

Assessment of Groundwater Quality and Evolution of Hydrochemical Facies around Tummalapalle Area, Cuddapah District, Andhra Pradesh, South India

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Abstract

Hydrogeochemical investigations were carried out in and around Tummalapalle uranium mining area in order to assess hydrogeochemistry and its evolution of hydrochemical facies. Forty groundwater samples were analyzed for various physicochemical parameters like pH, electrical conductivity (EC), Ca, Mg, Na, K, Cl, HCO₃, CO₃, SO₄, and F. The saturation indexes (SI) of minerals were calculated by employing Visual MINTEQ software. From this it is confirmed that most of the water samples were saturated with respect to carbonate minerals and under saturated with respect to sulfate minerals. The result saturation index calculated by Visual MINTEQ together with Gibbs diagram and Indices of Base Exchange (IBE) findings indicate that dissolution of dolomite and calcite, evaporation and cation exchangeable can be main mechanisms responsible for the chemical composition of the ground waters in the studied area.

Keywords: Hydrogeochemistry; Groundwater quality; Visual MINTEQ; Tummalapalle

Introduction

Water quality analysis is one of important issues in groundwater studies because groundwater has become an important water resource. The quality of water is of vital importance to humans, since it is directly linked with human welfare such as drinking, agricultural and industrial purposes. Groundwater is the major source of drinking water supply in rural and urban areas in India. Further, the groundwater represents a very significant source of fresh water for irrigation and drinking purposes and therefore preserving the availability and quality of this resource is extremely important [1]. Water management in agriculture is aiming for better tools to estimate risk assessment due to stricter legislation on soil and groundwater contamination, together with increasing population and demand in food production [2]. To protect the environment, there is need for baseline data to evaluate the potential impacts of pollutants to ecosystems.

The large amount of mining release tailing and waste containing heavy metals can pose severe threats to water sources, agricultural soils and food crops. Metals are leached out and carried downstream as water washes over the rock surface. Although metals can become mobile in neutral pH conditions, leaching is particularly accelerated in the low pH conditions such as are created by Acid Mine Drainage [3-6]. Mining activities has been reported to have impacts such as oxidation of metal sulphides which induces soil acidification, impeding natural colonization of vegetation causing soil erosion and degradation of aquatic ecosystem leading to destruction of aquatic life.

Thus, the demand for a country's economic, agricultural and industrial development needs a groundwater monitoring program for a safe and pure environment. Mining no doubt impacts negatively on

agriculture because of the complex of various interactions that occur as waste become part of the ecosystem into which it is deposited [7]. In furtherance acid mine water impacts on agricultural lands irrigated with it [8] Impacts such as deficiencies of essential micronutrients have been reported. [3,5]. Such effect results in the use of agrochemicals introduced as soil nutrients to improve soil fertility. Further, this study alerts the main processes that are responsible for these hydrochemical data including: (1) weathering of silicate minerals (2) Ion exchange between alkalies and alkaline earths (3) precipitation and (4) anthropogenic activities agricultural activities such as irrigation practices and fertilizations.

In order to discover anomalous samples or values within a collection of analyses they may be examined by using graphical methods. Mixed sources may be discovered by using factor analysis, a statistical procedure of multivariate analysis [9,10]. In this context, thermodynamic water equilibrium studies are usually made with sophisticated computer programs, such as MINTEQ [11].

Mining and agriculture are directly linked through agriculture's dependence on mined inputs, land and water resources, and workers. They are also indirectly linked where mining firms have improved infrastructure in a way that supports agricultural development. The outcomes of this interaction appear mixed. There is evidence that agriculture is growing in some areas as a result of mining and declining in others, depending on local circumstances. Water Use Conflict may also arise between agriculture and mining over access to water resources. Concerns relate to both the total amount of water used, especially in areas with limited fresh water resources, and changes in water quality due to mining activities [12]. This will determine if the solution is saturated or under saturated with respect to a variety of minerals, as well as determining the redox state of the water and speciation of the components in it. Groundwater is one of the primary sources of water for human consumption, agriculture and industrial uses in Tummalapalle area. Hence, the present study is

undertaken with the objective of assessment of groundwater hydrogeochemistry around Tummalapalle area, Cuddapah District, Andhra Pradesh, South India.

Hydrogeology and Geomorphology of the Study Area

The study site that surrounds the Tummalapalle area (14° 18' to 14° 21' N; 78° 15' to 78° 17' E) is located in Pulivendla Taluk of Cuddapah District of Andhra Pradesh (Figure 1). The study area is included in the survey of India top sheet No. 57 J/7. Geologically, Tummalapalle area is in the south western part of the Cuddapah basin. The geological formations of this area are hosted by carbonate rock formations. Lithologically, the Vempalle formation consists of purple shale, massive limestone, intraformational conglomerate, dolostone (uraniferous), shale and cherty limestone. The radioactive minerals identified in the ore zone are pitchblende, coffinite, and U-Ti complex [13,14] Coffinite is fine grained and associated with pyrite. Other associated minerals are pyrite, chalcopyrite, molybdenite and colophonane. The gangue minerals are dolomite, quartz and microcline. The crescent-shaped Cuddapah Basin of Andhra Pradesh, south-eastern Peninsular India, has a maximum width of 145 km (in the middle) and 440 km long, and is exposed over an area of 44,000 sq km. On the western margin of the basin the undisturbed Proterozoic sediments rest on an Archaean gneissic complex enclosing the greenstone belts of Kadiri, Veligallu and Gadwal with a profound nonconformity [15]. The lithostratigraphy of the Cuddapah Basin is composed dominantly of argillaceous and arenaceous sediments with subordinate calcareous sediments

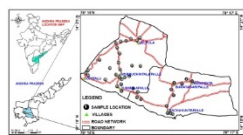


Figure 1: Map of the study area with water sample locations.

Sampling and Analytical Methodology

Water samples were collected from seven sites around the Tummalapalle area. A plastic bottle rinsed with perchloric acid and distilled water were used for the sample and brought to laboratory. A total of 40 water samples were collected in the study area and field parameters such as electrical conductivity (EC), pH were measured. Sample collection and preservation prior to laboratory analysis, in every case, followed a procedure according to the standard methods presented by American Public Health Association [16]. The major cations (calcium, magnesium, sodium, and potassium) and anions (bicarbonate, carbonate, sulfate, fluoride and chloride) were determined adopting the analytical techniques, based on the methods proposed by APHA [16].

The potential chemical reactions in the groundwater with respect to mineral phases were calculated using the geochemical model Visual MINTEQ version 3.00 [17]. This software is a chemical equilibrium computer program that has an extensive thermodynamic database that allows for the calculation of speciation, solubility, and equilibrium of solid and dissolved phases of minerals in an aqueous solution [17]. This program is the Windows version of MINTEQ that was originally developed by the US EPA [18].

Results and Discussion

Geochemical properties and principles that govern the behaviour of dissolved chemical constituents in groundwater are referred to as hydrogeochemistry. The dissolved constituents occur as ions, molecules or solid particles. The chemical composition of groundwater is related to the solid product of rock weathering and changes with respect to time and space. In the present study, the following observations were made for different parameters and have been discussed.

Groundwater chemistry

The chemical quality data showing minimum, maximum and average values of different constituents of water samples is shown in Table 1. Further, Visual MINTEQ software has been utilized in order to calculate the saturation index (SI) of minerals and depicted in Table 2. The major ion chemistry of groundwater from Tummalapalle area was statistically analyzed and the results summarized by minimum, maximum, mean in Table 1. Among the cations, the concentrations of Ca^{2+} , Mg^{2+} , Na^+ and K^+ ions ranged from 25 to 173; 27 to 133; 6 to 86 and 2 to 73 ppm with a mean of 77, 66, 33 and 14 ppm, respectively. Among the anions, the concentrations of HCO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} and F^- ions range from 130 to 509; 38 to 222; 21 to 207; 8 to 94 and 0.25 to 0.62 ppm with a mean of 303, 113, 71, 17 and 0.41 ppm, respectively. Hard water minerals primarily consist of calcium (Ca^{2+}), and magnesium (Mg^{2+}) metal cations, and sometimes other dissolved compounds such as bicarbonates and sulfates. Calcium usually enters the water as either calcium carbonate (CaCO_3), in the form of limestone and chalk, or calcium sulfate (CaSO_4), in the form of other mineral deposits. In the present study, the predominant source of magnesium is dolomite

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 hydrogeochemical modeling, Indices of Base Exchange (IBE) and Gibbs ratio methods.

Hydrogeochemical modeling

Interactions between the groundwater and the host rocks are the main processes responsible for variation in the groundwater chemistry [19]. Further, the summary statistics of the modeling are presented in Table 2 by employing Visual MINTEQ software.

To evaluate the potential chemical reactions in the groundwater, the saturation indices (SI) of the water with respect to mineral phases were calculated using the geochemical model Visual MINTEQ version 3.00 [17] Summary statistics of the modeling.

The saturation index provides information about the dissolution and precipitation reactions occurring in the groundwater. The negative, zero and positive values of the index, respectively indicate undersaturation, equilibrium and oversaturation of water with respect to dissolved minerals [20,21].

As shown in Table 2, most of the surveyed groundwaters were oversaturated with respect to dolomite (82% of all water samples with SI mean value 0.63), calcite (77% and 0.17) and aragonite (65% and 0.02). Further, all water samples were under saturated with respect to sulphur-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 the dissolution of dolomite and calcite can be a main mechanism responsible for the chemical composition of the ground waters in the study area. The HCO_3^- and CO_3^{2-} may derive from carbonate and silicate minerals dissolution. In

the current study, a plot (Figure 2) of $\text{Ca}^{2+} + \text{Mg}^{2+}$ against $\text{CO}_3^{2-} + \text{HCO}_3^-$ shows that nearly all of the water samples fall along the 1:1 equiline ($r=0.94$). These findings indicate that dissolution of carbonate minerals are a source of the observed Ca^{2+} , Mg^{2+} , CO_3^{2-} and HCO_3^- in the water samples [22].

S. No	Constituents	Min	Max	Average
1	Calcium (Ca) (ppm)	25	173	77
2	Magnesium (Mg) (ppm)	27	133	66
3	Sodium (Na) (ppm)	6	86	33
4	Potassium (K) (ppm)	2	73	14
5	Bicarbonate (HCO_3^-) (ppm)	130	509	303
6	Carbonate (CO_3) (ppm)	38	222	113
7	Sulphate (SO_4) (ppm)	8	94	17
8	Chloride (Cl) (ppm)	21	207	71
9	Fluoride (ppm)	0.25	0.62	0.41
10	pH	6.7	7.9	7.3
11	Specific conductance (μmhoscm^{-1})	1210	4590	3638
12	Total dissolved solids (ppm)	787	2984	2364
13	Indices of base exchange (IBE) Cal1	-0.58	0.7	0.03
14	Indices of base exchange (IBE) Cal2	-0.12	0.39	0.03
15	Gibbs ratio I	0.11	0.6	0.27
16	Gibbs ratio II	0.1	0.55	0.31

Table1: Minimum, maximum and average values of different constituents of water samples

These results are supported by the fact that the basement minerals in this area are mainly carbonates and saturation indices for calcite and dolomite in most of the water samples were positive.

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, [25,26] suggested two chloro-alkaline indices CaI1 and CaI2 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 and Ca of the rocks, and is negative when there is an exchange of Mg and Ca of the waters with Na and K of the rocks.

From the Table 1, it can be put forth that the CaI1 values range from -0.58 to 0.70 with an average value 0.03 and CaI2 values vary from -0.12 to 0.39 with an average value 0.03. From these values it can be interpreted that some of the samples in the study area fall into negative zones and some fall into positive zones. They indicate that the exchange of Na and K from the water with Mg and Ca in its host environment is prevalent in the studied area. It may explain the excess Mg concentration in the water samples. The result suggests that cation exchange can also be one of the mechanisms responsible for the chemical composition of the ground waters in the studied area [27].

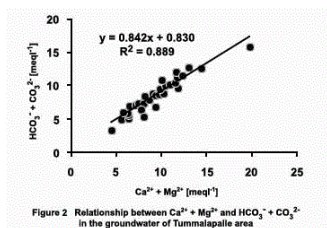


Figure 2: Relationship between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and HCO_3^{2-} in the groundwater of Tummalapalle area Indices of Base Exchange (IBE)

Control of the dissolution of undesirable constituents in waters is impossible during subsurface run off, but it is essential to know the changes undergone by the waters during its movement [23,24]. The

S No	Mineral saturation Index (SI)	Min	Max	Mean	Std. deviation
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1	Aragonite	-1	0.74	0.02	0.35
2	Artinite	-7.54	-3.72	-6	0.79
3	Brucite	-6.34	-3.96	-5.35	0.47
4	Calcite	-0.86	0.89	0.17	0.35
5	Dolomite (disordered)	-1.44	1.69	0.08	0.67
6	Dolomite (ordered)	-0.89	2.24	0.63	0.67
7	Epsomite	-5.25	-3.97	-4.84	0.26
8	Epsomite	-5.25	-3.97	-4.84	0.26
9	Gypsum	-3.11	-1.74	-2.52	0.25
10	Huntite	-5.63	0.6	-2.79	1.35
11	Hydromagnesite	-15.55	-7.12	-12.08	1.81
12	Lime	-22.5	-19.89	-21.1	0.5
13	Magnesite	-1.44	0.2	-0.69	0.34
14	Mirabilite	-10.19	-8.09	-8.96	0.44
15	Natron	-11.44	-9.02	-9.93	0.54
16	Nesquehonite	-4.23	-2.58	-3.48	0.34
17	Periclase	-10.82	-8.44	-9.83	0.47
18	Portlandite	-12.5	-9.9	-11.11	0.5
19	Thenardite	-11.62	-9.53	-10.39	0.44
20	Thermonatrite	-13.39	-10.97	-11.88	0.54
21	Vaterite	-1.42	0.32	-0.39	0.35

Table: 2 Summary statistics of mineral saturation index (SI) of Tummalapalle groundwater calculated by Visual MINTEQ*, *Positive values indicate saturation, and negative ones indicate under saturation

Indices of base exchange (IBE)

Control of the dissolution of undesirable constituents in waters is impossible during subsurface run off, but it is essential to know the changes undergone by the waters during its movement [23,24] 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, [25,26] suggested two chloro-alkaline indices CaI1 and CaI2 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 and Ca of the rocks, and is negative when there is an exchange of Mg and Ca of the waters with Na and K of the rocks.

From the Table 1, it can be put forth that the CaI1 values range from -0.58 to 0.70 with an average value 0.03 and CaI₂ values vary from -0.12 to 0.39 with an average value 0.03.

From these values it can be interpreted that some of the samples in the study area fall into negative zones and some fall into positive zones. They indicate that the exchange of Na and K from the water with Mg and Ca in its host environment is prevalent in the studied

area. It may explain the excess Mg concentration in the water samples. The result suggests that cation exchange can also be one of the mechanisms responsible for the chemical composition of the ground waters in the studied area [27].

Gibbs ratio

Reactions between groundwater and aquifer constituent minerals have a significant role on water quality. Further, these studies are useful to understand the genesis of groundwater [28,29] To know the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, [30] has suggested these types of diagrams. In this diagram the ratio of dominant anions and cations are plotted against the value of TDS. These diagrams are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation, rock, and evaporation dominance [31]. A similar study has been carried out by [11] and emphasized the mechanisms that control the chemistry of groundwater in Karnataka. The Gibbs ratios are calculated with the formulae given below:

$$\text{Gibbs Ratio I (for Anion)} = \text{Cl}^- / (\text{Cl}^- + \text{HCO}_3^-) \quad (1)$$

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

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

In the present study area, in order to know whether the ground water chemistry is due to rock dominance, evaporation dominance or precipitation dominance, the dominant anions (Cl^- and HCO_3^-) and cations (Na^+ , K^+ and Ca^{2+}) are plotted against their respective total dissolved solids (Figure 3),

Gibbs ratio I values in the present study varies from 0.11 to 0.60 with an average value of 0.27 and Gibbs ratio II values varies from 0.10 to 0.55 with an average value of 0.31. It can be elucidated that in the study area the samples fall into the evaporation dominance and samples viz. 6, 7 and 15 are falling in the rock dominance area.

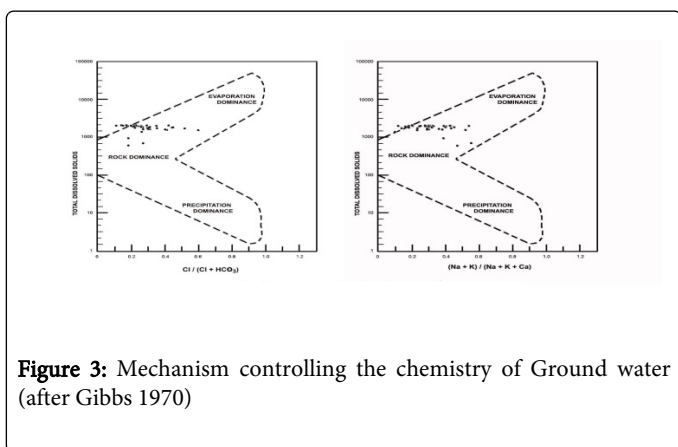


Figure 3: Mechanism controlling the chemistry of Ground water (after Gibbs 1970)

Conclusions

The groundwater sources in the Tummalalpalpe areas, evaluated for their hydrogeochemistry and its evolution of hydrochemical facies. The abundance of the major ions is as follows:



The host rock dolomite is responsible for contributing large amounts of magnesium in ground water. The results of calculations of Saturation indices (SI) by Visual MINTEQ software shows that most of the water samples were saturated with respect to carbonate minerals (dolomite, calcite and aragonite) and undersaturated with respect to sulfate minerals (gypsum, epsomite, mirabilite and thenardite). This study suggests that the dissolution of dolomite and calcite can be a main mechanism responsible for the chemical composition of the ground waters in the study area. The Gibbs diagram and Indices of Base Exchange (IBE) reveal that evaporation and cation exchangeable can also be responsible for concentration and composition of dissolved ions found in the groundwater, respectively.

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