry of groundwater in the study area (Figure 4a,b).

On the plot of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2-})$, samples fall close to 1:1 line if the dissolution of calcite, dolomite and gypsum are the dominant reactions in a system. However, fall above the equiline probably due to excess of $Ca^{2+} + Mg^{2+}$ ions in water and these ions can be potential release by the silicate weathering (e.g., $CaMgSiO_6 + 4H^+ = Ca^{2+} + Mg^{2+} + 2SiO_2 + 2H_2O$) or possibly by the reverse ion exchange processes. Moreover, fall below the aquiline, indicate the significant contribution from non-carbonate source (Cerling et al. 1989; Fisher and Mullican 1997; Rajmohan and Elango 2004, Tiwari et al. 2019b). In the present case, the scatter plot of $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$ (Figure 5a) shows that the groundwater chemistry of the area was mainly controlled by the weathering of carbonate and silicate minerals, as well as reverse ion exchange processes. Poor correlation (0.22) between Ca^{2+} and SO_4^{2-} (Table 2) suggested that the gypsum dissolution could not be the major contributor of Ca^{2+} in the present case. The molar ratio of Ca/Mg = 1 if the dissolution of dolomite, while if the ratio between 1 to 2, indicate calcite dissolution (Mayo and Loucks 1995; Kuldip-Singh et al., 2011). Furthermore, if ratio >2, suggest the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater (Katz et al. 1997). The plot of Ca/Mg ratio reveals that the 14.3% and 39.3% of the samples had dominance dolomite and calcite dissolution, while 46.4% of the water samples had dominance of silicate weathering in the study area (Figure 5b). Similarly, the plot of Mg/Na versus Ca/Na support that the carbonate and silicate minerals weathering were the controlling factors of the groundwater chemistry in the area (Figure 5c). Positive correlation of HCO_3^- with Na^+ (0.55) and Ca^{2+} (0.53) (Table 2) were verified the above observation.

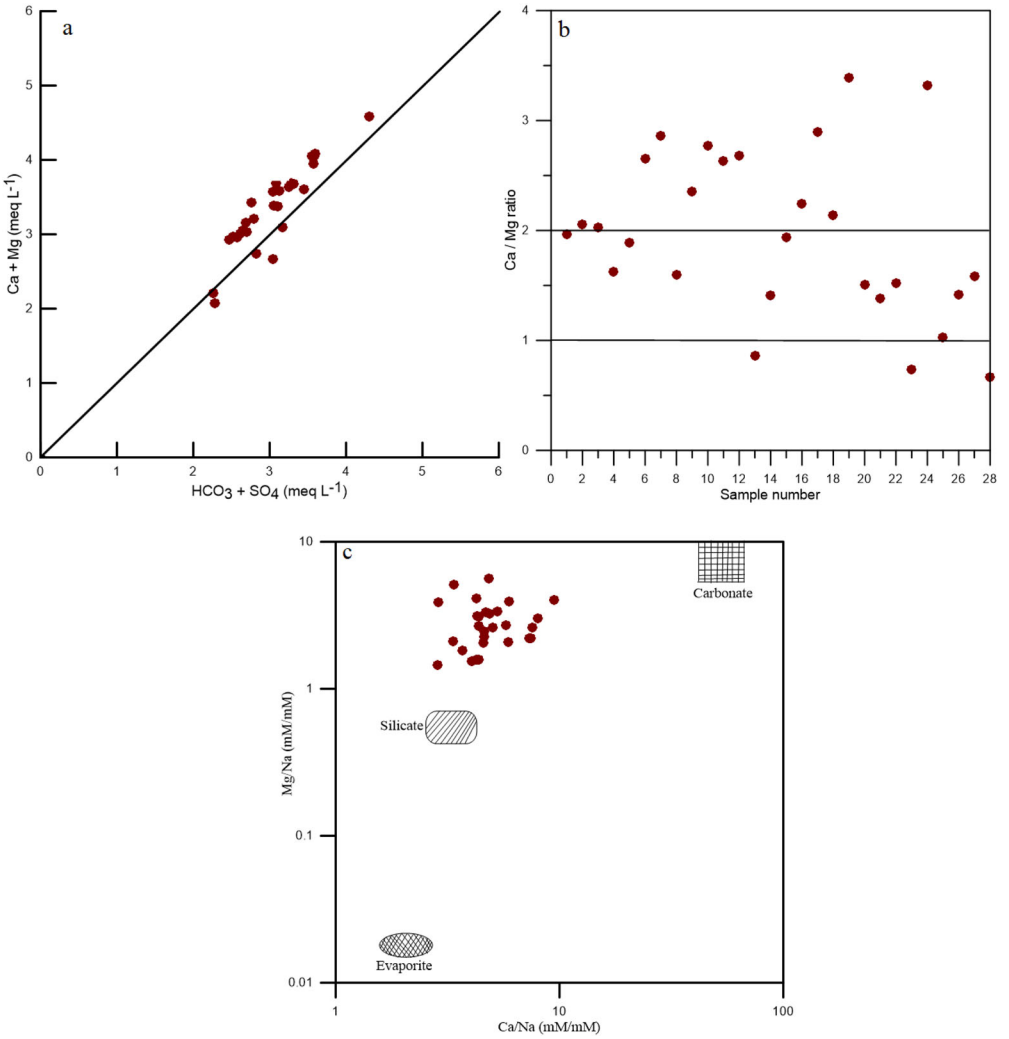


Figure 5. (a) Plot of (Ca^{2+} + Mg^{2+}) versus (HCO_3^- + SO_4^{2-}), (b) Ca/Mg ratio, (c) Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ relating carbonate and silicate end members (mM).

Table 2. Inter-elemental correlation matrix of dissolved ions (n = 28).

	pH	EC	TDS	F^-	Cl^-	HCO_3^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
pH	1.00	−0.27	−0.01	−0.05	−0.49	0.47	−0.63	−0.38	0.23	−0.40	0.18	−0.23
EC		1.00	0.75	−0.08	0.55	0.44	0.50	0.43	0.64	0.17	0.42	0.41
TDS			1.00	−0.29	0.70	0.70	0.53	0.47	0.76	0.36	0.56	0.13
F^-				1.00	−0.33	0.09	−0.34	−0.53	−0.47	0.17	0.08	−0.16
Cl^-					1.00	0.06	0.88	0.69	0.36	0.54	0.42	0.06
HCO_3^-						1.00	−0.14	−0.20	0.55	0.14	0.54	0.03
SO_4^{2-}							1.00	0.58	0.22	0.56	0.07	−0.05
NO_3^-								1.00	0.47	0.09	0.11	0.30
Ca^{2+}									1.00	−0.31	0.36	0.20
Mg^{2+}										1.00	0.13	−0.16
Na^+											1.00	0.23
K^+												1.00

Table 3. Principal component loadings (varimax normalized) of the groundwater samples (n = 28).

Elements	Factor_1	Factor_2	Factor_3
As	−0.81	−0.33	0.29
Ba	0.09	0.26	0.84
Cr	−0.59	−0.30	−0.57
Cu	0.64	−0.27	0.01
Fe	0.07	0.20	−0.77
Mn	0.04	0.95	0.03
Ni	0.85	−0.01	0.22
Zn	−0.03	0.89	0.05
Eigenvalues	2.2	2.1	1.8
%Total variance	27	26	22
Cumulative variance	27	53	75

The chloro-alkaline indices (CAI-I and CAI-II) provide significant evidence concerning the ion exchange reactions among the aquifer materials and groundwater of any area. The chloro-alkaline indices were proposed by Schoeller (1977) and expressed as:

$$\mathrm{CAI - I} = \mathrm{Cl^- - (Na^+ + K^+)/Cl^-} \quad (6)$$

$$\mathrm{CAI - II} = \mathrm{Cl^- - (Na^+ + K^+) / SO_4^{2-} + HCO_3^- + NO_3^-} \quad (7)$$

The chloro-alkaline indices could be either negative or positive. When Na^+ and K^+ ions in water are exchanged with Mg^{2+} and Ca^{2+}, the value of CAI will be positive, and it shows a reverse ion exchange reaction (Zaidi et al. 2015). However, low salt waters give negative value indicating chloro-alkaline disequilibrium, and it shows a cation-anion exchange phenomenon (Srinivasamoorthy et al. 2014). In the study area, the CAI-I and CAI-II show that 71% of samples had positive values and suggested a reverse ion-exchange reaction. Moreover, the rest of the water samples had negative values of the CAI-I and CAI-II, revealing chloro-alkaline disequilibrium, and it is a cation-anion exchange reaction.

Metal distribution and sources

Table 1 shows the statistical results of the analyzed metals (As, Ba, Cr, Cu, Fe, Mn, Ni and Zn) in the groundwater samples and compared with the World Health Organization (WHO 2017) drinking water guideline. The results, as shown in Table 1, the concentrations of metals in water samples were within the drinking water limits established by the WHO (2017). Concentrations of analyzed metals have followed the sequence of Zn > Fe > Ba > Ni > Mn > Cu > Cr > As in the study area.

The principal component analysis (PCA) of analyzed metals confirm that the lithogenic origin were the main sources of metals in the first factor. The second factor of PCA shows high loading of Mn and Zn and probably it was due to the non-lithogenic origin (Table 3). In the study area, around 65% of the area is occupied by the agricultural field and support this observation. A similar observation has been reported by the Rajmohan and Elango (2005) in groundwater of the Cheyyar river basins, South India. They have reported that the leaching of agricultural fertilizers was the major source of high concentration of these metals in groundwater of the area. The third factor of PCA had high loading of Ba and possibly it was due to the vehicular pollution. Hopke et al. (1980) and Kennedy and Gadd (2000) have reported that the Ba element is present in

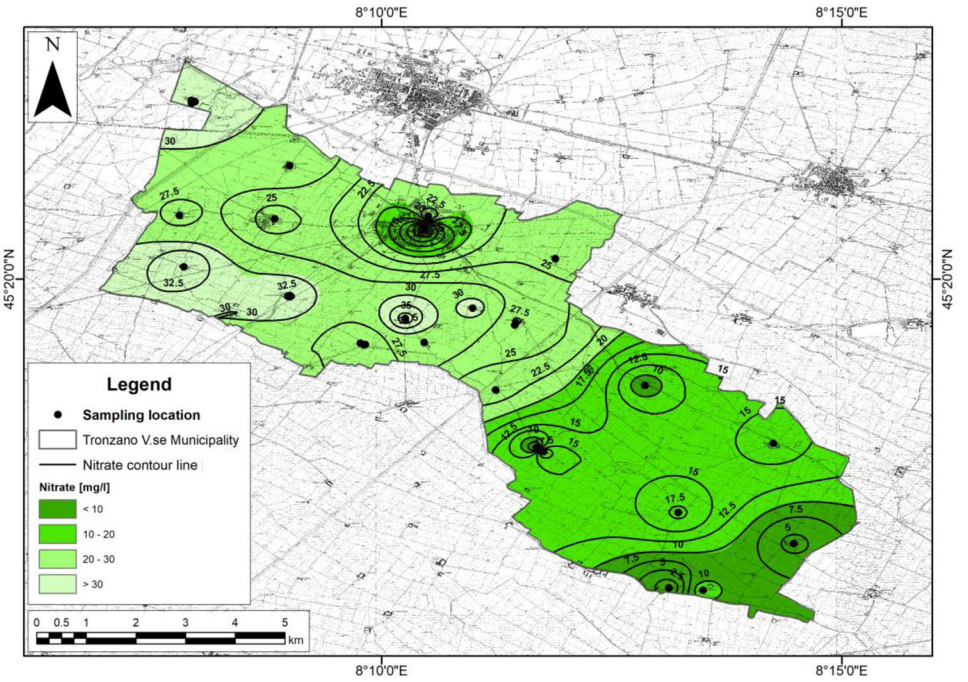


Figure 6. Spatial distribution map of NO_3^- in the area.

fuel additives, as well as in filters, which are utilized in the brake linings (barite form) and tires of vehicles.

Water suitability for drinking and domestic uses

The pH values of the groundwater samples in the study area were within the World Health Organization (WHO 2017) drinking water guideline, except one location. As per the WHO (2017) drinking water guidelines, TDS value of <600 mg/L is good for drinking uses, and increasingly unpalatable at >1000 mg/L. In the present case, groundwater samples had a maximum TDS value of 335 mg/L (Supplementary Fig. 2; Table 1). There are no health-based guideline values for SO_4^{2-}, Ca^{2+}, Mg^{2+} and total hardness (TH) in the WHO (2017) guidelines. Concentrations of F^-, Cl^-, and Na^+ in the groundwater samples were within the recommended drinking water limit of 1.5 mg/L, 250 mg/L, and 200 mg/L by the WHO (2017). The concentration of NO_3^- ranged from 1.2 mg/L to 36.1 mg/L in the water samples and below the WHO guidelines of NO_3^- (50 mg/L) ion. The sample number one had the lowest NO_3^- value and sample number 22 had highest NO_3^- concentration in the area (Figure 6). Furthermore, some samples (7, 8, 10, 11, 12, 22 and 23) had a moderate contamination (>30 mg/L) in the study area (Figure 6). The concentration of nitrate in the groundwater at farming region depends on the type of crop, type and control of surface manure loadings, soil nitrate levels etc. (Di and Cameron 2002). In the present study, nitrate concentrations were varied from a low level to a moderate level and this probably due to modulated fertilizers used by the farmers to produce the different variety of crop in the area (Zavattaro et al. 2006).

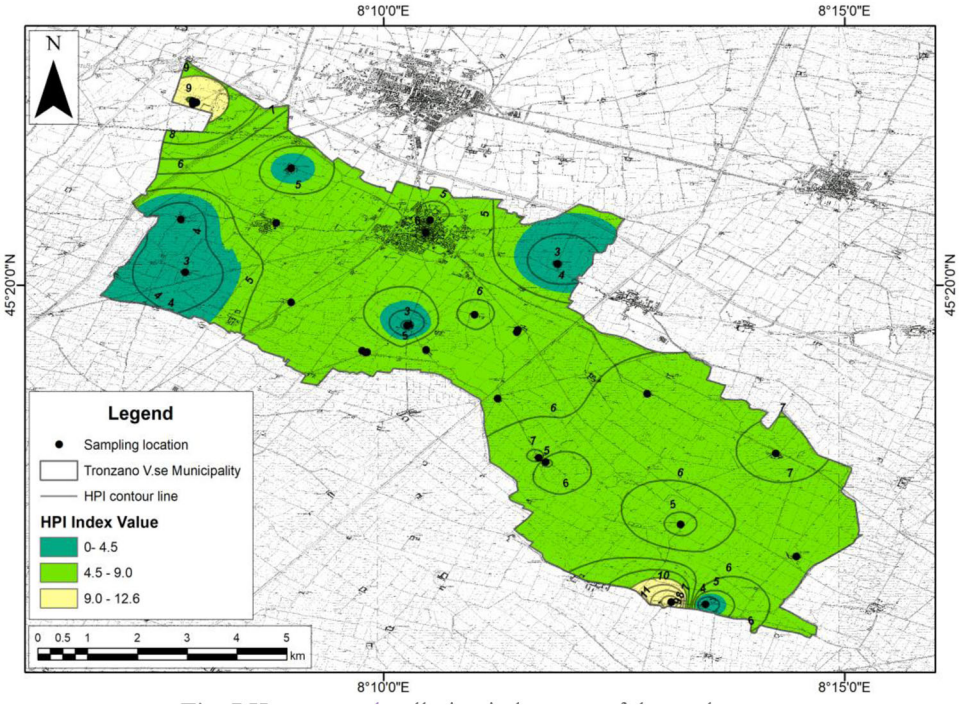


Figure 7. Heavy metal pollution index map of the study area.

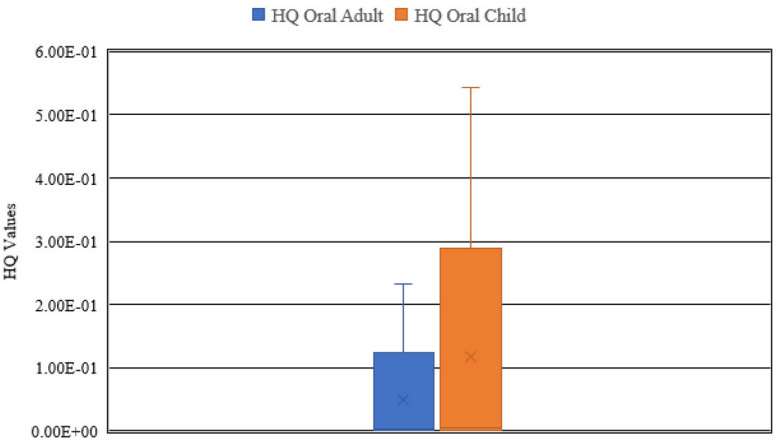


Figure 8. Box diagram of the hazard quotient for the adult and child.

Heavy metal pollution index (HPI)

The HPI was calculated to evaluate the extent of pollution and suitability of the groundwater for drinking uses. The concentration of the analyzed metals (As, Ba, Cr, Cu, Fe, Mn, Ni and Zn) were considered during the calculation of HPI values. The HPI values ranged from 2.7 to 12.6 (mean 5.9) in the groundwater of the study area. The highest HPI values were found in location 1, 10, 11 and 12 in the study area (Figure 7). As per Prasad and Bose (2001), 100 is the critical pollution index of HPI value for drinking

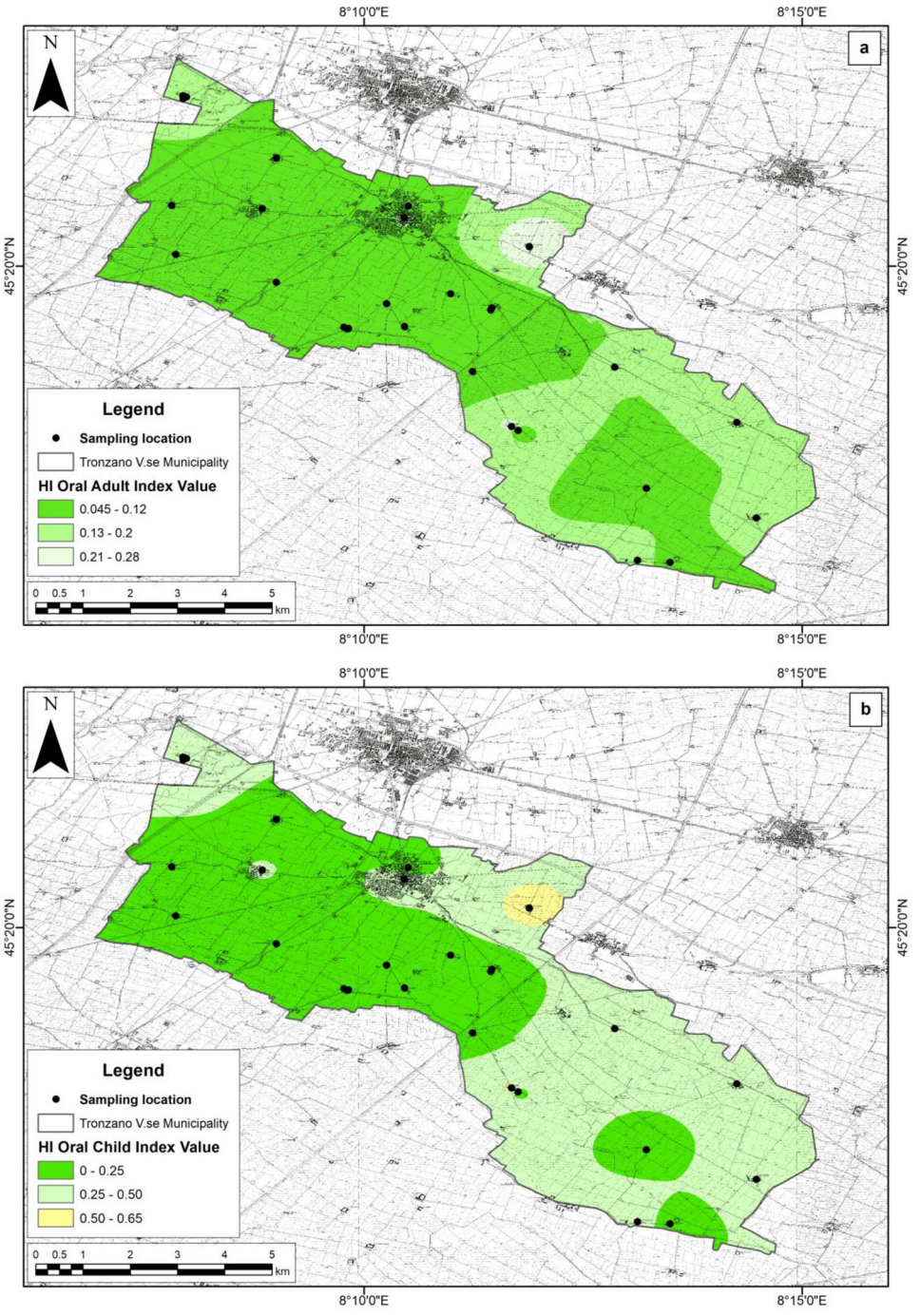


Figure 9. (a, b) HI oral index for the adult and child in the study area.

water. Moreover, Edet and Offiong (2002) suggested a modified scale using three classes based on HPI values, such as low, medium and high for HPI values < 15, 15–30 and > 30, respectively. In the present study, the HPI values in the water

samples were below the critical HPI value and belonged to low class and indicate suitable for drinking uses.

Health risk assessment

The hazard quotient (HQ) and hazard index (HI) level for the oral pathway relating to adult and child of the study area were estimated. The HQ values for the adult varied from 3.91E-06 to 2.33E-01 (mean 1.38E-02) and for the child ranged from 9.13E-06 to 5.43E-01 (mean 3.23E-02) in the study area (Figure 8). However, in the case of the HI values, the groundwater samples had a minimum of 0.05 and maximum of 0.28 with an average 0.11 for the adult (Figure 9a) and 0.11 to 0.65 (avg. 0.26) for the child (Figure 9b) in the water samples, respectively. In the study area, the sample 19 had the highest HQ and HI values for the adult and child and followed by the samples 4, 1, 11, 12 and 10, respectively (Figure 9a,b). We observed that the HQ and HI values were higher for the child as compared to the adult case in the groundwater of the area. The HQ and HI values were below the <1 for both adult and child in the study area. The water samples had maximum HQ value of 0.23 and 0.54 and the HI value of 0.28 and 0.65 for the adult and child, suggesting that these elements posed little hazard individually in the case of the child as compared to the adult in the study area, respectively.

Conclusion

The groundwater of the Tronzano V.se. was near neutral to slightly alkaline and had HCO_3-Ca, HCO_3-Ca-Mg, Ca- HCO_3 and HCO_3-Mg-Ca types water. The analyzed parameters were below the drinking water guidelines established by the WHO 2017 in the study area. Furthermore, the HPI values were within the critical pollution index limit and suggested that water was suitable for drinking and domestic uses. Estimated HQ and HI values were below the <1 for both adult and child in the groundwater samples of the area. The HQ and HI values were higher for the child as compared to the adult and suggesting that the elements posed little hazard individually in the case of the child. Lithology was the primary sources of most of the analyzed parameters in the groundwater samples. Weathering and dissolution of carbonate and silicate minerals and reverse ion-exchange reaction were the main controlling factor of the groundwater chemistry in the study area. Furthermore, anthropogenic activities were responsible for contribution in concentrations of some elements (Zn, Mn, Ba, NO_3^- and K^+) in the groundwater of the study area.

From the environmental degradation and groundwater management point of view: a) there was no contaminant observed in the groundwater of the area that would have a detrimental effect on the environment; b) the outcome of the present research suggests that the combined approach of hydrogeochemical, statistical, human health risk and GIS provided a significant knowledge to the management of current and future groundwater resources of the area; c) this kind of combined approach research could be important for agricultural areas of other similar regions; d) our research recommends that the monitoring of groundwater program is required in future to assess the variations in the concentration of elements and their impact on human health in the area.

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