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ORIGINAL ARTICLE

Metal Pollution Assessment in Ground Water

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ABSTRACT
The study is carried out to find the heavy metal contamination in the ground water of Batlagundu, Dindigul District, Tamilnadu. To get the extend of heavy metals contamination, water samples were collected from nine different locations in the study area and the concentrations of heavy metals such as Zinc, Copper, Cadmium, Iron and lead were determined using Atomic Absorption Spectrophotometer (AAS). Assessment of heavy metal contamination in ground water required knowledge of pre anthropogenic metal concentrations to act as a reference against which measured values can be compared. Groundwater contamination by heavy metal was carried out using Enrichment Factor (EF),Contamination Factor (Cf), Contamination degree (Cd), modified Contamination Degree (mCd), Pollution load Index(PLI), Metal Pollution Index(MPI), Metal Contamination Index (MCI) and Geo accumulation Index (Igeo) .Based on the above indices, the study area is found to be very low degree of heavy metal pollution.
Keywords : Enrichment Factor (EF),Contamination Factor (Cf), Contamination degree (Cd) and Geo accumulation Index (Igeo) .

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INTRODUCTION

Pollution of the natural environment by heavy metals is a worldwide problem because these metals are permanent and most of them have toxic effects on living organisms when they exceed a certain concentration [1]. Heavy metals are one of the most poisonous and serious groups of pollutants due to their high toxicity, abundance, and ease of accumulation from various plants and animals. It has been accepted that heavy metals can exist in the environment deriving from a variety of natural and anthropogenic sources. Heavy metals are introduced anthropogenic ally as pollutants into lotic and lentic aquatic ecosystems from industrial, agricultural and domestic wastewater / effluents . Discharge of greater quantity pollutants into the aquatic environment may result into deterioration of ecological imbalance, changes the physical and chemical nature of the water and aquatic biota [2].

The natural occurrence of heavy metals in aquatic environments and their movement through the hydro cycle in addition to the inputs from anthropogenic activities reflect their ubiquity and complexity. Their origins may be classified into various sources including terrigenous derived from continents (weathering and erosion), biogenic derived from organism decays (skeletal parts, carbonaceous orsiliceous), authigenic derived from seawater (chemical or biochemical precipitation and Fe-Mn nodules), volcanogenic, extra-terrestrial or cosmogonies, and anthropogenic derived from human activities. Industrialization, urbanization, agriculture (food production), and natural resources exploitation (mining and energy exploration) are basic activities associated with the modern living and vibrant society [3]. However, these anthropogenic activities can contribute to the environmental impacts of aquatic habitat, decrease in fishery and aquatic plant resources, fish migration and human health concerns. Heavy metals are natural constitutes of natural waters; some are present at low concentrations and are biologically important in aquatic environment, but some are toxic. Metals in natural waters are induced from various sources. Natural geological weathering of rocks and soils, directly exposed to surface waters, is usually the largest natural source. Several studies have shown that metals exist at low concentrations in natural waters, partially in soluble ionic forms and partially forms bound to inorganic or organic particulate matters, and their toxicity can be attributed mainly to their soluble forms .Besides the natural processes, metals may enter into the aquatic system due to anthropogenic factors such as mining operations, disposal of industrial wastes and applications of biocides for pest. Anthropogenic sources of elemental

contamination and pollution released into the environment have been summarized by many researchers [4].

The increasing contaminations of aquatic environment by heavy metals released from various sources as a consequence of industrialization and urbanization in this era are major environmental concern of all countries. Heavy metals are some of the main source of toxicity problems in the aquatic environment when they occur above the threshold concentrations. The behavior of heavy metals in the environment depends on their inherent chemical properties. Trace metal contaminations are important due to their potential toxicity for the environment and human beings. Some of the metals are the essentials for metabolic activity in organisms to sustaining aquatic biodiversity, but there is a narrow gap between their essentiality and toxicity. Toxic heavy metals can accumulate in the bodies of aquatic organisms, including fish, making them unfit for human consumption Various pollution indices have been calculated from the point of view of the suitability of groundwater for human consumption with respect to metal contamination. Ground water is one of the major sources of drinking water in the study area so it was important to assess the ground water quality with respect to heavy metal contamination.

The main objectives of this study were:

1. Determining background concentrations of the investigated heavy metals.
2. Assessing the water contamination by heavy metals and prioritizing contaminated areas for further investigation.
3. Distinguishing between natural and anthropogenic sources of the studied metals.

The results of this study can be used by authorities for directing environmental monitoring, management, and remediation programs.

MATERIALS AND METHODS

Study area

Batlagundu is a block of DindigulDistrict.It is geographically located at Longitude and Latitude is 77 ^{0} 45' 33.84" E and 10 ^{0} 9' 55.80"N with an average elevation of 320 meters(1049 feet).In the 2001 India census, Batlagundu had a population of 22,007.The main occupation of this study area is agriculture. The source of water supply in the area is hand pumps, bore holes and dug wells. The precipitation which is the sole source of ground water recharges in the study area is very low due to less rain fall. The area is very humid (86%) and warm with an average temperature 22 ^{0}C.In order to determine the heavy metal contamination, nine sites were chosen for sample collection in this study area.The map of the study area is given in Fig.1.

Analysis of the samples

The samples taken from different sampling sites have been analyzed for various heavy metals such as Zinc, Copper, Lead, Cadmium and Iron as per the suggestions given by APHA [5]. Concentrations of heavy metals in water samples were determined with an atomic absorption spectrophotometer (GCB-Avanta) with a specific lamp for particular metal. Average values of three replicates were taken for each determination. Appropriate drift blank was taken before the analysis of samples. The working wave length for the heavy metals are 248.3 nm for Fe, 213.9 nm for Zn, 324.7 nm for Cu, 228.8 nm for Cd, 217 nm for Pb.

Data analysis

Many authors prefer to express the metal contamination with respect to average shale to represent the degree of quantification of pollution. Some authors have considered the background value of their area of study to be the geometric mean of concentration at the different sample sites, which is the antilog of the arithmetic average of log10 (log to the base 10) of the concentration values. According to them, the geometric mean reduces the importance of a few high values in a sample group and therefore, is numerically less than the arithmetic mean, making it a useful indicator of background for most geochemical data. Such background value, however, varies from place to place. As such, this methodology of determining background value has not been considered in the present study. Instead, the world surface rock average [6] of individual metal has been taken to be the background following the recent works of some authors. Mean concentration of metals at selected sampling stations and their world surface rock average is given in Table 1.The degree of contamination in water is determined with the help of following parameters Enrichment Ratio (ER), Contamination factor (*Cf*),Contamination degree(*Cd*),Modified contamination degree(*mCd*), Pollution Load Index (PLI), Metal pollution index(MPI) , Metal contamination Index(MCI) and Geo accumulation Index(*Igeo*).

Enrichment Factor (EF):

Enrichment factor analysis, a method proposed by Simex and Helz [7] to assess trace element concentration, is mathematically expressed as:

$$Enrichment Factor(EF) = \frac{(C_x/Fe)_{sample}}{(C_x/Fe)_{Background}} \text{----------(1)}$$

where, Cx stands for concentration of metal 'x'. The background value is that of the world surface rock average [6] given in Table 1. According to Forstner and Wittmann [8] in case of Fe, particularly the redox sensitive iron-hydroxide and oxide under oxidation condition constitute significant sink of heavy metals in aquatic system. Even a low percentage of $Fe(OH)_3$, in aquatic system, has a controlling influence on heavy metal distribution. Fe is used as the normalized metal as it is an acceptable normalization element to be used in the calculation of enrichment factor since Fe distribution was not related to other heavy metals [9]. Fe usually has a relatively high natural concentration and is therefore not expected to be substantially enriched from anthropogenic sources in estuarine sediments . Therefore, Fe is taken as a normalization element while determining enrichment factor (EF). Five contaminant categories based on the EF value [10] is given in Table 2

Contamination factor (*Cf*) :

The contamination factor can be calculated from the following relation.

$$Contamination factor(Cf) = \frac{C_{sample}}{C_{Background}} \text{----------(2)}$$

Where C_{sample} and $C_{background}$ refers the measured concentrations of a pollutant and the average shale respectively. Table 3 presents the Contamination factor (Cf) based on Hakonson [11].

Contamination degree (*Cd*)

The numeric sum of the k specific contamination factors expressed the overall degree of contamination (*Cd*) by Hakanson [11] using the following formula.

$$Contamination degree(Cd) = \sum_{i=1}^{k} Cf \text{----------(3)}$$

The *Cd* is aimed at providing a measure of the degree of overall contamination in a particular core or sampling site. Furthermore, all n species must be analysed in order to calculate the correct *Cd* for the range of classes defined by Hakanson[11] (Table 4). Modified and generalised forms of the equation for the calculation of the overall degree of contamination are presented by equation 3 at a given sampling. The modified formula is generalized by defining the degree of contamination (*mCd*) as the sum of all the contamination factors (*Cf*) for a given set of pollutants divided by the number of analysed pollutants. The modified equation for a generalised approach to calculating the degree of contamination is given below.

$$Modified contamination degree(mCd) = \frac{\sum_{i=1}^{k} Cf}{n} \text{----------(4)}$$

Where *n* is number of analysed elements and *i*is *i*thelement (or pollutant) and *Cf* is contamination factor. Using this generalized formula to calculate the *mCd* allows the incorporation of as many metals as the study may analyse with no upper limit. For the classification and description of the modified degree of contamination *(mCd)* are proposed in (Table 5).

Pollution Load Index (PLI)

Pollution load index (PLI), for a particular site, has been evaluated following the method proposed by Tomilson [12]. This parameter is expressed as

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 - - - - - - \times Cf_n)^{1/n} \text{----------(5)}$$

where, n is the number of metals (five in the present study) and *Cf* is the contamination factor.

Metal Pollution Index (MPI)

MPI has been calculated to enable presentation of all results from the metal concentrations (Cd, Cu, Zn, Pb and Fe) as one value if possible, yet overcoming the difficulties with both application and understanding of demanding statistical analysis. According to Jorgensen and Pedersen [13], this implies that the five metal concentrations must be normalised to make it possible to sum up and average the different metal concentrations into one value.MPI has been calculated as

$$MPI = log \sum_{i=1}^{5} \frac{[X]}{ref_i} - - - - - - - - - - - (6)$$

Where ref_i represents a normalizer, or a reference value for each of five chosen metals (Cd, Cu, Pb, Zn and Fe) in selected sites, while x represents mean value of metal concentration from the chosen sampling site. If calculated as proposed, MPI distinguishes "polluted" from "non-polluted" ecosystem: if this combined index is above 1 the concentrations of trace metals would be considered elevated and ecosystem could be regarded as "polluted".

Elemental contamination index (ECI) and overall metal contamination index (MCI)

Elemental contamination index (ECI) and overall Metal Contamination Index (MCI) are expression of single metal contamination within a sample or combined metal contamination for a sample relative to the back-ground values of the respective metal and are expressed as

$$ECI = \frac{[C_n - B]}{B} \text{----------(7)}$$

$$MCI = \sum\left(\frac{(C_x - B)}{B}\right)$$ ----------(8)

where, Cx, and B metal concentration and Background value of the metal. According to Meybeck[14] MCI was designed to describe general trace elements contamination on a scale from 0 to 100, with MCI of <5 implies very low contamination; 5–10 = low contamination; 10–25 = medium contamination; 25–50 high contamination; 50–100 = very high contamination and >100 implies extremely high contamination.

Geo accumulation index (I_{geo})

A common approach to estimate the enrichment of metal concentrations above background or baseline concentrations is to calculate the geo accumulation index *(I_{geo})* [15]. The method assesses the degree of metal pollution in terms of seven enrichment classes based on the increasing numerical values of the index. This index is calculated as follows:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$ ----------(9)

Where C_n is the concentration of the element in the enriched samples, and the B_n is the background or pristine value of the element. The factor 1.5 is introduced to minimise the effect of possible variations in the background values which may be attributed to lithological variations in the sediments. Therefore, if the concentration of element in a sample be five times greater than the concentration of it in the background the sample is extremely polluted. Muller proposed the following descriptive classes for increasing I_{geo} values in Table (6).

Table 1:Mean concentration of metals at selected sampling stations and their world surface rock average

Metals	Mean concentration of metals in ppm	World surface rock average
Fe	0.6033	4.72
Zn	0.1889	95
Cu	0.0777	45
Pb	0.05	20
Cd	0.0144	0.3

Table 2. Five contaminant categories based on EF value

Enrichment factor(EF) value	Contamination degree
<2	Deficiency to low enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

Table 3: Contamination factor (*Cf*) based on Hakonson classification

Contamination factor(Cf)	Classification
<1	Low contamination factor
1-3	Moderate contamination factor
3-6	Considerable contamination factor
>6	Very high contamination factor

Table 4: Contamination degree (*Cd*) based on Hakanson (1980) classification

Contamination degree(Cd)	Classification
<6	Low contamination degree
6-12	Moderate contamination degree
12-24	Considerable contamination degree
>24	Very high contamination degree

Table 5: Hakanson(1980) classification of the modified degree of contamination

Modified contamination degree(mCd)	Classification
<1.5	Very Low degree of contamination
1.5-2	Low degree of contamination
2-4	Moderate degree of contamination
4-8	High degree of contamination
8-16	Very high degree of contamination
16-32	Extremely degree of contamination
>32	Ultra degree of contamination

Table 6: Enrichment factor of heavy metals in selected sampling stations

Sample number	Zn	Cu	Pb	Cd
S_1	0.0133	0.0886	0.0199	0.6646
S_2	0.0172	0.0464	0.0681	0.9087
S_3	0.0198	0.0336	0.0378	0.3149
S_4	0.0155	0.0224	0.0232	0.2582
S_5	0.0963	0.0214	0.0722	0.1607
S_6	0.01	0.0112	0.01	0.1675
S_7	0.0248	0.0138	0.0621	0.4144
S_8	0.0157	0	0.0414	0.2763
S_9	0.0429	0.0143	0.0107	0.7158

RESULTS AND DISCUSSIONS

Enrichment Factor (EF)

A common approach to estimating anthropogenic impact on water and sediments is to calculate a normalized enrichment factor (EF) for metal concentrations above uncontaminated background levels. The EF measured in heavy metal content with respect to a reference metal such as Fe or Al. Due to the lack of geochemical background values of the study area an alternative of the average crustal concentrations as reference material. Deely and Fergusson [9] proposed Fe as an acceptable normalization element to be used in the calculation of the enrichment factor since they consider the Fe distribution which was not related to other heavy metals. EFs close to unity point show crustal origins while those greater than one are related to non-crustal source.(Table 7). In this study the EFs obtained for all heavy metals are less than unity that reveals these elements are depleted in some of the phases relative to crustal abundance in the study area.(Fig.2).

Table 7: Contamination factor, contamination degree, modified contamination degree and Pollution load index for selected sampling stations

Samplig stations	Contamination factor(Cf)					Contamination degree(Cd)	Modified contamination degree(mCd)	PLI
	Fe	Zn	Cu	Pb	Cd			
S_1	0.1504	0.0020	0.0133	0.0030	0.1	0.2687	0.0537	0.0164
S_2	0.1102	0.0189	0.0511	0.0750	0.1	0.3552	0.0710	0.0603
S_3	0.1059	0.0210	0.0356	0.040	0.0333	0.2358	0.472	0.0402
S_4	0.1292	0.02	0.0289	0.03	0.0333	0.2414	0.0483	0.0375
S_5	0.2076	0.02	0.0044	0.02	0.0333	0.2853	0.0571	0.0261
S_6	0.1992	0.02	0.0022	0.02	0.0333	0.2745	0.0549	0.0226
S_7	0.0805	0.02	0.0111	0.005	0.0333	0.1499	0.0301	0.0197
S_8	0.1208	0.0189	0	0.005	0.0333	0.178	0.0356	0.0520
S_9	0.0466	0.02	0.0067	0.005	0.0333	0.1116	0.0223	0.0160

Contamination factor, contamination degree and modified degree of contamination of analyzed metals

Table 8 shows the contamination factor (*Cf*) of each element the degree of contamination (*Cd*) and also modified degree of contamination for each sampling site. On the basis of Hakanson classification, the contamination factor for all the sampling sites falls under low contamination factor and the values of contamination degree indicates low degree of contamination. The *mCd* for the individual metal lie in the range 0.02-0.07 that is less than 1.5 show nil to very low degree of contamination. The *mCd* data indicates non-anthropogenic impact in all the sites.

Pollution Load Index (PLI)

The pollution load index does not show much fluctuation. Lower values of PLI imply no appreciable input from anthropogenic sources. There is, in general, a decrease in PLI values of study area indicating dilution and dispersion of metal content with increasing distance from source areas. The PLI value of >1 is polluted whereas <1 indicates no pollution. The values of PLI summarized in Table 8.

Metal Pollution Index (MPI)

Table 8 presents the metal concentrations of Zn, Cu, Pb, Cd and Fe and the reference values. Also, the values of x/ref. ratio are presented and MPI is calculated. According to its value (0.6596) the study area could be regarded as "non polluted" when trace metals are concerned as it is given in Table 9

Elemental contamination index (ECI) and overall metal contamination index (MCI)

According to [14], MCI of all the sampling sites less than 5 implies very low contamination and it is presented in Table 10.

Geo accumulation Index(Igeo)

The *Igeo* method was used to calculate the heavy metal contamination levels for study area. The geo accumulation index (Igeo) scale consists of seven grades (0-6) ranging from unpolluted to highly pollute. The average *Igeo* class falls less than zero for all sampling sites indicating unpolluted levels of study area(Fig.3). The result of geo accumulation indices for the sampling sites as given in Table 10.

Table 8: Mean concentration of metals, Reference value and MPI

Metals	Mean concentration(x)	Reference values(Ref)	x/ref
Fe	0.6033	0.3	2.0111
Zn	0.1889	5	0.0378
Cu	0.0777	1	0.0777
Pb	0.05	0.05	1
Cd	0.0144	0.01	1.44
		$\sum$	4.5666
		MPI = log$\sum$	0.6596

Table 9:Metal contamination index values based on Meybeck*et al*

Sample number	MCI	Classification
S_1	4.74	Very low contamination
S_2	4.77	Very low contamination
S_3	4.85	Very low contamination
S_4	4.83	Very low contamination
S_5	4.76	Very low contamination
S_6	4.76	Very low contamination
S_7	4.88	Very low contamination
S_8	3.84	Very low contamination
S_9	4.92	Very low contamination

Table 10: Index of Geo accumulation (*Igeo*) in the sampling sites

Sample No	Fe	Zn	Cu	Pb	Cd
S_1	-3.322	-9.5517	-10.1367	-8.9667	-3.9073
S_2	-3.7675	-9.6297	-8.1979	-7.6446	-3.9073
S_3	-3.8241	-9.4777	-8.7215	-8.5516	-5.4924
S_4	-3.5372	-9.5517	-9.0211	-8.9667	-5.4924
S_5	-2.8532	-9.5517	-11.7218	-9.9668	-5.4924
S_6	-2.9133	-9.5517	-12.7219	-9.5517	-5.4924
S_7	-4.2201	-9.5517	-10.3997	-12.7219	-5.4924
S_8	-3.6350	-9.6297	0	-12.7219	-5.4924
S_9	-5.0087	-9.5517	-11.1368	-12.7219	-5.4924

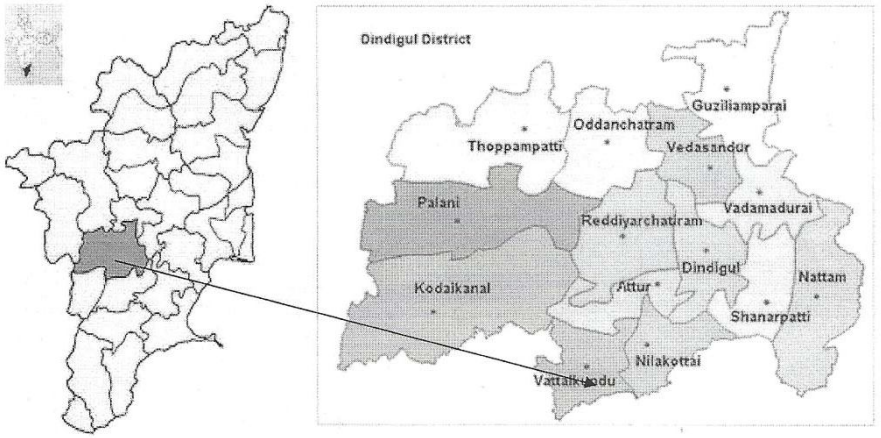

Fig.1 Map of the study area

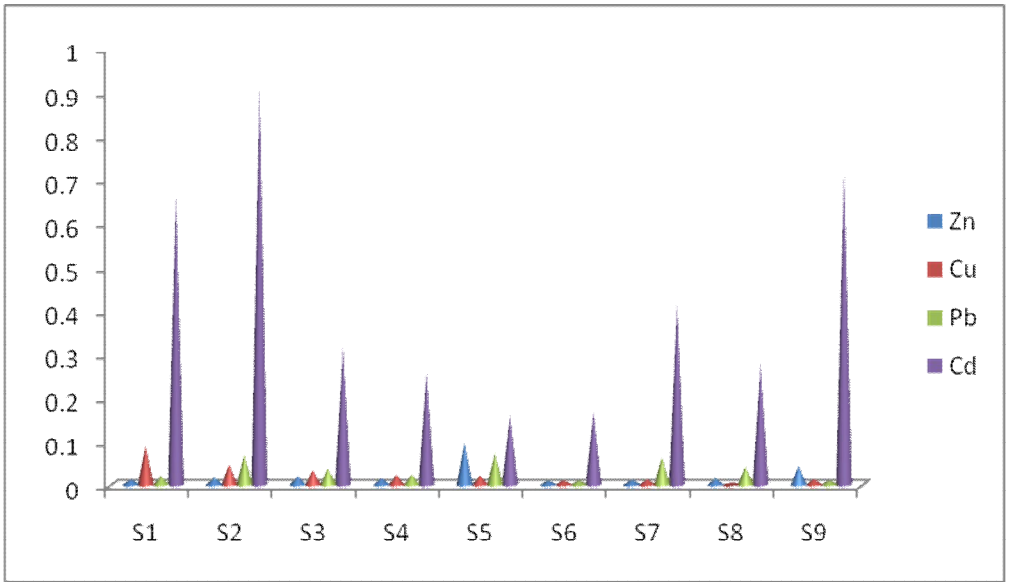

Fig.2 Enrichment factor at all the sampling sites

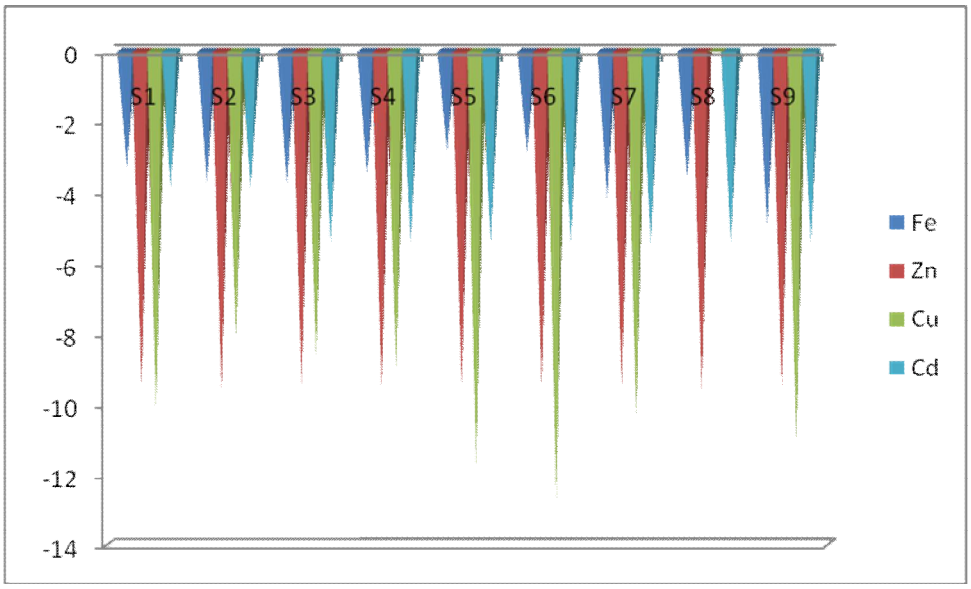

Fig.3 Geoaccumulation index at all the sampling sites

CONCLUSION

The impact of anthropogenic heavy metal pollution in the sampling sites was evaluated using Enrichment Factor (EF),Contamination Factor (*Cf*), Contamination degree (*Cd*), modified Contamination Degree (*mCd*), Pollution load Index(PLI), Metal Pollution Index(MPI), Metal Contamination Index (MCI) and Geo accumulation Index (*Igeo*) at nine sampling sites of Batlagundu. EF values for heavy metals were calculated for the area using the continental or average shale abundance of Fe. The results show that EF of all sampling sites was found to be less than 2 indicates the study area falls in the category of deficiency to low enrichment. The results of Contamination Factor (*Cf*), Contamination degree (*Cd*), and modified Contamination Degree (*mCd*) show that the study area falls under nil to very low contamination, Calculation of Pollution load Index(PLI), Metal Pollution Index(MPI), Metal Contamination Index (MCI) and Geo accumulation Index (*Igeo*) indicates the study area is regarded as non-polluted. The present study suggests that these indices are useful tools for identification of anthropogenic source of contamination of ground water.

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