

## **Groundwater quality deterioration due to clay mining industry in a midland region of Kerala**

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### **Abstract**

Groundwater represents a significant and in many places predominant proportion of the drinking water source. In Kerala State, open dug wells are the sole source of drinking water especially in rural areas where surface water based protected water supply systems are scanty. The availability of this precious resource is diminishing in recent past not only due to over exploitation but also due to pollution arising from different origin. Indiscriminate disposal of sewage and solid wastes on lands coupled with agricultural and industrial activities pose great threat to domestic wells. Groundwater quality deterioration due to industrial activities needs special mention as industries discharge enormous quantities of untreated or partially treated wastes containing toxic chemicals into the environment which ultimately reaches subsurface water sources. A study conducted to assess the quality of selected wells around a clay mining industry in Kannur, Kerala revealed that over 61% of the observation wells has been polluted due to the presence of high level of sulphate or chloride and become non-potable. The wells located within one km distance are more affected than the wells beyond. The predominant pollutant is observed to be sulphate with a maximum recorded concentration of 1875 mg/l in the well water. The mine discharge effluent was characterised by high acidity with pH value as low as 2.4 and of sulphate as high as 2860 mg/l. The sulphur bearing overburden materials of the mining site especially iron pyrite was observed to be the major cause of the pollution. Few wells located east and western side of the mining area were observed to have the influence of salinity intrusion also.

The study deals with the impact of indiscriminate discharge of mine effluents on the groundwater quality especially in open dug wells around clay mining industry at Madayi, Kannur District of Kerala. The nature and extent of pollution and , the temporal variations are discussed. An attempt was also made to use the stable isotope technique using  $^{34}\text{S}/^{32}\text{S}$  ratio to identify the source of sulphate in this area.

### **INTRODUCTION**

Groundwater use is continuously increasing in many parts of our country to meet the ever growing domestic, municipal, agricultural and industrial demands. In Kerala, groundwater mainly in the form of open dug wells are the sole source of drinking water especially in the rural areas where the protected water supply schemes, based on surface water sources are scanty. Extensive use of groundwater has led to problems like lowering of water table, salt water intrusion etc. People often over look the groundwater problems until the problems are well advanced. The groundwater quality is affected by both natural and man-made activities. Among various problems, industrial activities pose great threat to these precious sources as wide variety of chemicals contained in waste effluents are

discharged into the environment without proper treatment. The different kinds of pollutants altering the quality of the water are of diverse in nature which mainly depend on the type of the industry, the various chemicals in use, the processes involved and the transformation that would take place after the effluents reach the environment. Pollution of freshwater bodies due to major industries like pulp & paper mills, tanneries, sugar industries and textile industries are well documented. Mining industry, though does not involve any chemical process, too fall in this category causing degradation of both terrestrial and aquatic environment in a local and regional scale. The deterioration of the drinking water quality and pollution of aquatic environment due to mine discharge around the mining area has been reported in many parts of the world (Blevins, 1989; Gray, 1996). The investigations on the effect of coal mining on water quality showed that acidity and the concentration of sulphate, iron, manganese and aluminium were generally higher around mined areas. The overflowing water from water filled mines and open pits in pyrite and coal mined areas was observed to be acidic and severely polluted by metals and sulphate (Christensen et al., 1996).

In this paper, the results of an investigation carried out to assess the impact of effluents on groundwater sources around a clay mining industry in Kannur, Kerala are reported. The nature and extent of pollution and the seasonal trends in the quality of well water are discussed.

## **STUDY SITE DESCRIPTION**

### **Location, Physiography and Climate**

The study area, Madayippara is located 29 kms north-west of Kannur city. It lies between 75° 15' 0" and 75° 15' 50" East longitude and between 12° 0' 13" and 12° 0' 51" North latitude (Figure 1). This place is about 2.5 km east from the shoreline. The mining area comprises of mostly flat topped or gently undulating hills of laterite with a maximum elevation of 41m above mean sea level. The general gradient of Madayippara plateau falls from northern side to the southern side with gentle slope at the low lying areas with moderate to steep slope at higher elevations. The low lying land surrounding the terrace is sea regressed area and many layers of sea shells could be seen beneath the sandy layer or clay layer.

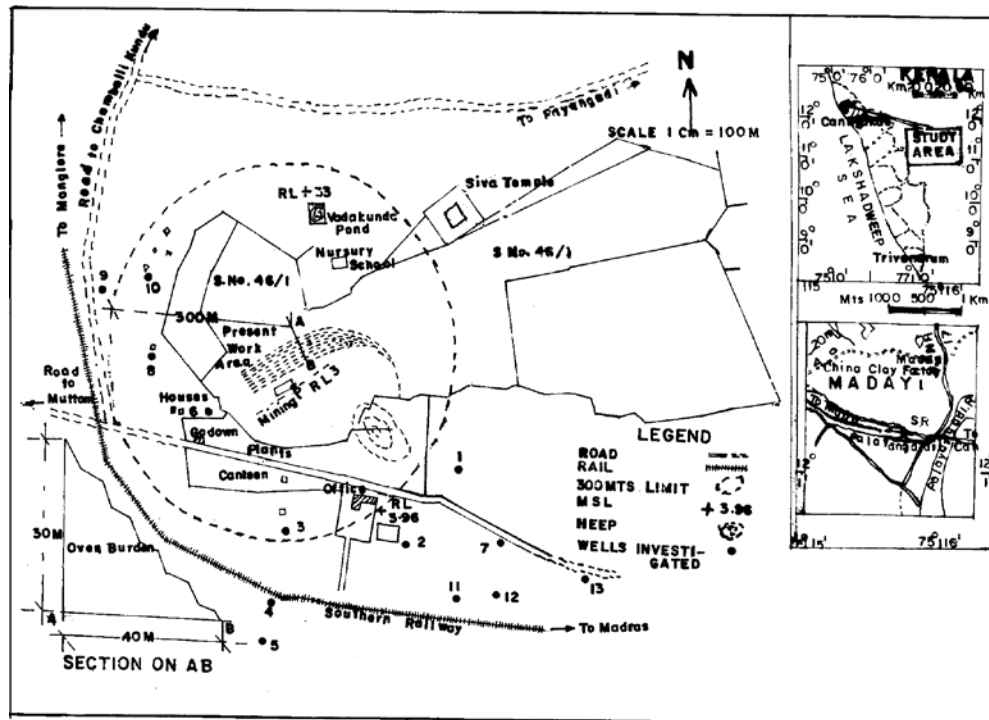
The study area receives an average annual rainfall of 3308 mm with 81.2% being received during south-west monsoon alone. The mean daily temperature is 25.4°C. The month of May is the hottest with the maximum recorded temperature of 34.2°C.

## **MATERIALS AND METHODS**

### **Preliminary Survey**

A survey was conducted around Madayi clay mining area to collect details on the physical environment, mining activities, the various processes involved in mining, mode of disposal of mine effluents etc. The survey revealed that apparently no waste effluent is observed to be generated during the process of clay extraction and purification. However, it was observed that the open pits developed as a result of open-cast mining are filled

with rain water which are discharged through channels/open drains after the rainy season. The water ultimately finds its way to the nearby groundwater sources in the low lying areas through percolation. The heap of over-burden materials dumped outside the mining area is also transported by wind and storm run-off to nearby lands leading to environmental problems.



**Figure 1. Location map of the study area.**

The open wells in this low lying area are shallow with a total depth ranging from 2.8 – 3.7 m and having diameter ranging between 1.1 and 2.1 m. All the wells in these area are lined with laterite and few wells are plastered too.

### **Mining Process**

The Kerala Clays and Ceramic Products Ltd. is carrying out mining operations at Madayi in Kannur since 1952 and the Kerala Government undertook the industry in 1976 with a total lease land of 34 acres. The mining land comprises of hard laterite to a depth of 10 m followed by high aluminium laterite to 2 m, alternate layers of ball clay and lignite to 10 m and finally the China clay to a depth of 10.5 m. Clays are extracted by open-cast mining by digging the clay dry and washing with water to remove impurities. The water carrying the clay, sand and impurities are conveyed into shallow channels called sand pits. The sand gets deposited at the bottom and overflow containing the clay conveyed through channels are led to settling tanks. The settled clay slurry is pumped off to the pressing unit where it is filtered and clay is removed as cake. The same water is re-circulated throughout the process. During the process of separation of clay from impuri-

ties, apparently no waste effluents are observed to be generated. However, it was observed that during monsoon season, the rain waters get accumulated in the open pits developed as a result of open-cast mining. Once the pits get filled, the excess rain water overflows and taken as surface runoff to the nearby stream through open drains around the mining area. The left out water which was accumulated in the pits are pumped off to the drains after the rainy season is over during the month of September-October. The water was observed to be brownish in colour. It ultimately finds its way to the nearby groundwater sources in the low lying areas through percolation .

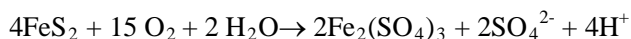
### Sample collection and analysis

Based on the survey, a network of 13 representative wells were identified around the mining area for water quality monitoring. The locations of the observation wells are marked in Figure 1. The water samples were collected in July, October 1996 and , January and April 1997. They were subjected to analyses for physico-chemical characteristics. Mine discharge effluent samples were also collected to ascertain the quality of the mine effluents. Samples were collected in pre-washed plastic containers after proper rinsing. Samples were preserved wherever necessary. All the analyses were carried out as per the standard methods available in literature (APHA, 1995).

## RESULTS AND DISCUSSION

### Quality of mine drainage

The physico-chemical quality of the mine drainage is presented in Table 1. The quality of the effluents discharged from the mine area were observed to be highly acidic with pH ranging from 2.4 – 2.5 and were rich in sulphate and iron. The sulphate content ranged between 2800 – 2860 mg/l and iron 350 – 360 mg/l during the period of observation. The high sulphate and low pH may be due to the formation of sulphuric acid resulting from the oxidation of iron sulphide minerals. During mining, the sulphur bearing over burden materials are uncovered and are exposed to air and moisture. The exposure of iron sulphides especially, pyrites (FeS<sub>2</sub>) in the tracts, to water and oxygen results in the production of acid and iron sulphate( Powell and Larson1985; Blevins, 1989)



These effluents when discharged untreated, lead to the pollution of groundwater sources around the area.

**Table 1. Physico-chemical quality of the mine drainage observed during 1996.**

Period	PH	Total Dissolved Solids	Total Hardness (as CaCO <sub>3</sub> )	Chloride	Sulphate	Nitrate	Iron	Calcium	Magnesium
July	2.4	3725	600	20	2800	2.8	360	176	35.4
October	2.5	3840	1100	20	2860	5.8	350	364	46.4

NB: All values except pH are expressed in mg/l.

### **Quality of well water**

The observed levels (ranges) of different constituents in the water of selected wells during 1996-97 are presented in Table 2. The results indicate that high acidity in a few wells, and high sulphate content observed in most of the wells, are the main causes for the water quality deterioration. Water in over 61% of the observation wells is non-potable with the presence of high concentration of sulphate or chloride, and in some cases with very low pH also. The wells, MDY2 and MDY6 which are in close vicinity to the mine boundary are observed to be highly polluted with very low pH, and very high sulphate content. The extent of pollution is observed to decrease as the distance from the mine area/drains increases. Some of the wells in the low lying area are already observed to be under the influence of sea water intrusion, especially during summer months. The wells, MDY8, MDY9 and MDY10 located western side of the mining area are suspected to be intruded by sea water as evidenced by the higher level of chloride than sulphate in these wells. Moreover, in these cases, the ratio of  $SO_4/SO_4+Cl$ , an index generally used to discriminate the source of sulphate (Robinson and Bottrell, 1995) is found to be greater than 0.12, the value for sea water, which confirms that sulphate, originating from other source is also present. The other source could most probably be the mine effluents in this location. Thus, these wells have the impact of both sea water as well as the mine drainage.

### **Temporal variations in water quality**

Temporal trends in concentrations of selected water quality constituents viz. TDS, chloride and sulphate, for the observation wells (MDY-1 to MDY-12) are presented in Figure 2a & 2b. It may be noted that all the wells do not follow similar pattern in temporal variations. In well Nos. MDY1, MDY2 and MDY3, the level of dissolved solids and sulphate increases from July 96 to April 97 and reaches maximum in April. The level of increase from January to April is steep in case of well nos. MDY1, MDY2 whereas, it is gradual in well No. MDY3. The first two wells are located very near to the mining boundary than the third well, which may be the possible reason for the above. Variations in chloride are not significant in these wells. The water quality data indicates that the wells with numbers MDY8, MDY9 and MDY10 have higher levels of chloride than of sulphate in their waters during all the observations, and follow a similar trend. These three wells are located in the western part of the mine pits and may have the influence of sea water also. Among the three wells, MDY8 is observed to have more influence due to sea water intrusion as evident from the high level of chloride compared to the others. In case of the wells, MDY4 and MDY7, it is found that they contain significantly high levels of sulphates during January than in April, contrary to the expected trend. The possible reasons for these variations may be that the well waters are subjected to high water level fluctuations due to variations in the flow of effluents through the open drains, sea-water intrusion, surface run-off from precipitation, and uneven topography of the terrain.

### **Identification of source of sulphate using stable isotopic data**

Dissolved sulphates in rivers, lakes and other water resources are derived generally from either of the following sources:

1. Sulphate in rain water
2. Oxidation of pyrite and other forms of reduced sulphur

3. Leaching of sulphate minerals
4. Other natural sources such as geothermal water
5. Sulphates of agricultural and industrial origin such as fertilizers and industrial effluents (Robinson and Bottrell, 1995)

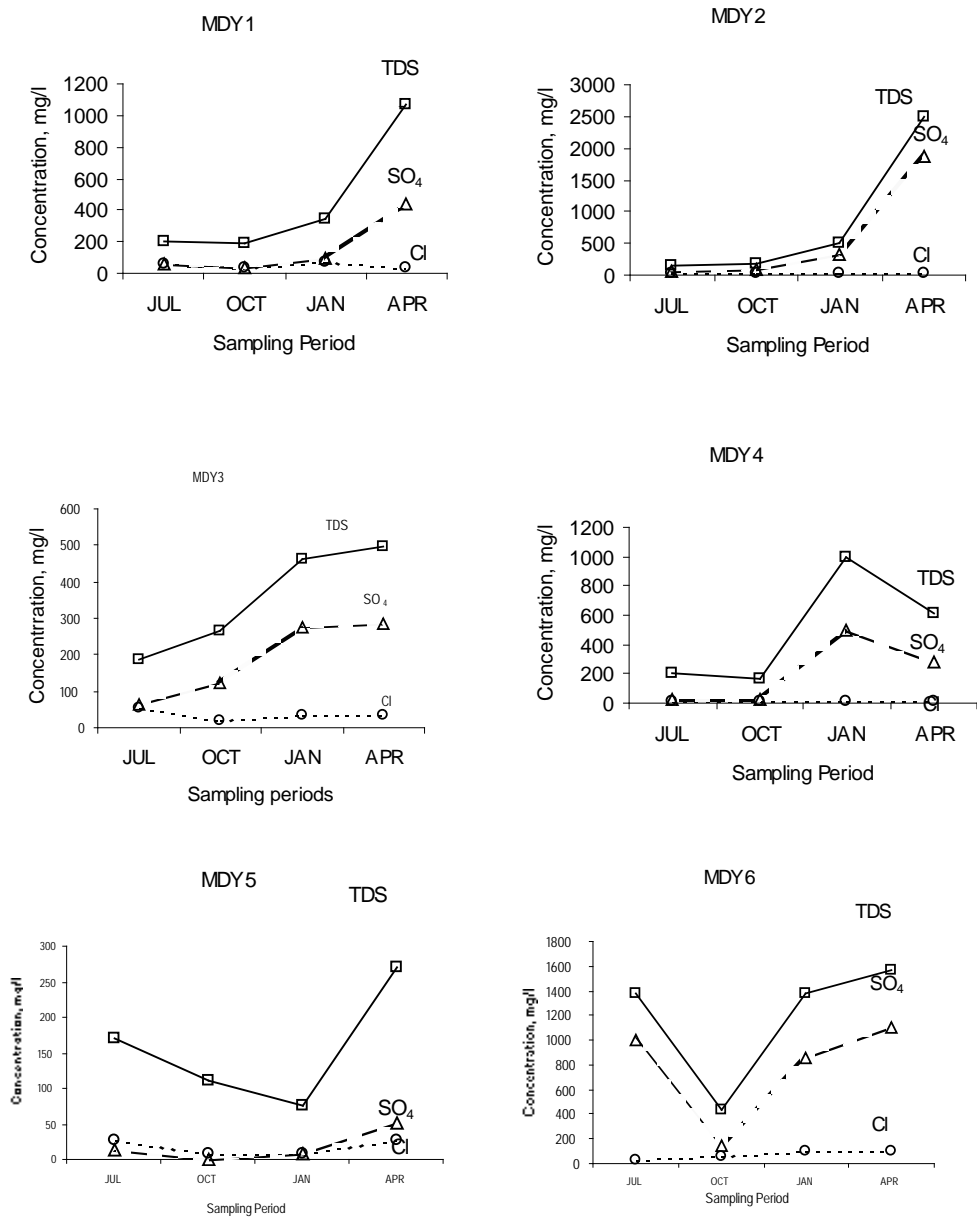
**Table 2. Physico-chemical characteristics (Ranges) of well water during 1996-97.**

Sl No	Sample Code	PH	Total Dissolved Solids	Total Alkalinity (as CaCO <sub>3</sub> )	Total Hardness (as CaCO <sub>3</sub> )	Chloride	Sulphate	Nitrate	Iron	Calcium	Magnesium
1	MDY-1	6.9-8.0	186-1075	12-65	52-520	34-66	38-438	9.1-12.7	0.05-0.64	14.4-152	3.9-34.2
2	MDY-2	2.5-4.1	142-2496	---	56-520	16-36	60-1875	2.0-8.4	0.09-1.7	14.4-60.8	3.9-90.3
3	MDY-3	6.0-8.1	188-499	44-48	96-340	22-52	63-288	0.8-6.8	ND-0.29	30.4-94.4	4.9-29.2
4	MDY-4	7.7-8.4	172-998	90-116	100-644	14-16	25-500	1.0-11.6	ND-0.28	36.8-235.2	2.0-26.8
5	MDY-5	7.9-8.5	77-267	44-116	44-250	8-28	1-53	1.4-1.6	ND-0.29	12.8-68	2.9-19.5
6	MDY-6	2.7-3.9	430-1574	--	252-830	28-108	150-1100	1.6-10.8	0.15-1.65	65.6-256	14.6-97.6
7	MDY-7	7.6-8.2	348-1267	62-110	234-608	28-354	38-313	2.4-12.0	ND-0.6	67.2-188.8	16.1-32.2
8	MDY-8	7.7-8.4	932-1498	142-180	390-516	230-560	78-173	3.2-12.8	ND-0.42	92.0-145.6	27.3-39.0
9	MDY-9	7.7-8.4	430-614	104-146	200-348	68-86	31-70	2.4-10.8	ND-0.49	70.4-118.4	5.9-14.6
10	MDY-10	7.7-8.5	265-538	88-150	140-200	32-76	15-40	2.8-9.0	ND-0.35	43.6-61.6	7.6-11.2
11	MDY-11	6.8-8.5	154-353	24-96	76-230	10-20	36-145	1.1-3.4	0.06-0.9	24.0-68.0	2.9-14.6
12	MDY-12	7.8-8.5	430-922	62-158	266-490	42-90	100-300	2.6-8.5	ND-1.4	68.8-144.0	12.7-31.7
13	MDY-13	7.6-8.4	111-207	60-92	64-112	12-28	4-16	1.4-3.6	ND-0.4	20.8-36.8	2.9-8.3

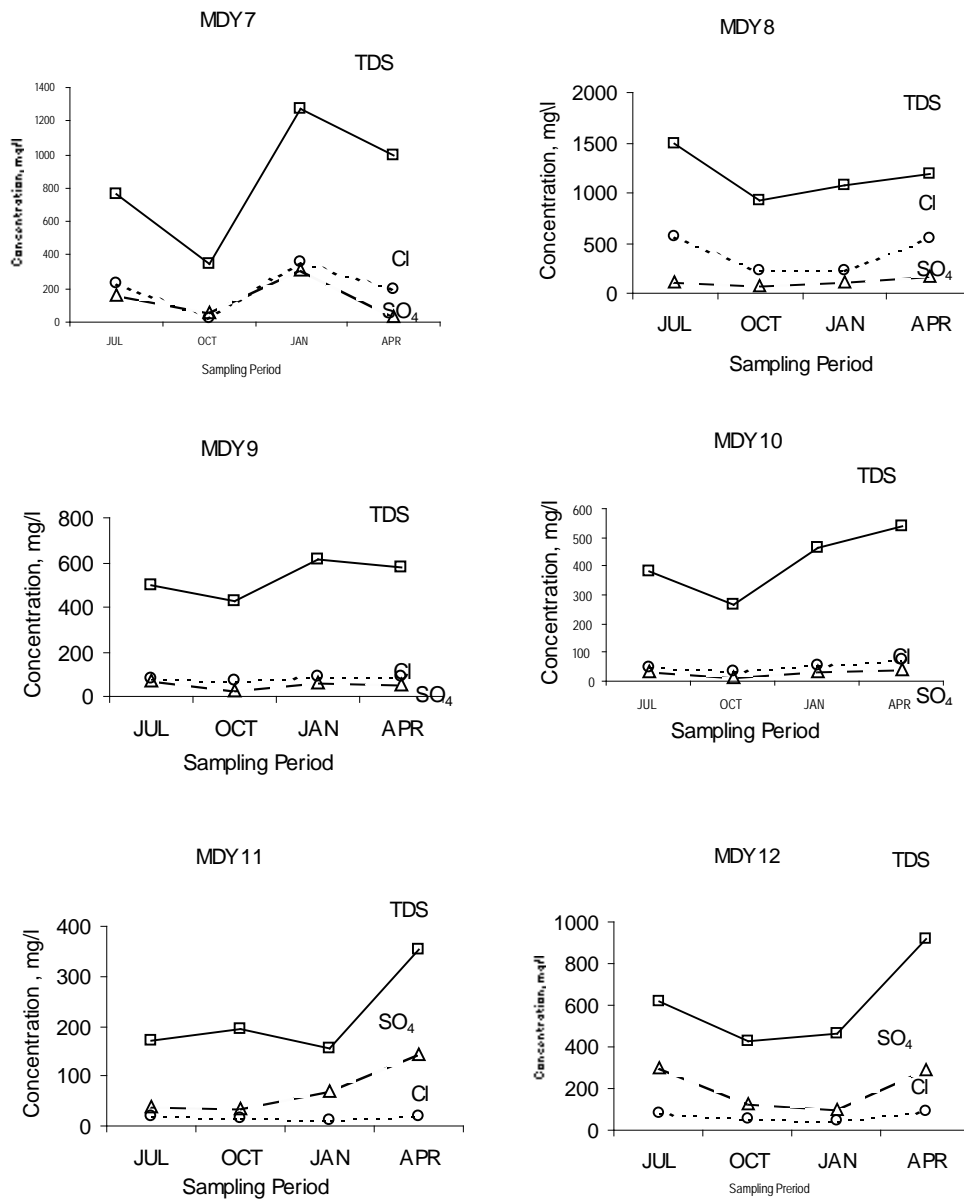
NB : All values except pH are expressed in mg/l ; ND : Non –detectable

The amount of sulphate in water may correlate directly with one main input or may be from multiple sources. Environmentally stable isotopic data provide authentic information on the actual source. In the case of sulphate, its sulphur and oxygen carry variable isotopic signatures (<sup>34</sup>S/<sup>32</sup>S, <sup>18</sup>O/<sup>16</sup>O), which can help to delineate the exact source of its origin.

Isotopically the sources represent two groups:relatively heavy sulphate (<sup>34</sup>S- enriched) from evaporate minerals, and relatively light sulphate (<sup>34</sup>S-depleted) derived from reduced sulphur sources such as sulphide minerals or organic sulphur in soil. The investigations on the isotopic composition of sulphate sources to the Xingwen Karst aquifer, Peoples Republic of China, revealed that rain and percolation sulphate have uniform  $\delta^{34}\text{S}$  ranging from +0.4 to +1.6‰, mine drainage sulphate has  $\delta^{34}\text{S}$  values from +2 to +3 ‰, and sulphate in shale drainage around +6‰ (Bottrell and Robinson, 1993).



**Figure 2 (a). Temporal variations in concentrations of selected constituents in well water (MDY-1 to MDY-6).**



**Figure 2(b). Temporal variations in concentrations of selected constituents in well water (MDY-7 to MDY-12).**

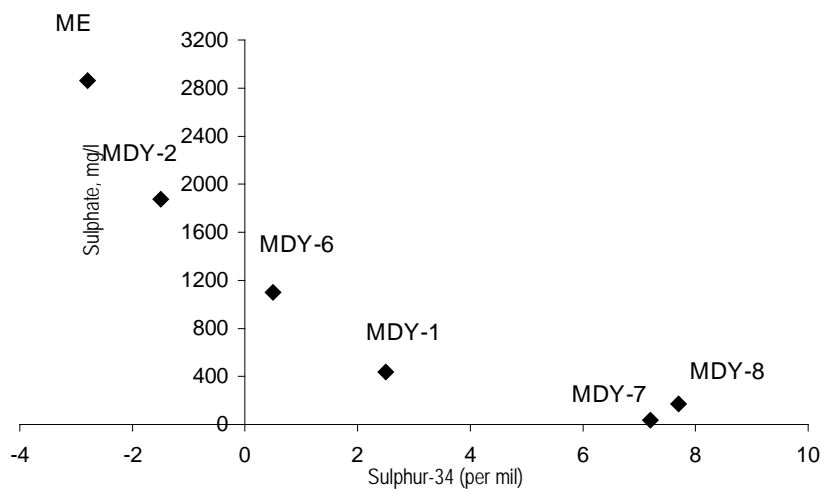
In the present study, a set of five well water samples and a sample from the mine effluent were subjected to stable isotope, <sup>34</sup>S/<sup>32</sup>S analyses and the results of isotopic composition and the sulphate level in these samples are presented in Table 3.



**Table 3. Stable isotopic ratio  $\delta^{34}\text{S}$  of selected well water samples.**

Sl.No.	Sample Code	Conc. of Sulphate, mg/l	$\delta^{34}\text{S}\text{‰}$
1.	MDY-01	437	+2.5
2.	MDY-02	1875	-1.5
3.	MDY-06	1100	+0.5
4.	MDY-07	38	+7.2
5.	MDY-08	173	+7.7
6.	Mine Effluent(ME)	2860	-2.8

A plot of sulphate concentration versus  $\delta^{34}\text{S}$  for the above (Figure 3) indicates that the well Nos.1,2 and 6 have sulphate contamination derived from clay mine effluents as evidenced by the  $\delta^{34}\text{S}$  values of  $-1.5$  to  $+2.5$ , which are close to the value of mine effluent. The remaining wells show values around  $+7\text{‰}$ , which are markedly different from the range of the earlier ones. These enhanced  $\delta^{34}\text{S}$  values may be due to intrusion of sea water.



**Figure 3. Sulphur-34 versus Sulphate.**

## CONCLUSIONS

The study conducted to investigate the effect of clay mine drainage on the quality of groundwater sources revealed that over 61% of the observation wells were polluted with

high sulphate or chloride and in few cases with low pH. The wells located in the southern part in the low lying area and close to the mining boundary were observed to be severely affected. The  $\delta^{34}\text{S}$  values of sulphate along with the index on  $\text{SO}_4/\text{SO}_4+\text{Cl}$  clearly indicated that though the wells in the area are influenced by sea water intrusion also, the predominant source of pollution is from the effluents of clay mining industry. The mining activities expose fresh strata of the overburden containing sulphur bearing materials, especially pyrites ( $\text{FeS}_2$ ) to the action of oxygen and water resulting in the oxidation of sulphides to ferrous sulphate and sulphuric acid. This acidic and sulphate rich effluent, when discharged through open drains finds its way to nearby wells leading to pollution. It was also observed that the temporal variations in water quality do not follow any regular pattern which may be attributed to reasons such as the uneven topography of the terrain, location of wells, effect due to sea-water intrusion, variation in the flow of effluent through the drains and distance of the drains from the wells etc.

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