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Hydrogeochemistry of Waters of Mangampeta Barite Mining Area, Cuddapah Basin, Andhra Pradesh, India

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Abstract

The study is undertaken in the barite mining area of Mangampeta (Lat. 14° 01' N; Long. 79° 19' E), which is located in the Kodur Mandal of Cuddapah District, Andhra Pradesh, India. The important geological formations in this area are quartzites (quartz veins), carbonaceous tuff and dolomites. The paper presents the assessment of water quality for its suitability for agricultural and domestic purposes. The results of chemical analyses for the major ions of 50 water samples collected from the entire study area (mining and adjacent virgin area) are presented. The quality analysis is performed through the estimation of silica, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, sulphate, chloride, total dissolved solids, pH, specific conductance, alkalinity and hardness. Based on the analyses, certain parameters like noncarbonate hardness, sodium adsorption ratio, percent sodium, potential salinity, residual sodium carbonate, Kelly's ratio, magnesium ratio, index of base exchange, permeability index and Gibb's ratio were calculated. The striking difference is in the sulphate content of mine water samples, which ranges from 211 to 589 mg/l, and is due to the presence of barites, the source for the high content of sulphates in the mining area. In contrast, in the virgin area water samples show 1-20 mg/l sulphate content. The bicarbonates (262 to 1100 mg/l) and alkalinity (198 to 953 mg/l) are very high and this is due to the presence of tuff and dolomitic rocks in the virgin area. According to the Gibb's diagram all the samples of both the virgin and mining area fall in the rock dominance field. From the evaluation it is known that the water quality is suitable for both domestic and irrigation purposes.

Key words: Hydrogeochemistry, Water quality, Mangampeta barite deposit, Andhra Pradesh.

Introduction

The Earth's immediate subsurface is a reaction front between the atmosphere (generally oxidising and acidic) and the geosphere (generally reducing and basic). Groundwater is the circulating medium which carries atmospheric reactants (oxygen, carbon dioxide) into the geosphere. The zone of groundwater circulation is typically the zone where redox and acid-base reactions occur. In normal groundwater environments, the contents of oxidisable minerals (e.g., pyrite) are so low or the access to oxidising species (e.g., oxygen) is so poor, that acid-base reactions (which consume protons) dominate over redox oxidation reactions (which may generate protons). Thus, "normal" groundwaters have typically neutral to slightly alkaline pH (Frengstad and Banks, 2000), dominated by base cations (Ca++, Mg++, Na+) and bicarbonate. 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 waters) their characteristic chemical signatures.

Groundwater forms one of the primary resources for developmental activity. Several interrelated processes control the chemical composition of the water and it is essential to understand the processes in order to arrive at the distribution and quality of various types. Underground water plays an important role in the overall water balance of the environment. The main factors that control the quality of water are associated with lithology and soil. Water quality may vary depending upon variations in geological formations. The ratio of different elements in the subsurface water is dependent on the associated rocks and sediments that form the aquifers and the time it has been in contact with this geological material. The shallow aquifers tap groundwater down to 50 m depth, while deep aquifers are 125 m deep. The aquifers are being tapped for augmentation of the drinking water supply and agriculture.

Human activities such as industrialisation, mining and urbanisation may also alter the water quality by polluting the environment (Pojasek, 1977; Salomons, 1995; Banks et al., 1997). The quality of water plays a prominent role in affecting both agricultural production and human health. Surface mining inevitably produces major environmental disturbances since vegetation, top soil and underlying soil mantle have to be removed to gain access to the minerals beneath. In underground mining, large quantities of waste are produced, which commonly exceed the volume of minerals (Plumlee et al., 1993; Salomons, 1995; Younger, 1997). Not only is there local destruction of the eco-system and loss of productive areas, but there can also be serious pollution problems caused by wind- and water-borne materials. The problem can be further aggravated as natural water courses may be disturbed due to disruption of surface and groundwater circulations. Various living communities may also be affected (Smith et al., 1983). Earlier studies have examined the environmental and occupational health implications of barites (Seaton et al., 1986; Thomas and Gary, 1992).

Mining affects water resources, both surface and groundwater, at various stages of the life cycle of the mine and even after its closure. The mining process itself, mineral processing operations, mine dewatering, seepage of contaminated leachates, flooding of mine workings, and discharge of untreated water are some important processes with related mine water problems (Younger et al., 2002).

This paper examines the water quality of a barite mining area and its adjacent virgin area and attempts to see whether chemical parameters have any impact on water quality.

Mangampeta barite deposit

The Mangampeta barite deposit is located in the Kodur Mandal of Cuddapah district, Andhra Pradesh (Lat. 14° 01' N; Long. 79° 19' E) and is included in the survey of India toposheet no. 57 N/8 (Figure 1). This is the single largest bedded deposit in the world. The deposit occurs as 2 separate lensoid bodies within the upper Carbonaceous tuff zone of the middle Proterozoic Cuddapah Supergroup. The granular barite beds overlain by a zone of lapilli barite constitute the economically significant deposit, with an estimated reserve of over 74 million tons. The ore deposit at some places is associated with copper mineralisation primarily consisting of pyrite, chalcopyrite, azurite and malachite.

Barite is mined by opencast mining and the deposit is a bedded deposit with tuff as hanging wall and dolomite as foot wall. The general strike of the deposit is $N30^0W - S30^0E$ and dips $20^{\circ}-30^{\circ}$ towards N-E. The top strata consist of soil and tuff, which forms the overburden. Under this strata there is a bed known as rosette barite (inferior barite) of specific gravity 4.2. Below it lies the good quality barite (specific gravity more than 4.27). Below this bed lie the black tuff and dolomite beds. The ore to overburden ratio is 1:3. Earlier workers studied mineralogical (Kurien et al., 1977), geochemical (Neelakantam, 1987; Basu, 1997), and petrological (Viswanath and Sastry, 1983) aspects of this mineralised area and confirmed that the deposit is of volcanic origin.

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Figure 1. Geology of the study area with sample locations.

Materials and Methods

The present study provides a detailed description of the chemical criteria of groundwater. Fifty representative samples (20 samples from the mining area [sample Nos. M1 to M20] and remaining 30 samples from the virgin area surrounding the mine [sample Nos. K21 to YK 50]) were collected in June 2003 and analysed for silica, calcium, potassium, sodium, magnesium, chloride, bicarbonate, sulphate, total hardness, alkalinity, TDS, EC, and pH. Further the sodium adsorption ratio, percent sodium, potential salinity, residual sodium carbonate, noncarbonate hardness, Kelly's ratio, magnesium ratio, permeability index, indices of base exchange and Gibb's ratio were calculated. The techniques and methods followed for collection, preservation, analysis and interpretation are those given by Rainwater and Thatcher (1960), Brown et al. (1970), ICMR (1975), Hem (1985), Raghunath (1987), Karanth (1989) and APHA (1995). The chemical quality data are shown in Tables 1-3. The sample locations in the study area are depicted in Figure 1. Various methods and graphs were used to study and interpret the water analyses data (Figures 2-5).

Results and Discussion

From Tables 1-3 the following observations were made for different parameters:

$\mathbf{p}\mathbf{H}$

The pH values in the water samples of the study area range from 7.34 to 8.17 in the mining area and from 6.84 to 7.84 in the adjacent virgin area. There are no very significant differences in pH values observed between mine water and adjacent virgin area samples.

Specific conductance (EC)

A high concentration of salts in irrigation water renders the soil saline. This also affects the salt intake capacity of the plants through the roots. Specific conductance of water samples ranges from 1020 to 1740 μ mhos/cm in the mining area samples and in the virgin area samples it varies between 646 and 1573 μ mhos/cm.

	Potential	$_{\rm salinity}$	9.42	9.60	8.61	7.22	6.96	6.55	4.96	7.09	5.18	8.15	7.36	7.53	7.77	4.06	7.43	6.89	7.18	7.34	7.05	7.51	2.26	1.70	1.47	2.97	3.50
	Percent	sodium	25.60	25.30	26.90	33.00	32.90	33.90	33.40	39.78	31.97	28.87	35.20	38.60	37.80	34.40	32.90	32.10	34.37	34.91	34.05	35.22	26.00	15.40	15.80	10.90	29.90
Alkalinity	as CaCO ₃	(mg/l)	133	163	150	134	138	136	227	139	195	150	141	142	170	144	140	154	242	142	175	134	388	639	783	953	440
Hardness	as CaCO ₃	(mg/l)	665	686	618	463	436	416	389	397	386	571	445	416	438	468	463	450	469	448	463	445	380	614	721	984	430
	TDS	(mg/l)	1078	1112	1016	819	766	741	699	782	655	966	809	816	819	848	817	786	836	811	826	813	498	712	662	1007	621
	SO_4	(mg/l)	558	589	509	374	316	320	211	318	216	474	340	290	280	380	344	326	378	342	336	342	,	1	,	3	,
	G	(mg/l)	128	124	118	118	130	114	98	134	104	114	136	160	172	126	136	124	115	134	126	140	180	09	52	104	124
	CO_3	(mg/l)	8	4	9	9	×	9	23	7	20	9	9	4	8	9	10	4	9	6	11	7	18	-	12	31	12
	HCO_3	(mg/l)	148	154	172	152	152	154	230	156	197	167	160	192	192	164	150	180	173	155	190	149	436	780	932	1100	512
	Na+K	(mg/l)	124	127	123	123	117	116	110	135	104	126	129	152	140	125	126	121	122	127	133	131	82	29	83	75	103
	К	(mg/l)	45	48	45	44	45	43	49	35	50	45	43	61	43	30	52	50	22	40	56	48	50	38	50	48	45
	Na	(mg/l)	62	62	78	62	72	73	61	100	54	81	86	01	26	95	74	11	100	87	22	83	32	29	33	27	58
	Mg	(mg/l)	132	139	120	106	95	26	74	85	72	109	96	86	89	92	98	96	94	95	98	96	74	105	156	224	78
	Ca	(mg/l)	49	46	50	11	17	7	34	19	36	49	20	25	29	36	24	22	33	23	24	20	23	73	32	25	43
	Si	(mg/l)	9	7	9	9	8	5	9	7	9	9	4	5	2	3	5	5	3	5	5	4	2	24	2	9	10
	$_{\rm pH}$		8.17	8.15	7.92	8.12	8.03	8.05	7.60	8.02	7.70	8.00	7.35	7.45	7.34	7.34	7.36	7.38	7.34	7.37	7.35	7.34	7.80	7.15	7.84	7.46	7.12
EC	$(\mu \text{ mhos})$	$^{\mathrm{cm}}$	1685	1740	1600	1280	1200	1160	1045	1225	1020	1510	1264	1276	1280	1325	1276	1230	1305	1270	1290	1270	778	1112	1218	1573	0.26
	Sample	No.	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M11	M12	M13	M14	M15	M16	M17	M18	M19	M20	K21	K22	K23	K24	K25
	SI.	No.	1	2	3	4	5	9	7	×	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
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 Table 1. Chemical analyses of water samples of the study area.

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		EC													Hardness	Alkalinity		
SI.	Sample	$(\mu \text{ mhos})$	μd	Si	Ca	Mg	Na	К	Na+K	HCO ₃	CO ₃	5	SO_4	TDS	as CaCO ₃	as CaCO ₃	Percent	Potential
No.	No.	cm		(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	sodium	$_{ m salinity}$
26	K26	1510	7.18	9	24	176	76	43	119	820		228	10	965	784	672	21.90	6.54
27	K27	931	7.50	4	40	76	56	45	101	519	10	111		596	413	443	30.31	3.13
28	K28	1280	7.15	8	28	123	81	48	129	514	1	276	3	819	576	422	29.20	7.82
29	K29	062	7.80	2	31	75	29	50	62	431	16	86	1	505	386	380	24.76	2.53
30	K30	1110	7.16	22	65	107	34	36	20	222	,	64		708	602	635	16.61	1.80
31	K31	808	7.82	7	33	73	36	45	81	502	21	57		518	383	447	26.20	1.60
32	K32	1035	7.14	11	47	80	62	51	113	524	14	137	1	659	455	461	30.95	3.86
33	K33	1341	7.50	4	28	134	64	53	132	009	,	251	15	858	621	492	27.84	7.24
34	A34	1386	7.13	5	50	53	42	35	27	404	29	68	3	887	343	380	28.40	1.95
35	A35	646	7.30	9	29	44	45	38	83	309	22	20	2	413	253	290	33.70	2.17
36	A36	1262	7.06	5	34	49	62	32	94	332	30	96	5	808	286	322	38.00	2.76
37	A37	730	7.05	8	42	43	55	30	85	262	33	106	20	465	282	270	35.90	3.20
38	A38	710	7.30	9	32	44	47	51	98	302	45	62	20	455	260	198	41.80	1.96
39	A39	1220	7.66	2	26	147	52	31	83	0.29	40	144	3	778	0.29	616	18.60	4.10
40	A40	1162	7.20	5	24	149	44	29	73	620	,	184	5	744	676	622	16.40	5.24
41	A41	710	7.13	5	47	46	49	21	20	264	36	107	14	454	307	277	30.33	3.31
42	A42	1200	7.20	5	23	151	46	31	27	686	44	127	3	200	678	635	17.07	3.61
43	A43	730	7.06	5	34	49	65	25	06	369	31	73	5	468	286	354	37.70	2.11
44	YK44	1140	6.88	11	21	152	27	32	59	738	1	120	3	728	678	605	12.80	3.42
45	YK45	1110	7.20	9	29	149	29	29	58	702	1	108	5	602	685	575	14.15	3.10
46	YK46	1140	6.84	11	21	152	28	31	59	741	ı	119	3	728	678	608	12.92	3.39
47	YK47	1175	7.25	9	31	150	32	30	62	722	ı	142	5	750	694	591	7.70	4.06
48	YK48	1150	7.20	9	27	147	30	36	99	740	1	122	5	736	672	909	14.20	3.49
49	YK49	1130	7.24	5	25	149	26	33	59	743		115	3	720	675	609	12.76	2.27
50	YK50	1150	7.20	5	23	153	31	29	60	751	,	122	3	734	687	616	13.20	3.47

Table 1. Contunied.

 $\rm M1-M20:$ Mine water samples; K21 – K33, A34 – A43, YK44 – YK50: Virgin area water samples

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Total Dissolved Solids (TDS)

Gorrel (1958) presented a very simple classification based on the total dissolved solids. The water samples in the present area belong to the "Fresh water" category, having a range of 655 to 1112 mg/l in the mining area, and 413 to 1007 mg/l in the virgin area samples. Out of the 50 samples collected, 46 samples fall into the "Fresh water" category while 4 samples (3 samples from the mine area and 1 sample from the virgin area) fall into the "Brackish water" category.

Waters can be classified based on the concentration of TDS (Wilcox, 1955; ICMR, 1975) as given below:

Up to 500 mg/l Desirable for drinking

Up to 1000 mg/l Permissible for drinking

Up to 3000 mg/l Useful for irrigation

Above 3000 mg/l Useful for drinking and irrigation $\,$

Based on the above classification, almost all samples in both mining and virgin areas will come under desirable and permissible for drinking.

Hardness

Hardness results due to the presence of divalent cations of which Ca and Mg are the most abundant in groundwater. Hardness in water is also derived from the solution of carbon dioxide released from the bacterial action in soil in percolating water (Sawyer and McCarty, 1967). The waters of the study area are classified according to hardness as suggested by Hem (1985). All the 50 samples collected in the study area fall into the very hard category. In the present study, the hardness of water samples ranged from 386 to 686 mg/l in the mine area samples and from 253 to 984 mg/l in the adjacent virgin area samples. This high amount of hardness in the virgin area samples is due to the presence of carbonate rocks, i.e. dolomites.

Alkalinity

Most of the natural waters contain substantial amounts of dissolved carbon dioxide, which is the principal source of alkalinity, and this can be conveniently evaluated by acid titrations. An increase in the temperature or decrease in the pressure causes a reduction in the solubility of CO_2 in water. In the present study, alkalinity ranges between 133 and 242 mg/l in the mine area and in the virgin area it ranges from 198 to 953 mg/l. The high amount of alkalinity in the virgin area samples is due to the presence of country rocks, i.e. carbonaceous tuff and dolomites.

Non-carbonate hardness (NCH)

Hardness of water relates to the reaction with soap, since Ca and Mg ions precipitate soap. Hardness is expressed as mg/l of CaCO₃. If the hardness as CaCO₃ exceeds the difference between the alkalinity as CaCO₃ and hardness as CaCO₃, it is called 'Noncarbonate hardness' (NCH). Non-carbonate hardness is further called permanent hardness. The NCH values range between 162.30 and 531.55 mg/l in the mine area samples and between -67.70 and 154.30 mg/l in the adjacent virgin area samples.

Sodium adsorption ratio (SAR)

Excess sodium in waters produces the undesirable effects of changing soil properties and reducing soil permeability (Kelly, 1951). Hence, the assessment of sodium concentration is necessary while considering the suitability for irrigation. The degree to which irrigation water tends to enter into cation-exchange reactions in soil can be indicated by the sodium adsorption ratio (U.S. Salinity Laboratory, 1954). Sodium replacing adsorbed calcium and magnesium is a hazard as it causes damage to the soil structure. It becomes compact and impervious. SAR is an important parameter for the determination of the suitability of irrigation water because it is responsible for the sodium hazard (Todd, 1980). The waters were classified in relation to irrigation based on the ranges of SAR values (Richards, 1954). According to Richard's classification all the samples of the study area have been classified as excellent for irrigation. SAR values of the water samples in the virgin area vary from 0.38 to 1.67 and in the mine area from 1.20 to 2.18.

Integrated effect of EC and SAR

The SAR and EC values of water samples of the study area were plotted in the graphical diagram of irrigated water (U.S. Salinity Laboratory, 1954) (Figure 2). The entire water samples of the mine area fall into C_3S_1 (high salinity with low sodium), and among the 30 water samples from the surrounding virgin areas, 5 samples fall into C_2S_1 (medium salinity with low sodium) and the remaining samples fall into C_3S_1 (high salinity with low sodium). The waters are satisfactory for irrigation use in almost

all soil types. All these waters are being used for irrigation, as they facilitate good soil drainage.

Percent sodium

Sodium concentration is important in classifying irrigation water because sodium reacts with soil to reduce its permeability. Soils containing a large proportion of sodium with carbonate as the predominant anion are termed alkali soils; those with chloride or sulphate as the predominant anion are saline soils. The role of sodium in the classification of groundwater for irrigation was emphasised because of the fact that sodium reacts with soil and as a result clogging of particles takes place, thereby reducing the permeability (Todd, 1980; Domenico and Schwartz, 1990). Percent sodium in water is a parameter computed to evaluate the suitability for irrigation (Wilcox, 1948). The percent sodium values of the mine area samples vary from 25.30 to 39.78 and in the virgin area it ranges from 7.70 to 41.80.

Percent sodium is plotted against conductivity,

which is designated as a Wilcox diagram (Figure 3). From this figure, it is clear that 20 mine samples and most virgin area samples fall into the category of 'Good to permissible', while 5 virgin area samples fall into the category of 'Excellent to good'.

Potential salinity

This is defined as the chloride concentration plus half of the sulphate concentration. Doneen (1954) pointed out that the suitability of water for irrigation is not dependent on the concentration of soluble salts. Doneen (1962) is of the opinion that the low solubility salts precipitate in the soil and accumulate with each successive irrigation, whereas the concentration of highly soluble salts increases the salinity of the soil. The potential salinity of the water samples ranges from 4.06 to 9.60 in the mine area and in the adjacent area it varies from 1.47 to 7.82. This huge amount of potential salinity is due to the presence of sulphates, which are derived from the ore mineral, i.e. barites.



Figure 2. The quality of water in relation to salinity and sodium hazard (after US Salinity Laboratory, 1954).



Figure 3. The quality of water in relation to electrical conductivity and percent sodium (Wilcox diagram).

Residual sodium carbonate

In addition to total dissolved solids, the relative abundance of sodium with respect to alkaline earths and boron, and the quantity of bicarbonate and carbonate in excess of alkaline earths also influence the suitability of water for irrigation. This excess is denoted by 'Residual sodium carbonate' (RSC) and is determined as suggested by Richards (1954).

The water with high RSC has high pH and land irrigated by such waters becomes infertile owing to deposition of sodium carbonate as known from the black colour of the soil (Eaton, 1950). According to the U.S. Salinity Laboratory (1954), an RSC value less than 1.25 meq/l is safe for irrigation, a value between 1.25 and 2.5 meq/l is of marginal quality and a value more than 2.5 meq/l is unsuitable for irrigation. In the present study, the waters in both virgin areas and the mine show RSC values of -11.06 to 1.35 meq/l, which includes both the safe and marginal quality categories for irrigation. Further, continued usage of high residual sodium carbonate waters affects crop yields.

Permeability Index (PI)

The soil permeability is affected by long-term use of irrigation water. Sodium, calcium, magnesium and bicarbonate content of the soil influence it. Doneen (1964) evolved a criterion for assessing the suitability of water for irrigation based on a permeability index (P.I.) where

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

Accordingly, waters can be classified as Class I, Class II, and Class III orders. Class I and Class II waters are categorised as good for irrigation with 75% or more of maximum permeability. Class III waters are unsuitable with 25% of maximum permeability. Accordingly, all the samples fall into the Class I category of Doneen's chart. In the present study, P.I. values vary from 29.29 to 48.40 in the mining area samples and from 26 to 61.80 in the virgin area samples. These values are more pronounced in the virgin area than in the mining area samples.

Indices of base exchange (IBE)

Control of the dissolution of undesirable constituents in waters is impossible during the subsurface run off but it is essential to know the various changes undergone by waters during the travel (Pojasek, 1977; Johnson, 1979). The ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloro-alkaline indices. To know the direction of exchange during the path of groundwater through the aquifer, Schoeller (1965, 1977) suggested 2 chloroalkaline 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 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.

In the present study, CaI_1 values range from - 0.51 to -0.09 in mine area samples and from -0.91 to 0.49 in virgin area samples. CaI_2 values vary from -0.16 to -0.05 in mine area and from -0.23 to 0.36 in the adjacent area samples. In the study area, all the samples in the mining area fall into the category of negative zones, while some samples fall into positive zones in the virgin area. This indicates that in some water samples in the virgin area, the exchange of Na and K from the water with Mg and Ca of the dolomitic rocks is taking place.

Kelly's ratio

Based on Kelly's ratio waters are classified for irrigation. Sodium measured against calcium and magnesium was considered by Kelly (1940) and Paliwal (1967) to calculate this parameter. A Kelly's ratio of more than one indicates an excess level of sodium in waters. Therefore, waters with a Kelly's ratio less than one are suitable for irrigation, while those with a ratio more than one are unsuitable. Kelly's ratio in the present study varies from 0.06 to 0.49 in the virgin area and from 0.25 to 0.55 in mining area samples. Therefore, according to Kelly's ratio, all of the water samples are suitable for irrigation.

Magnesium ratio

Generally, calcium and magnesium maintain a state of equilibrium in most waters. In equilibrium more Mg in waters will adversely affect crop yields. As the rocks of the study area consist of dolomites, it is observed that most waters contain more Mg than Ca. In the present study 98% of samples contain a Mg ratio more than 50%. This would adversely affect the crop yield as the soils become more alkaline. In the present study, the 'Magnesium ratio' values vary from 14.99 to 95.81 in the mining area samples and from 61.74 to 93.66 in the virgin area samples. These high values are because of the presence of dolomite in these areas.

Gibbs ratio

Gibbs (1970) proposed a diagram to understand the relationship of the chemical components of waters from their respective aquifer lithologies. Viswanathaiah et al. (1978) emphasised the mechanism of controlling the chemistry of groundwater of Karnataka. Further, Ramesam and Barua (1973) carried out similar research work in the northwestern regions of India. Three distinct fields, namely precipitation dominance, evaporation dominance, and rock dominance areas, are shown in the Gibbs diagram (Figure 4).

The Gibbs ratios are calculated with the formulae given below.

Gibbs Ratio I (for anion) = $Cl/(Cl+HCO_3)$

Gibbs Ratio II (for cation) = Na+K/(Na+K+Ca)where all ions are expressed in meq/l.



Figure 4. Mechanism controlling the quality of groundwater (after Gibbs, 1970).

Gibbs ratios for the study area samples are plotted against their respective total dissolved solids as shown in Figure 4 to know whether the ground water chemistry is due to rock dominance, evaporation dominance or precipitation dominance. In the present study, Gibbs ratio values for adjacent virgin and mine area samples are shown in Tables 2 and 3. It is observed from the diagrams that both virgin and mining area samples fall into the rock dominance area, indicating the interaction between rock and water in the subsurface.

Graphical methods of representing analyses

Piper diagram Collins (1923) first proposed a graphical method of representation of chemical analysis. The method was later modified by Piper (1944, 1953), based on the concentration of dominant cations and anions, and a trilinear diagram was proposed to show the percentages at milli equivalents per litre of cations and anions in water samples. The Piper diagram was modified by Davis and Dewiest (1967). The trilinear diagrams of Piper are very useful in bringing out chemical relationships among groundwaters in more definite terms (Walton, 1970). This is useful to understand the total chemical character of water samples in terms of cation-anion pairs.

			- -	N				LJL T			
			Residual	-HONI				Indices of Da	ase excitange		
SI.	Sample	SAR	sodium	carbonate	Permeability	Kelly's	Magnesium	Chloroalka-	Chloroalka-	Gibb's	Gibb's
No.	No.		carbonate	hardness	index	ratio	ratio	line indices 1	line indices 2	Ratio I	Ratio II
1	M1	1.33	-10.63	531.55	29.80	0.26	81.62	-0.27	-0.07	0.60	0.65
2	M2	1.31	-11.06	522.95	29.29	0.25	79.22	-0.33	-0.08	0.58	0.67
3	M3	1.36	-9.36	467.90	32.16	0.27	79.82	-0.37	-0.09	0.54	0.64
4	M4	1.60	-6.58	328.80	39.48	0.37	94.07	-0.37	-0.12	0.57	0.89
5	M5	1.50	-5.97	298.30	39.73	0.36	90.28	-0.17	-0.07	0.60	0.83
9	M6	1.56	-5.60	280.25	41.42	0.38	95.81	-0.33	-0.11	0.56	0.92
7	M7	1.35	-3.25	162.30	44.02	0.34	78.20	-0.41	-0.13	0.42	0.70
8	M8	2.18	-5.15	257.55	48.40	0.55	88.06	-0.39	-0.16	0.60	0.85
6	M9	1.20	-3.82	191.20	41.18	0.30	76.73	-0.24	-0.08	0.48	0.67
10	M10	1.46	-8.43	421.30	34.58	0.30	78.57	-0.44	-0.11	0.54	0.66
11	M11	1.77	-6.07	303.70	42.42	0.39	88.78	-0.26	-0.10	0.59	0.83
12	M12	1.89	-5.49	274.40	46.68	0.48	14.99	-0.22	-0.11	0.59	0.82
13	M13	2.02	-5.36	267.75	46.15	0.48	83.49	-0.09	-0.05	0.61	0.79
14	M14	1.91	-6.38	323.95	42.76	0.44	80.82	-0.38	-0.12	0.57	0.73
15	M15	1.50	-6.46	323.05	38.38	0.35	87.06	-0.18	-0.07	0.61	0.79
16	M16	1.46	-5.91	295.60	39.77	0.34	87.79	-0.25	-0.09	0.54	0.80
17	M17	2.01	-4.54	227.20	43.95	0.46	82.44	-0.51	-0.13	0.53	0.75
18	M18	1.79	-6.12	306.20	42.19	0.42	87.19	-0.27	-0.10	0.60	0.81
19	M19	1.56	-5.76	288.10	40.60	0.36	87.07	-0.34	-0.12	0.53	0.80
20	M20	1.71	-6.20	311.00	41.36	0.41	88.78	-0.22	-0.09	0.62	0.83
21	K21	0.72	0.16	-7.70	45.24	0.18	80.55	-0.18	-0.05	0.41	0.70
22	K22	0.51	0.21	-25.25	35.72	0.10	70.34	-0.32	-0.04	0.12	0.38
23	K23	0.54	1.24	-62.20	33.68	0.09	88.93	-0.85	-0.08	0.09	0.63
24	K24	0.38	-0.61	30.60	26.00	0.06	93.66	0.18	0.03	0.14	0.66
25	K25	1.22	0.20	-9.85	48.75	0.29	75.03	-0.05	-0.02	0.29	0.63

Table 2. Hydrogeochemical parameters of water samples of the study area.

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	Gibb's	Ratio II	0.79	0.64	0.77	0.62	0.42	0.62	0.63	0.77	0.52	0.67	0.67	0.60	0.68	0.70	0.69	0.53	0.71	0.67	0.65	0.58	0.66	0.58	0.62	0.61	0.64
	${\rm Gibb's}$	Ratio I	0.32	0.27	0.48	0.26	0.12	0.16	0.31	0.42	0.22	0.30	0.33	0.41	0.26	0.27	0.34	0.41	0.24	0.25	0.22	0.21	0.22	0.25	0.22	0.21	0.22
se exchange	Chloroalka-	line indices 2	0.15	-0.05	0.36	-0.01	-0.05	-0.12	-0.01	0.23	-0.10	-0.13	-0.12	-0.03	-0.23	0.08	0.25	0.06	0.06	-0.20	0.11	0.07	0.11	0.15	0.10	0.10	0.11
Indices of ba	Chloroalka-	line indices 1	0.31	-0.15	0.39	-0.04	-0.33	-0.69	-0.03	0.32	-0.42	-0.37	-0.30	-0.06	-0.91	0.25	0.49	0.12	0.22	-0.68	0.41	0.26	0.40	0.46	0.35	0.39	0.39
	Magnesium	ratio	92.63	75.80	87.86	79.95	73.07	78.48	73.73	88.75	63.59	71.43	70.37	62.79	69.38	90.33	91.13	61.74	91.54	70.38	92.27	89.44	92.27	87.08	89.97	90.76	91.64
	Kelly's	ratio	0.21	0.29	0.31	0.16	0.12	0.20	0.30	0.28	0.27	0.39	0.47	0.42	0.39	0.17	0.14	0.35	0.15	0.49	60.0	0.09	60.0	0.10	0.10	0.08	0.10
	$\operatorname{Permeability}$	index	36.73	50.10	42.73	43.65	37.29	43.60	48.42	28.32	50.69	59.92	59.70	55.63	58.80	35.62	33.07	50.98	34.39	61.80	31.59	30.65	31.84	31.63	32.47	31.52	32.20
Non-	$\operatorname{carbonate}$	hardness	111.80	-29.55	154.30	5.95	-32.85	-63.75	-6.45	129.30	-36.75	-36.60	-35.65	12.00	61.65	53.60	53.60	30.10	43.00	-67.70	72.80	109.90	70.30	102.65	65.55	66.30	71.25
Residual	sodium	$\operatorname{carbonate}$	-2.24	-0.59	-3.09	-0.12	0.66	1.27	0.12	-2.59	0.74	0.73	0.71	-0.24	0.99	-1.07	-3.35	-0.60	-0.86	1.35	-1.46	-2.20	-1.41	-2.05	-1.31	-1.33	-1.42
	SAR		1.18	1.20	1.47	0.64	0.60	0.80	1.27	1.38	0.99	1.23	1.59	1.43	1.27	0.87	0.74	1.22	0.77	1.67	0.45	0.48	0.47	0.53	0.50	0.43	0.51
	Sample	No.	K26	K27	K28	K29	K30	K31	K32	K33	A34	A35	A36	A37	A38	A39	A40	A41	A42	A43	YK44	YK45	YK46	YK47	YK48	YK49	YK50
	SI.	No.	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50

Table 2. Contunied.

M1 – M20: Mine water samples; K21 – K33, A34 – A43, YK44 – YK50: Virgin area water samples

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Sl.							
No.	Constituents	Min	Max	Mean	SD	SE	'r' value
1	Silica (SiO_2) (mg/l)	3	8	5.45	1.28	0.29	-0.62
2	Calcium (Ca) (mg/l)	7	50	28.70	12.31	2.75	-0.29
		(4)	(24)	(7.67)	(4.53)	(0.82)	(-0.31)
3	Magnesium (Mg) (mg/l)	72	139	98.45	16.17	3.61	0.46
		(43)	(224)	(110.27)	(48.70)	(8.89)	(0.15)
4	Sodium (Na) (mg/l)	54	100	80.85	11.82	2.64	0.29
		(26)	(81)	(44.73)	(16.36)	(2.99)	(-0.24)
5	Potassium (K) (mg/l)	22	61	44.70	8.36	1.87	0.05
		(21)	(53)	(38.17)	(9.04)	(1.65)	(-0.71)
6	Bicarbonate (HCO_3) (mg/l)	148	230	169.35	21.04	4.70	0.13
		(262)	(1100)	(593.33)	(205.50)	(37.52)	(-0.03)
7	Carbonate (CO_3) (mg/l)	4	23	8.25	4.79	1.07	-0.02
		(10)	(45)	(26.11)	(11.11)	(2.03)	0.75
8	Sulphate (SO_4) (mg/l)	211	589	362.15	97.53	21.81	0.42
		(1)	(20)	(6.09)	(5.54)	(1.01)	(-0.02)
9	Chloride (Cl) (mg/l)	98	172	127.55	16.70	3.73	0.30
		(52)	(276)	(120.70)	(54.90)	(10.02)	(-0.05)
10	Total dissolved solids (mg/l)	655	1112	839.25	115.60	25.85	-0.38
		(413)	(1007)	(686.93)	(154.61)	(28.23)	(-0.07)
11	Hardness as $CaCO_3(mg/l)$	386	686	476.60	85.19	19.05	-0.46
		(253)	(984)	(538.63)	(187.96)	(34.32)	(0.09)
12	Alkalinity as $CaCO_3(mg/l)$	133	242	157.45	30.10	6.73	0.16
		(198)	(953)	(510.97)	(165.14)	(30.15)	(-0.04)
13	Non-carbonate hardness (mg/l)	162.30	531.55	319.15	95.17	21.28	-0.47
		(-67.70)	(154.30)	(27.68)	(60.37)	(11.02)	(0.39)
14	Specific conductance (μ mhos/cm)	1020	1740	1312.55	181.95	40.68	-0.38
		(646)	(1573)	(1073.60)	(241.17)	(44.03)	(-0.06)
15	рН	7.34	8.17	7.67	0.33	0.07	0.88
10		(0.84)	(7.84)	(7.28)	(0.26)	(0.05)	(-0.47)
16	Sodium adsorption ratio (SAR)	1.20	2.18	1.62	(0.27)	(0.05)	0.45
17	Dansant as diama	(0.38)	(1.07)	(0.90)	(0.39)	(0.07)	(-0.19)
17	Percent sodium	20.0 (7.70)	39.78 (41.80)	33.03	3.81	(1.70)	(0.34)
19	Potential calinity	(1.10)	(41.80)	(23.04)	(9.31)	(1.70)	(-0.20)
10	r otentiai samiity	(1.47)	(7.82)	(3.33)	(1.50)	(0.29)	-0.29 (0.02)
19	Residual sodium carbonate	-11.06	-3.25	-6.41	1.07	(0.23)	(0.02)
15	rtesiduar sourum carbonate	(-3.35)	(1.35)	-0.41 (-0.60)	(1,31)	(0.24)	(-0.33)
20	Permeability Index	29.29	48.40	40.21	5 10	1 14	0.51
20	i crineability index	(26)	(61.80)	$(41 \ 42)$	(10.54)	(1.92)	(-0.16)
21	Chloroalkaline indices 1	-0.51	-0.09	0.12	-0.30	-0.06	0.10
		(-0.91)	(0.49)	(-0.01)	(0.40)	(0.07)	(0.43)
22	Chloroalkaline indices 2	-0.16	-0.05	-0.10	0.02	0.01	-0.11
		(-0.23)	(0.36)	(0.02)	(0.13)	(0.02)	(0.22)
23	Kellev's ratio	0.25	0.55	0.37	0.07	0.02	0.23
~		(0.06)	(0.49)	(0.22)	(0.12)	(0.02)	(-0.10)
24	Magnesium ratio	14.99	95.81	81.54	16.13	3.61	-0.01
	5	(61.74)	(93.66)	(81.16)	(10.29)	(1.88)	(0.23)
25	Gibbs ratio I	0.42	0.62	0.56	0.05	0.01	0.11
		(0.09)	(0.48)	(0.27)	(0.09)	(0.02)	(-0.02)
26	Gibbs ratio II	0.64	0.92	0.77	0.08	0.02	0.29
		(0.38)	(0.79)	(0.63)	(0.08)	(0.01)	(0.02)

Table 3. Minimum, maximum and average values of different constituents of water samples.

Values in parentheses are virgin area water samples; Values outside parenthesis are mine area water samples

The Piper diagram (Figure 5) consisting of 2 triangular and 1 intervening diamond-shaped field. All 3 sides of the 2 triangular fields and the 4 sides of the diamond-shaped field are divided into 100 parts. The percentage reacting values at the 3 cation groups— Ca, Mg and (Na+K)—are plotted as a single point in the left triangular field and the 3 anion groups— (HCO_3+CO_3) , SO₄ and Cl—similarly on the right triangular field. The 2 points in each triangular field show the relative concentration of several dissolved constituents of the water sample. Later a third point is plotted in the central diamond-shaped field after computing percentage reacting values for anions and cations separately. This field shows the complete chemical character of the water samples that gives the relative composition of groundwater about the cation-anion point. These 3 fields reflect the chemical character of groundwater according to the relative concentration of its constituent but not according to the absolute concentrations.

Later Piper (1953) classified the diamond-shaped field of the trilinear diagram into 9 areas to know quickly the quality of water and they are given below.

Area-1: Alkaline earth's (Ca+Mg) exceeds alkalies (Na+K) (includes areas 5, 6 and 9a)

Area-2: Alkalies exceed alkaline earth's (includes areas 7, 8 and 9b)

Area-3: Weak acids (CO_3+HCO_3) exceed strong acids (SO_4+Cl+F) (includes areas 5, 8 and 9b)

Area-4: Strong acids exceed weak acids (includes areas 6, 7 and 9a)

Area-5: Carbonate hardness (secondary alkalinity) exceeds 50%.

Area-6: Non-carbonate hardness (secondary salinity) exceeds 50%

Area-7: Non-carbonate alkali (primary salinity) exceeds 50%

Area-8: Carbonate alkali (primary alkalinity) exceeds 50%

Area-9: None of the cation and anion pairs exceed 50%



Figure 5. Piper diagram for representing the analysis of groundwater quality.

In the present study, it is noted that all the samples of both virgin mining area fall under area-1, no samples fall under area-2; all virgin area samples fall under area-3; all samples from the mine area come under area-4; all virgin samples falls under area-5; 4 samples from the mine area fall under area-6; 16 samples from mine area fall under area-9; and no samples fall under area-8.

Conclusions

- 1. The water samples in the virgin area show enrichment of magnesium and calcium among cations and of bicarbonate among anions. Geochemically the behaviour of magnesium is different from that of calcium. Magnesium ions are smaller than Na or Ca ions and therefore have a stronger change density and greater attraction for water molecules. This enrichment is due to the dissolution of mineral dolomite [(Mg, Ca) CO₃]. Generally, the concentration of magnesium in waters ranges from 72 to 139 mg/l in the mining area and from 43 to 224 mg/l in the virgin area samples. The desirable range for drinking is 30-100 ppm (Indian Standards Institution, 1991).
- 2. Sulphate is predominant in the waters of the

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Davis, S.N. and Dewiest, R.J.M., Hydrogeology. John Wiley and Sons, New York, p 463, 1967. mining area and this enrichment of sulphate in mine waters is due to barite $(BaSO_4)$.

3. Quartz (the crystalline form of silica) and the feldspars, amphiboles, pyroxenes and mica (the silicate minerals) are the chief sources of silica in groundwater. When the water is fresh, silica comes next in abundance to bicarbonate, but at higher concentrations the silica content is usually less than that of sodium, bicarbonate, sulphate and chloride. Silica in the present study area varies between 4 and 24 ppm in the virgin area samples and between 3 and 8 ppm in the mining area water samples.

The minerals are responsible for the release of the above-mentioned elements predominantly in large amounts. These cations are solubilised and removed by leaching, leaving a residue deprived of its easily soluble bases. Based on concentration of TDS, about 92% of the samples are within the permissible limit both for drinking and irrigation, while 8% are useful only for irrigation but not for drinking. Although soluble salts of barium are regarded as extremely poisonous to higher animals, barite (barium sulphate) is only slightly soluble in water (approximately 2 mg/l) (Thomas and Gary, 1992).

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