

Assessment of groundwater quality for irrigation: a case study from Bandalamottu lead mining area, Guntur District, Andhra Pradesh, South India

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Abstract Quality of water resources in the Bandalamottu area of Guntur District of Andhra Pradesh in South India is facing a serious challenge due to Pb mining. Therefore, 40 groundwater samples were collected from this area to assess their hydrogeochemistry and suitability for irrigation purposes. The groundwater samples were analyzed for distribution of chemical elements Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , CO_3^{2-} , F^- , Cl^- , and SO_4^{2-} . It also includes pH, electrical conductivity, total hardness, non-carbonate hardness and total alkalinity. The parameters, such as sodium absorption ratio (SAR), adjusted SAR, sodium percentage, potential salinity, residual sodium carbonate, non-carbonate hardness, Kelly's ratio, magnesium ratio, permeability index, indices of base exchange (IBE) and Gibbs ratio were also calculated. The major hydrochemical facieses were Ca– HCO_3 , Ca–Na– HCO_3 and Ca–Mg–Cl types. The result of saturation index calculated by Visual MINTEQ software combined with Gibbs diagram and IBE findings indicate that, dolomite and calcite dissolution and reverse ion exchange can be a major process controlling the water chemistry in the study area. The results also showed that the salinity (85 %, C3 class) and alkalinity due to high concentration of HCO_3^- and CO_3^{2-} and low Ca:Mg molar ratio (97.5 %, <1), are the major problems with water for irrigation usage. As a result, the quality of the groundwater is not suitable for sustainable crop production and soil health without appropriate remediation.

Keywords Groundwater quality · Hydrogeochemistry · Irrigation · Salinity hazard · Alkalinity hazard · Bandalamottu area · South India

Introduction

India is endowed with abundant mineral resources which have contributed immensely to the national wealth with associated socio-economic benefits. Mineral resources are an important source of wealth for a nation, but before they are harnessed, they have to pass through the stages of exploration, mining, and processing (Adekoya 2003). Anthropogenic activities such as mining and smelting of metal ores have increased the occurrence of heavy metal contamination at the Earth's surface. Abandoned mines have been observed to be major sources of metals into the environment. Mining activities have a serious environmental impact on soils and water streams by generating millions of tons of sulfide-rich tailings (Banks et al. 1997; Younger 1997; Passariello et al. 2002; Younger and Robins 2002; Younger et al. 2002; Romano et al. 2003; Kovács et al. 2006; Bhattacharya et al. 2006). Sulfide ore tailings disposals result in the pollution of surface and groundwaters owing to uncontrolled discharge, i.e., removing from mining work (Kelly 1988). Mine tailings pose a special problem not only because these comprise the bulk of the generated waste from mining, but also due to the characteristically high metal concentrations (David 2002).

The activity such as metal mining release large amount of tailing and waste containing heavy metals which pose severe threat to water sources, agricultural soils and food crops (Jung 2001, 2008; Suresh et al. 2007; Aremua et al. 2010; Gutiérrez-Ginés et al. 2010; Tordoff et al. 2010). The natural occurrence of copper, zinc and lead at

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Bandalamottu and its commercial exploration potentially threatens local groundwater resources due to the leachate from the waste. Waste is commonly disposed on the earth's surface in rock dumps and spoil piles, and the barren remains of processing are contained in tailings. Mine waste can generate elevated levels of sulfate, metals and acidity. Unless mine waste sites are protected from oxidation and metal release, these sites represent a source of serious contamination to groundwater and aquatic systems for potentially hundreds to thousands of years (Marqués et al. 2001; Witkowski et al. 2003).

Water quality analysis is one of the most important aspects in groundwater studies. The hydrochemical study reveals quality of water that is suitable for drinking, agriculture and industrial purposes. Chemical analysis forms the basis of interpretation of the quality of water in relation to source, geology, climate, and use. Water being an excellent solvent, it is important to know the geochemistry of dissolved constituents and methods of reporting analytical data. The normal groundwater have typically neutral to slightly alkaline pH dominated by base cations (Ca^{2+} , Mg^{2+} , Na^+) and bicarbonate (Frengstad and Banks 2000). Groundwater is often defined as water occurring within the subsurface geological environment. Mine water is thus merely a type of groundwater, subject to the same geochemical processes as “normal” groundwater. We should start, however, by examining, in outline, some of the processes which give all groundwaters (including mine water) their characteristic chemical signatures.

The natural chemistry of the groundwater is largely controlled by the dissolution of the geologic materials through which the water flows. Contaminants enter groundwater from sources at the ground surface through chemical weathering soil leaching, decaying vegetation, etc. These dominant processes depend on the geological and geochemical conditions, as well as the chemical and biological characteristics of the contaminant. It is stated that the chemical composition of groundwater is affected by several diverse factors like topography, rock and soil compositions, rainfall pattern and temperature in the region, soil microbial diversity, land use pattern and several other anthropogenic processes, such as excess groundwater extraction for various applications, construction of storage reservoirs and canals, etc. (Handa 1974). The fate of chemical constituents in the groundwater is determined by their reactivity and migration capacity from the soil.

The inhabitants at Bandalamottu depend on the groundwater resources for drinking and agriculture. This study represents an initial effort to characterize the extent and nature of contamination in groundwater, as it potentially relates to the lead mining and processing. Surprisingly little attention has been given to this issue until recently.

Geology

The Bandalamottu base metal belt (Lat. $16^{\circ}13'15''\text{N}$: Long $79^{\circ}39'47''\text{E}$), is located in Vinukonda Taluk of Guntur District in the northeastern part of the Cuddapah Basin and constitutes one of the prominent base metal deposits in India. About 30 copper–lead–zinc occurrences are localized within this belt, with Bandalamottu, Nallakonda and Dhukonda constituting the main deposits. The present study represents the water quality studies related to Bandalamottu–Agnigundala mineralized belt and is included in the Survey of India Toposheet No. 56 P/12.

Earlier workers have studied on geology and genesis of the ore deposit (Ziauddin and Sharma 1968; Krishna Rao and Dhanu Raju 1974; Narayanaswami et al. 1977; Sivadas et al. 1985). In Bandalamottu block, the rock types are dolomite, cherty dolomite, phyllite with magnetite and chlorite. The zones of mineralization are confined mainly to the upper dolostone and dolomitic limestone, which crop out along the southern flank of the Bandalamottu hill, striking ENE–WSW and dipping 20° – 35° WNW. The dolostone bed is the thickest in the middle and thins down on either end. It is interbedded with cherty dolostone, sandstone and calcareous sandstone, belonging to the Cumbum formation of Nallamalai Group of the Cuddapah Super group. Galena is the important ore mineral in this block while pyrite and sphalerite are next in abundance. The important minerals occurring in this belt are Pb, Zn and Cu.

The biotite-schists and amphibolites of metamorphic origin are the oldest rocks in this area and they belong to the archaeans. In addition, granites and dolerite dykes are also found. The Bairankonda formation, represented by grey, fine-grained, hard and compact sandstones with intercalated shale/slate units, except at a few places, directly overlies the granitic basement. The Cumbum formation is an argillaceous unit comprising shale, slaty-shale, slate and phyllite interbedded with fine to medium and coarse sandstone and dolostone/dolomitic limestone at various levels. The Pb–Zn mineralized dolostone is rather restricted in occurrence as beds of varying thickness within the chlorite phyllite. The formations are folded, faulted and disturbed. Ore mineralization is concordant with bedding, though, in detail it occurs as lodes composed of veins, fracture-fillings and disseminations.

Topography, climate and soils

The general elevation of the area is 130–160 m above the sea level with hills and ridges rising from 300 to 600 m above the mean sea level. Climate of the area is tropical with hot summer and mild winter. The maximum temperature during summer is 45°C and the minimum temperature will be

16 °C. The average annual rainfall is 850 mm. The plains are almost wholly covered with red soils and mixed soils containing black loam, sand and clay in varying amounts. They often contain boulders, cobbles, and pebbles of quartzite and vein quartz. Ferruginous laterite is found to cap some hills; calcareous kankar is also present in the soil in fairly large amounts. The streams are covered by shallow alluvium composed of boulders, cobbles, pebbles, gravels, sand, silt, and clay in varying amounts.

Materials and methods

The present study elucidates the chemical criteria of groundwater and the sample locations in the study are depicted in Fig. 1. It is therefore essential to conduct field and laboratory investigations to characterize, understand and interpret observed anomalies in groundwater in the regional context. In this area, 40 samples of groundwater were collected to study the chemical quality of water present in the region. To know the suitability of water for irrigation, chemical parameters like pH, electrical conductivity (EC), Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , F^- and various chemical index such as total

dissolved solids (TDS), total hardness (TH), non-carbonate hardness (NCH), total alkalinity (TA), sodium absorption ratio (SAR), adjusted SAR (adj.SAR), sodium percentage (SP), residual sodium carbonate (RSC), permeability index (PI), indices of exchange (IBE), Kelly's ratio and magnesium ratio were analyzed by adopting the standard procedures of water analysis. Saturation index (SI) values for mineral species were calculated using the Visual MINTEQ version 3.00 (Gustafsson 2012). The techniques and methods followed for collection, preservation, analysis and interpretation are those given by Hem (1985), Raghunath (1987), Karanth (1989), APHA (2005) and Todd and Mays (2005). The data are presented in Table 1.

Results and discussion

Water quality evaluation for irrigation purpose

The major ion chemistry of groundwater from Bandalamottu area were statistically analyzed and the results summarized by minimum, maximum, mean in Table 1. Suitability of the groundwater for irrigation purpose was discussed by the following basic criteria.

Fig. 1 Map of the study area with water sample locations

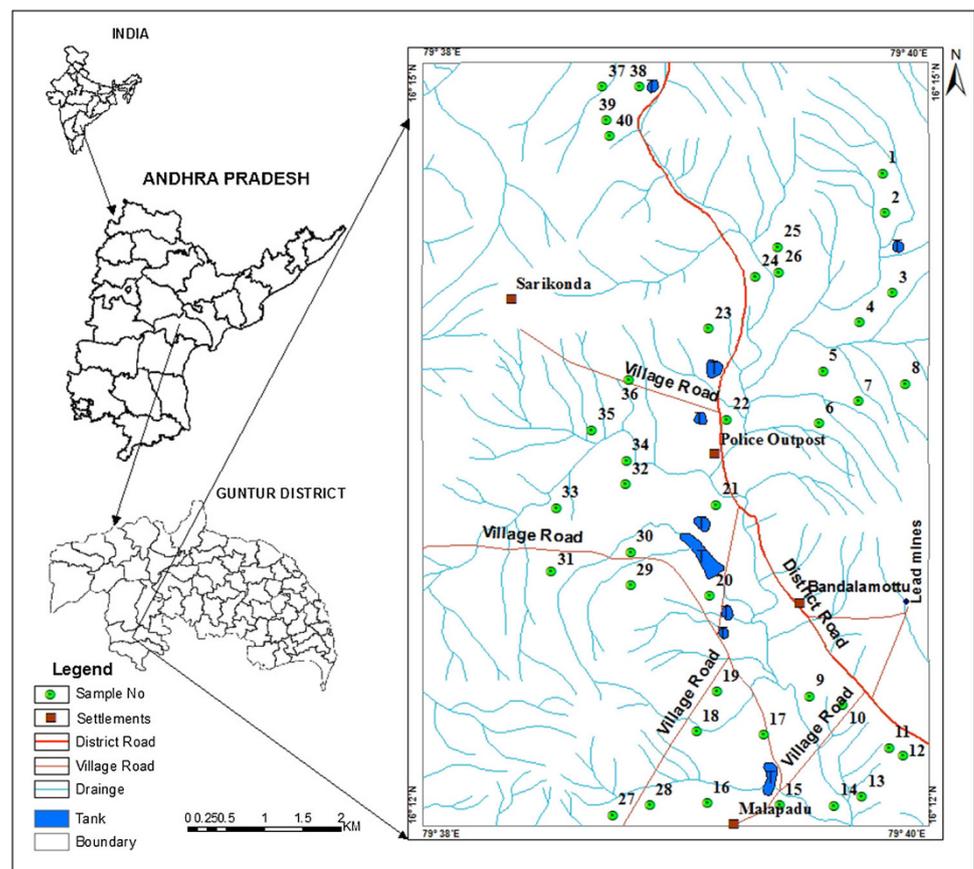


Table 1 Minimum, maximum and average values of different constituents of water samples of Bandalamottu area

S. no	Constituents	Min	Max	Average
1	Calcium (Ca ²⁺) (ppm)	11.0	84.0	32.9
2	Magnesium (Mg ²⁺) (ppm)	7.0	108.0	43.6
3	Sodium (Na ⁺) (ppm)	31.5	252.0	110.9
4	Potassium (K ⁺) (ppm)	2.0	96.0	15.8
5	Bicarbonate (HCO ₃ ⁻) (ppm)	144.0	598.0	368.9
6	Carbonate (CO ₃ ²⁻) (ppm)	6.0	49.0	15.2
7	Sulfate (SO ₄ ²⁻) (ppm)	76.0	475.0	151.6
8	Chloride (Cl ⁻) (ppm)	17.0	276.0	94.9
9	Fluorine (F ⁻) (ppm)	0.6	3.3	2.0
10	pH	7.0	7.7	7.4
11	Specific conductance (μmhoscm ⁻¹)	415.0	1,475.0	1,057.5
12	Total dissolved solids (ppm)	246.0	916.0	661.5
13	Hardness as CaCO ₃ (ppm)	124.0	512.0	274.0
14	Non-carbonate hardness as CaCO ₃ (NCH) (ppm)	-388.0	235.2	-64.7
15	Alkalinity as CaCO ₃ (ppm)	156.0	582.0	339.7
16	Sodium adsorption ratio (SAR)	1.1	8.0	3.3
17	Adjusted SAR (Adj.SAR)	2.1	18.6	7.3
18	Sodium Percentage (SP) (%)	21.6	77.4	49.2
19	Potential salinity (PS) (meql ⁻¹)	1.5	8.6	4.2
20	Residual sodium carbonate (RSC) (meql ⁻¹)	-4.7	7.8	1.3
21	Permeability index (PI) (%)	42.1	109.3	73.1
22	Kelly's ratio	0.27	3.05	1.15
23	Indices of base exchange (IBE) CaI	-4.4	0.3	-1.1
24	Indices of base exchange (IBE) CaII	-0.56	0.27	-0.25
25	Gibbs ratio I	0.12	0.61	0.3
26	Gibbs ratio II	0.38	0.94	0.73
27	Calcium to magnesium molar ratio	0.2	2.0	0.5
28	Magnesium ratio (%)	33.4	82.4	67.7

Water quality based on absolute amount of ions

Among the cations, the concentrations of Ca²⁺, Mg²⁺, Na⁺ and K⁺ ions ranged from 11 to 84, 7 to 108, 31.5 to 252 and 2 to 96 ppm with a mean value of 32.9, 43.6, 110.9 and 15.8 ppm, respectively (Table 1). The maximum permissible limit of Ca²⁺, Mg²⁺, Na⁺ and K⁺ in irrigation water is 80, 35, 200 and 30 ppm, respectively (Duncan et al. 2000 and Sharifi and Safari Sinigani 2012). On the basis of these permissible limits, 57, 7 and 15 % of the water samples are unsuitable for irrigation usage with respect to Mg²⁺, Na⁺ and K⁺, respectively. Among the anions, the concentrations of HCO₃⁻, CO₃²⁻, Cl⁻, SO₄²⁻ and F⁻ ions lie in between 144 and 598, 6 and 49, 17 and 276, 76 and 475, 0.6 and 3.3 ppm with a mean value of 368.9, 15.2, 94.9, 151.6 and 2.0 ppm, respectively (Table 1). The maximum permissible limit of HCO₃⁻, CO₃²⁻, Cl⁻, SO₄²⁻ and F⁻ in irrigation water is 250, 15, 250, 180 and 10 ppm, respectively (McKee and Wolf 1963; Duncan et al. 2000; Sharifi and Safari Sinigani 2012). According to the grading standards 85, 37, 2.5 and 17.5 % of the water samples are unsuitable for irrigation usage with respect to HCO₃⁻,

CO₃²⁻, Cl⁻ and SO₄²⁻, respectively. It should be noted that the absolute concentration of ions by itself is not enough for assessing suitability of ions for irrigation usage. Thus, the effects of interactions among the ions should also be considered for this issue. For this reason, to accurate estimate of the hazards of the ions in the water samples, in the next sections, we adopted the methods that include the interactions.

pH

pH is a term used universally to express the intensity of the acid or alkaline condition of a solution. From the Table 1, it is observed that the pH values of the water samples ranged from 7.0 to 7.7 with a mean value of 7.4 in the study area. All the water samples fall in the safe limit of pH standard (6–8.5) for irrigation purpose (Ayers and Westcot 1985).

Salinity hazard

Determination of salinity hazard is very important in irrigation water, as high salt content renders the soil saline.

This also affects the salt intake capacity of the plants through the roots. Electrical conductivity (EC) is a measure of water capacity to convey electric current. It signifies the amount of total dissolved salts (TDS). Thus, in the present study, the salinity hazard was evaluated by EC and TDS, their amounts varied from 415 to 1475 μhoscm^{-1} and 246–916 ppm with an average value of 1,057.5 μhoscm^{-1} and 661.5 ppm, respectively. Based on the classification of TDS as suggested by USSL (1954), most of the water samples (85 %) are classified as moderate water category. According to the EC grading standards as suggested by Wilcox (1955), most of the water samples (85 %) are classified as permissible water category. Therefore, the continuation use of this moderate saline water for irrigation in the long term may increase the salinity hazard in the soils of the studied area.

Potential salinity

Doneen (1964) explained that the suitability of water for irrigation is not dependent on soluble salts. Because, the low solubility salts precipitate in the soil and accumulate with each successive irrigation, the concentration of highly soluble salts increase the soil salinity. Potential salinity is defined as the chloride concentration plus half of the sulfate concentration as showed below:

$$\text{P.S} = \text{Cl}^- + 1/2\text{SO}_4^{2-} \quad (1)$$

All ionic concentration is in meq l^{-1} .

The potential salinity of the water samples range from 1.5 to 8.6 meq l^{-1} with an average of 4.2 meq l^{-1} . It suggests that the potential salinity in the groundwater of the studied area nearly is high, thus, making the water unsuitable for irrigation usage. High values of potential salinity in the area can be ascribed to high sulfate content derived from the lead mining, the major mineral mined in the studied area.

Total alkalinity

In the natural environment, carbonate alkalinity tends to make up most of the total alkalinity. Other common natural components that can contribute to alkalinity include borate, hydroxide, phosphate, silicate, nitrate, dissolved ammonia, the conjugate bases of some organic acids and sulfide. Alkalinity is important because it buffers pH changes that occur naturally during photosynthetic cycles, water exchanges, etc. From the Table 1, it is clear that the alkalinity ranges from 156.0 to 582.0 with an average value of 339.7 ppm as CaCO_3 . The high amount of alkalinity in the Bandalamottu area water samples can be due to the presence of calcareous rocks, such as dolomite in this area.

Sodium hazard

The excessive sodium content in water sample reduces the permeability, and hence, the available water for the plant is reduced. Sodium replacing adsorbed calcium and magnesium is a hazard, as it causes damage to the soil structure resulting in compact and impervious soil (Arveti et al. 2011). Excess absorption of sodium can cause sodium toxicity in sensitive plants, causing marginal leaf burn on older foliage and possibly defoliation and water containing excessive amount of sodium may immobilize other nutrient ions particularly calcium, magnesium and potassium, which can result in deficiencies of these elements in plants (NWQMS 2000; Kelly 1951; Domenico and Schwartz 1990; Todd and Mays 2005; Sharifi and Safari Sinegani 2012).

Irrigation water is classified on the basis of SAR (WHO 1989). Hence, the assessment of sodium hazard is necessary while considering the suitability for irrigation. One of the most important criteria in determining sodium hazard is sodium adsorption ratio (SAR) (Todd and Mays 2005). It is an easily measured property that gives information on the comparative concentrations of Na^+ , Ca^{2+} , and Mg^{2+} in soil solutions. Sodium adsorption ratio is computed as:

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

All ionic concentration is in meq l^{-1} .

As shown in Table 1, the SAR values of the groundwater samples varied from 1.1 to 8.0 with an average value of 3.3. The SAR values of the water samples of the studied area to be <10 and are classified as excellent for irrigation (Richards 1954).

Kelly (1940) and Wilcox (1958) have also determined the hazardous effect of sodium on water quality for irrigation usage in terms of Kelly's ratio (KR) and sodium percentage (SP), respectively. Kelly's ratio and SP are computed as:

$$\{\text{Kelly's ratio} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})\} \quad (3)$$

$$\text{SP} = \frac{(\text{Na}^+ + \text{K}^+)}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)} \times 100 \quad (4)$$

All ionic concentrations are in meq l^{-1} .

A Kelly's ratio of more than one indicates excessive sodium in water. Therefore, water with a Kelly's ratio less than one are suitable for irrigation, while those with a ratio more than one are unsuitable. From the Table 1, it can be suggested that the Kelly's ratio varies from 0.27 to 3.05 with an average value of 1.15. In the present study, 42 % of the water samples are unsuitable for irrigation with more than one of Kelly's ratio.

From the Table 1, it is observed that the sodium percentage values of the study area samples vary from 21.6 to 77.4 % with an average value 49.2 %. Sodium percentage is plotted against conductivity, which is designated as Wilcox diagram and is illustrated in Fig. 2. It is clear that water samples fall into the categories of “excellent to good” (15 %), “good to permissible” (52.5 %), and “permissible to doubtful” (32.5 %).

Carbonate and bicarbonates hazard

Water containing excessive amount of HCO_3^- and CO_3^{2-} , react with Ca^{2+} and Mg^{2+} in soil solution and will precipitate them as calcite and magnesite. This will allow sodium adsorbed to dominate onto the clay surfaces, to enhanced exchangeable sodium percentage (ESP) of soil, which increases sodium hazard and its related problems such as reducing soil permeability, soil aeration, high pH, inhibit root penetration, etc. (Bohn et al. 1985; Domenico and Schwartz 1990; Todd and Mays 2005). Thus, some of the researchers have attempted to present equations to show the effects of interactions among Ca^{2+} , Mg^{2+} , Na^+ ,

HCO_3^- and CO_3^{2-} on water quality for irrigation purpose. They are as follows:

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

$$\text{P.I.} = \frac{\text{Na}^+ + \sqrt{\text{HCO}_3^-}}{(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+)} \times 100 \quad (6)$$

Adjusted sodium adsorption ratio (adj.SAR) = $\text{SAR} [1 + (8.4 \text{ pH}_c)]$ (Ayers and Westcot 1985)

$$\text{pHc} = (\text{pK}_2 - \text{pK}_c) + \text{p}(\text{Ca} + \text{Mg}) + \text{p}(\text{Alk}) \quad (7)$$

where

pK_2 Negative logarithm of the second disassociation constant for carbonic acid

pK_c Solubility constant for calcite

p Negative logarithm of ion concentration

All ionic concentration is in meq l^{-1} .

From the Table 1, it can be interpreted that the groundwaters in the study area shows RSC values of -4.7 to 7.8 with an average value of 1.3 meq l^{-1} . Based on the US Salinity Laboratory (1954), over 16 samples have values $<1.25 \text{ meq l}^{-1}$ and are safe for irrigation; 11 samples have RSC values between 1.25 and 2.5 meq l^{-1} are marginal in quality and 13 samples have RSC values $>2.5 \text{ meq l}^{-1}$ and are unsuitable for irrigation. The water with high RSC has high pH and land irrigated by such water becomes infertile owing to deposition of sodium carbonate as indicated by the black color of the soil (Eaton 1950).

Water can be classified as Class I, Class II and Class III orders with regard to permeability index (PI). Class I and Class II waters are categorized as good for irrigation with 75 % or more of maximum permeability. Class III waters are unsuitable with 25 % of maximum permeability (Donnen 1964). From the Table 1, it can be demarcated that the PI values vary from 42.1 to 109.3 with an average of 73.1. Nearly 50 % water samples fall into the Class I Category of Donnen’s chart and are categorized as good for irrigation.

Although RSC and PI are useful parameters for assessing of carbonate and bicarbonates hazard, adj.SAR is basically used for assessment of alkalinity hazard in irrigation water, amount of which was 2.1–18.6 with a mean value of 7.3 (Table 1). The result showed that the concern due to sodium hazard of the water became more emphatic because in all water samples adj.SAR is higher than SAR. Based on Ayers and Tanji (1981) classification, 15 % of samples have adj.SAR values <3 and are safe for irrigation; 57.5 % of samples have adj.SAR values between 3 and 9 are increasing problem for irrigation and remained samples (27.5 %) have adj.SAR values >9 and are severe problems for irrigation.

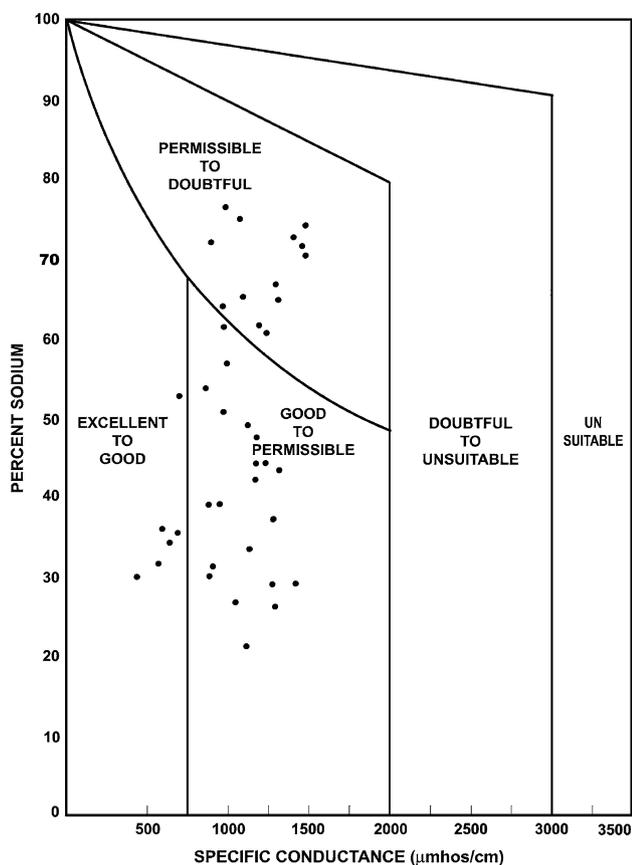


Fig. 2 The quality of water in relation to electrical conductivity and percent sodium (Wilcox diagram)

In general, the obtained results from the calculation of RSC, PI and adj.SAR suggest that there is tendency for calcium and magnesium to precipitate with carbonate and bicarbonate as calcite and magnesite in the soils irrigated by the water, resulting in an increased sodium hazard and its related problems in the area.

Salinity and alkalinity hazard class

According to US Salinity Laboratory’s diagram (Richards 1954) in Fig. 3, salinity and alkalinity hazard class of water samples were C3–S1 (70 %), C3–S2 (15 %) and C2–S1 (15 %). The result shows that a majority of the groundwaters possess high salinity with low sodium (C3–S1). Lauchli and Epstein (1990) have pointed out that salinity can have effect on growth and development of plants in different ways, such as osmotic effects, specific-ion toxicity and/or nutritional disorders. Thus, the excessive amount of salts can be one of the major problems with water used for irrigation in this area and the water cannot be used for irrigation with most crops without special circumstances for salinity control such as leaching requirement or cropping of salt-tolerant plants. In this study about 15 % of the water samples fall in high salinity and medium alkalinity hazard class (C3–S2), with continuous use of the such water samples in the long term will increase both salinity and alkalinity hazard in the soil.

Magnesium hazard

Generally, calcium and magnesium maintain a state of equilibrium in most waters. More magnesium in water adversely affects the crop yield. As the rocks of the study area comprise dolomites, most water possess more magnesium than calcium. For this reason, in this study magnesium hazard was evaluated by two following methods including “magnesium ratio” and “calcium to magnesium molar ratio”. From the Table 1, it is seen that the magnesium ratio $\{Mg^{2+} \text{ ratio} = [Mg^{2+}/(Ca^{2+} + Mg^{2+})] \times 100\}$ has varied from 33.4 to 82.40 with an average value of 67.7. In this study, nearly all of the water samples has Mg ratio more than 50 %, which adversely affect the crop yield as turn the soils more alkaline (Paliwal 1972). The high values of observed ‘magnesium ratio’ are due to the influence of dolomite in these areas. The result support that Ca:Mg molar ratio nearly in all of the surveyed water samples was <1 (range 0.2–2.0, mean 0.5). Jalali (2008) and Joshi et al. (2009) have pointed out that water with a Ca:Mg molar ratio <1, results in an increased SAR value, which adversely affects soil structure and crop yield as the soils become more saline.

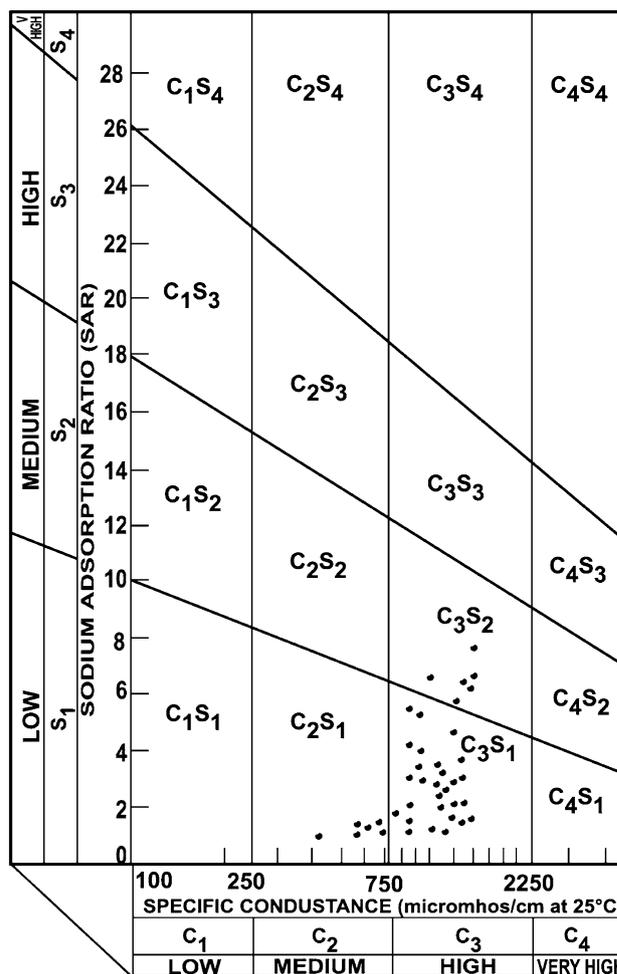


Fig. 3 The quality of water in relation to salinity and sodium hazard (after US Salinity Laboratory 1954)

Total hardness

Hard water is water that has high content of calcium and magnesium ions, and sometimes other dissolved compounds such as iron. Calcium usually enters the water as either calcium carbonate (CaCO₃), in the form of limestone and chalk, or calcium sulfate (CaSO₄), in the form of other mineral deposits. The predominant source of magnesium is dolomite (CaMg(CO₃)₂). Piper’s diagram confirms that all the groundwaters in the study area are characterized as alkaline earth’s (Ca + Mg) exceeds alkalis (Na + K) and all the groundwaters in the study area described as weak acids (CO₃ + HCO₃) exceed strong acids (SO₄ + Cl + F). In the present study, area hardness of water samples varied from 124.0 to 512.0 with a mean value of 274.0 ppm as CaCO₃. Based on Sawyer et al. (2003) classification the water are classified as moderately hard (5 %), hard (55 %) and very hard (40 %). In general, water with hardness more than 200 ppm as CaCO₃ will lead to scale deposits in the piping system (Van der Aa

2003). Thus, the result suggests that most of the water samples (72 %) can be problematic for plumbing of irrigation systems.

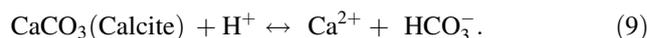
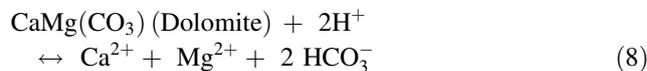
Non-carbonate hardness (NCH)

Hardness of water relates to the reaction with soap, since Ca and Mg ions precipitate soap. Hardness is expressed as ppm of CaCO_3 . If the hardness as CaCO_3 exceeds the difference between the alkalinity as CaCO_3 and hardness as CaCO_3 , it is termed as non-carbonate hardness. It is also called permanent hardness. From the Table 1, it can be delineated that the NCH values ranged from -388.0 to 235.2 with an average of -64.7 .

Geochemical classification and hydrogeochemical facies

In order to understand water composition and chemical relationship between dissolved ions, the concept of hydrochemical facies of the investigated area are used in Pipers (1953) trilinear diagram for graphical analysis (Fig. 4). This diagram reveals similarities and differences among water samples (Todd 1980). The facies mapping approach applied to the present study shows dominance of alkaline earth over strong acids (Fig. 4) and samples fall in the Ca–

HCO_3 type (35 %), Ca–Na– HCO_3 type (37.5 %) and Ca–Mg–Cl type (20 %). Remaining samples fall in the field of Na–Cl type. The results suggest that mixed cation- HCO_3 is the dominant hydrochemical facies for the surveyed groundwaters. The principal water type depicts rock–water interaction involving the dissolution of carbonates by weathered zone above the underlying rocks. There is a tendency in the groundwater to carbonate mineral saturation by dissolving dolomite and calcite in the soil and bedrock in the recharge area as:

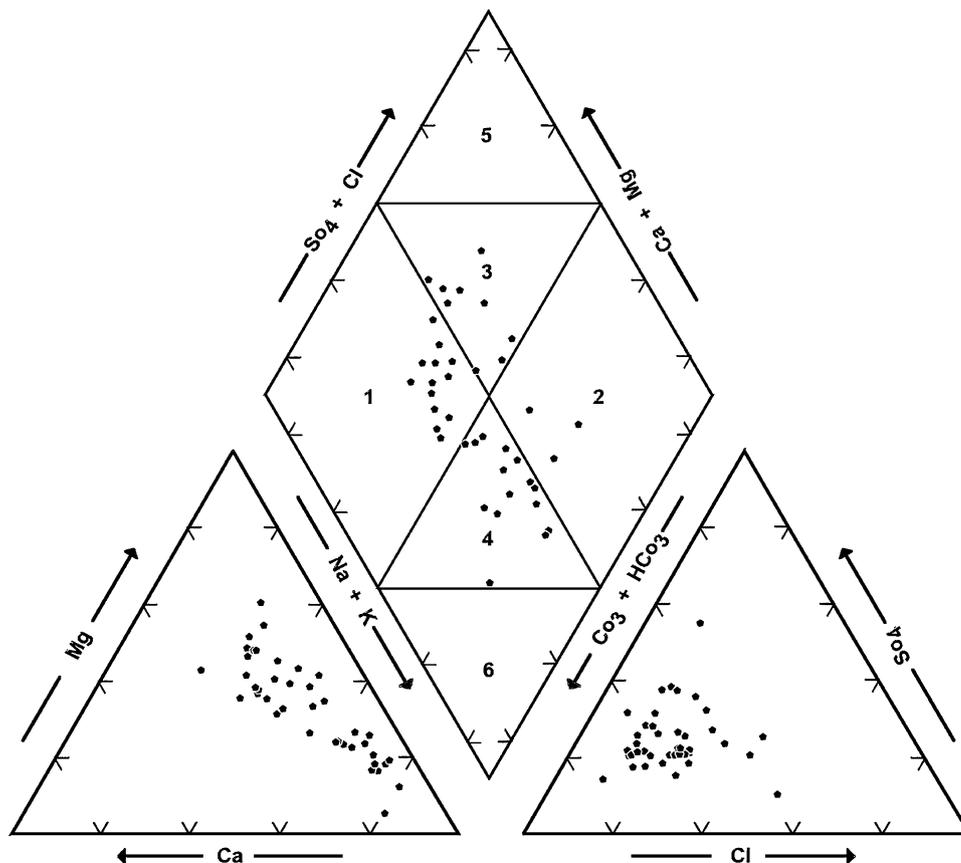


These results are supported by that the basement minerals in this area are mainly carbonates and saturation indices of 55, 30 and 10 % of the water samples, respectively, for dolomite, calcite and aragonite were positive.

The origin of solutes

In this section, the origin of solutes and the process that generated the observed water compositions in the water has been assayed by the following methods:

Fig. 4 Piper diagram for representing the analysis of ground water



1. Hydrogeochemical modeling
2. Indices of base exchange (IBE)
3. Gibbs ratio.

I. Hydrogeochemical modeling To evaluate the potential chemical reactions in the groundwater, the saturation indices (SI) of the water with respect to mineral phases were calculated using geochemical model Visual MINTEQ version 3.00 (Gustafsson 2012). The model has an extensive thermodynamic database that allows for the study ion speciation, solubility, equilibrium of solid and dissolved phases of minerals in an aqueous solution (Gustafsson 2012). This program is the windows version of MINTEQ that was originally developed by the US EPA (Allison et al. 1991). Summary statistics of the modeling are presented in Table 2. The saturation index (SI) quantitatively indicates about the dissolution and precipitation reactions occurring in the groundwater. The negative, zero and positive values of the index, respectively, indicate under-saturation, equilibrium and oversaturation of water with respect to dissolved minerals (Appelo and Postma 1996; Drever 1997).

As shown in Table 2, 55 % of the all water samples were oversaturated with respect to dolomite (SI ranged

Table 2 Summary statistics of mineral saturation index (SI) of Bandalamottu groundwater calculated by Visual MINTEQ

S no.	Mineral saturation index (SI)	Min	Max	Mean	Std. deviation
1	Aragonite	-0.87	0.21	-0.35	0.29
2	Artinite	-7.15	-5.28	-6.28	0.59
3	Brucite	-6.10	-4.73	-5.44	0.39
4	Calcite	-0.73	0.36	-0.21	0.29
5	Dolomite (disordered)	-1.35	0.44	-0.49	0.49
6	Dolomite (ordered)	-0.80	1.03	0.06	0.50
7	Epsomite	-4.80	-3.30	-4.05	0.27
8	Fluorite	-2.00	-0.51	-1.10	0.35
9	Gypsum	-2.44	-1.26	-1.91	0.25
10	Halite	-7.90	-6.00	-6.65	0.41
11	Hydromagnesite	-15.14	-10.80	-12.94	1.30
12	Lime	-22.37	-20.50	-21.39	0.50
13	Magnesite	-1.34	-0.50	-0.90	0.24
14	Mirabilite	-7.90	-6.00	-6.90	0.50
15	Natron	-10.00	-7.70	-8.83	0.54
16	Nesquehonite	-4.13	-3.27	-3.67	0.24
17	Periclase	-10.59	-9.30	-9.93	0.40
18	Portlandite	-12.40	-10.50	-11.40	0.47
19	Thenardite	-9.33	-7.40	-8.30	0.50
20	Thermonatrite	-11.94	-9.65	-10.78	0.54
21	Vaterite	-1.29	-0.21	-0.78	0.28

Positive values indicate saturation, and negative ones indicate under-saturation

–0.08 to 1.03, mean 0.06), 30 % with respect to calcite (SI ranged –0.73 to 0.36, mean –0.21) and 10 % with respect to Aragonite (SI ranged –0.87 to 0.25, mean –0.35), and all water samples were under-saturated with respect to sulfur-bearing minerals (gypsum, epsomite, mirabilite and thenardite). Thus, precipitation is expected for calcite and dolomite and dissolution is expected for gypsum, epsomite, mirabilite and thenardite. These findings indicate that dissolution of dolomite and calcite can be the main mechanism responsible for the chemical composition of the groundwaters in the studied area.

II. Indices of base exchange (IBE) Control of the dissolution of undesirable constituents in water is impossible during the subsurface run off, but it is essential to know the changes undergone by the water during its movement (Pojasek 1977; Johnson 1979). The ion exchange between the groundwater and its host environment during residence or travel are well understood by studying the chloro-alkaline indices. To know the direction of exchange during the path of groundwater through the aquifer, Schoeller (1967, 1977) suggested two chloro-alkaline indices CaI_1 and CaI_2 to indicate the exchange of ions between groundwater and its host environment. This is positive when there is an exchange of Na^+ and K^+ from the water with Mg^{2+} and Ca^{2+} of the rocks, and is negative when there is an exchange of Mg^{2+} and Ca^{2+} of the water with Na^+ and K^+ of the rocks.

From the Table 1, it can be put forth that the CaI_1 values range from –4.4 to 0.3 with a mean of –1.1 and CaI_2 values vary from –0.56 to 0.27 with a mean of –0.25. From these values, it can be interpreted that most of the samples (95 %) in the studied area fall into negative zones. They indicate that the exchange of Mg^{2+} and Ca^{2+} of the water with Na and K in its host environment is prevalent in the studied area. The result suggests that cation exchangeable can also be one of the mechanisms responsible for the chemical composition of the groundwaters in the studied area.

III. Gibbs ratio Gibbs (1970) proposed a diagram to understand the relationship of the chemical components of water from their respective aquifer lithologies. Viswanathaiah et al. (1978) emphasized the mechanisms that control the chemistry of groundwater in Karnataka. Ramesam and Barua (1973) have also carried out similar research work in the northwestern regions of India. The Gibbs diagram illustrates three distinct fields, namely precipitation dominance, evaporation dominance and rock dominance areas that are shown in Gibbs diagram (Fig. 5).

The Gibbs ratios are calculated with the formulae given below:

$$\text{Gibbs ratio I (for Anion)} = \text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-) \quad (10)$$

$$\text{Gibbs ratio II (for Cation)} = (\text{Na}^+ + \text{K}^+) / (\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}) \quad (11)$$

All ionic concentrations are in meq l^{-1} .

Gibbs ratios for the study area samples are plotted against their respective total dissolved solids as shown in Fig. 5 to know whether the groundwater chemistry is due to rock dominance, evaporation dominance or precipitation dominance. In the present study, Gibbs ratio I values in the present study vary from 0.12 to 0.61 with an average value

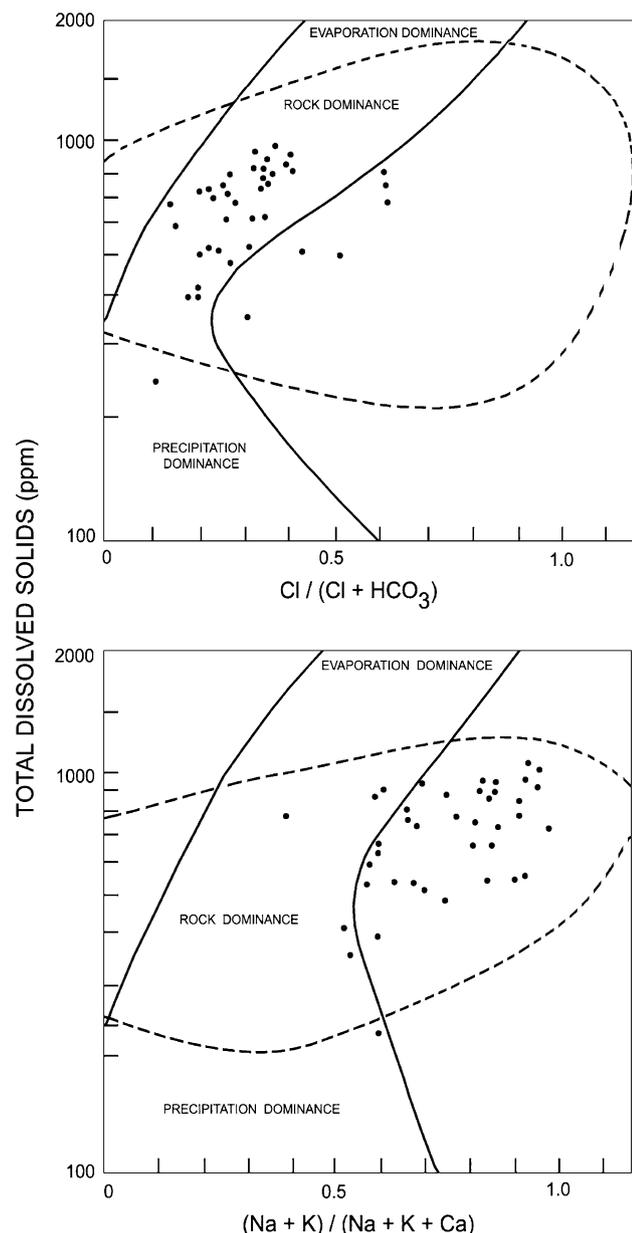


Fig. 5 Mechanism controlling the quality of ground water (after Gibb's 1970)

of 0.30 and Gibbs ratio II values vary from 0.38 to 0.94 with an average value of 0.73. From Fig. 5, it can be elucidated that in the study area the samples fall into the rock dominance area, indicating the influence of rocks on the groundwater in the aquifers.

Conclusion

The groundwater resources in the Bandalamottu region were evaluated for their chemical composition and suitability for irrigation. The abundance of the major ions is as follows: $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{CO}_3^{2-} > \text{F}^-$. Dolomite is the predominant source of the huge amounts of magnesium found in the groundwater. The major hydrochemical facieses were Ca–HCO₃, Ca–Na–HCO₃ and Ca–Mg–Cl types. The saturation index (SI) of minerals calculated by Visual MINTEQ software showed that 55 % of all water samples were oversaturated with respect to dolomite, 30 % with respect to calcite and 10 % with respect to Aragonite, and all water samples were under-saturated with respect to sulfur-bearing minerals. The result of SI together with Gibbs diagram and indices of base exchange (IBE) findings indicate that dissolution of dolomite and calcite and reverse ion exchange can be the main mechanisms responsible for the chemical composition of the groundwater in the studied area. The results also showed that the surveyed groundwater for irrigation purposes have a high salinity hazard (85 %, C3 class), high alkalinity hazard due to high concentration of HCO₃⁻ and CO₃²⁻ and low Ca:Mg molar ratio (97.5 %, <1), slight basic in nature and are very hard. Based on the results of this study, the quality of the groundwater is not suitable for irrigation and continuation of their use in the long term may increase the salinity and alkalinity problems in the soils.

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