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Monitoring of Heavy Metal Concentration in Groundwater of Mamundiyar Basin, India

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1. Introduction

Heavy metals designate a group of elements that occur in natural system in minute concentration and when present in sufficient quantities and are toxic to living organisms. The behavior of trace metals in groundwater is complicated and is related to source of group water and the bio-geochemical process in elemental conditions.

It is often assumed that natural, uncontaminated waters from deep (bedrock) wells are clean and healthy (Banks et al., 1998b). This is usually true with regards to bacteriological composition. The inorganic chemical quality of these waters is, however, rarely adequately tested before the wells are put into production. Due to variations in the regional geology and water rock interactions, high concentrations of many chemical elements can occur in such waters. During the last 5-10 years several studies have shown that wells in areas with particular geological features yield water that does not meet established drinking water norms (e.g. Varsanyi et al., 1991; Bjorvatn et al., 1992, 1994; Edmunds and Trafford, 1993; Banks et al., 1995a, b, 1998a; Sæther et al., 1995; Reimann et al., 1996; Edmunds and Smedley, 1996; Smedley et al., 1996; Williams et al., 1996; Morland et al., 1997, 1998; Midtga°rd et al., 1998; Misund et al., 1999; Frengstad et al., 2000) without any influence from anthropogenic contamination. These studies also document that quite a number of elements for which no drinking water guideline values (GL) or maximum acceptable concentration limits (MAC) have been established can occur at unpleasantly high levels in natural well waters (e.g. Be, Th, Tl). In Norway, F and radon (Rn) are the most problematic elements (see Frengstad et al., 2000) in terms of possible health effects. In Hungary, Bangladesh and India, arsenic represents one of the most drastic examples of unwanted natural chemical 'contamination' of groundwater. Several 100 000 people in these regions suffer skin cancer due to high As concentrations in drinking water from drilled wells (Chatterjee et al., 1995; Das et al., 1995; Smith et al., 2000; Smedley and Kinniburgh, 2002).

It has been established that various trace elements have certain health on living organisms (WHO, 1984). But the extent to which these elements affect health of living organisms depends on the chemical characteristics and the concentration of the element in the water consumed. Furthermore, the time of exposure will also determine the level of the element on

the organism. Some elements are biocumulative and therefore get increased with time in the body. The present paper reports analytical results for 6 chemical elements (trace elements) from 50 sampling stations of Mamundiyar basin, India.

2. Geography and geology of the study area

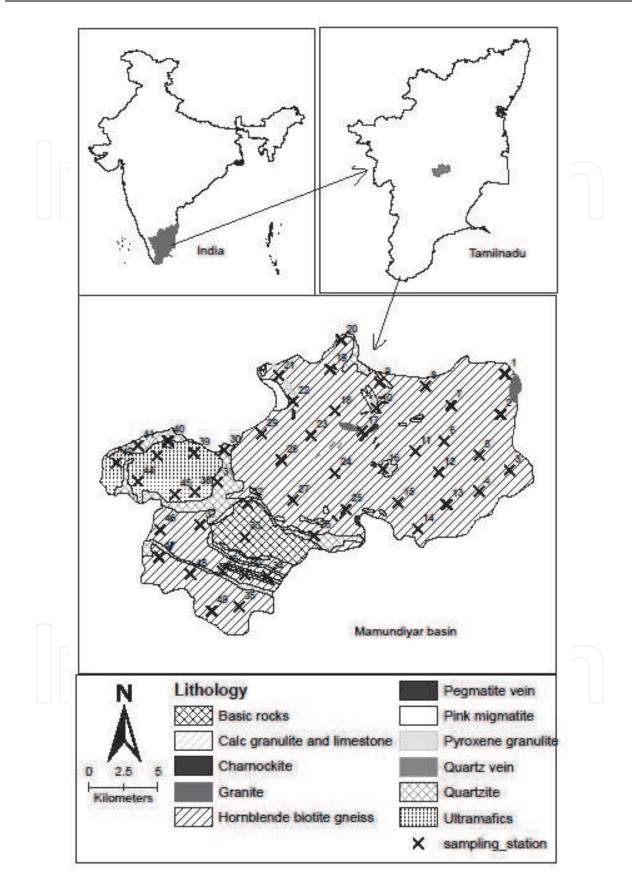
Mamundiyar basin, India lies in hard rock terrain. Groundwater is available only in weathered and fractured zones. In this area assured surface water supplies are nominal and most of the farmers depend on groundwater for drinking and irrigation purposes. Average annual rainfall is around 464 mm which is mostly lost as surface runoff and evaporation. Only one-fifth of it is recharging to groundwater. Therefore, groundwater development assumes great significance in improving the quality of life of the most deprived and vulnerable people of this basin by improving their access to safe drinking water.

The Mamundiyar basin extends over approximately 720 km² and lies between 10^o 25` and 10^o 40`N latitudes and 78^o 10` and 78^o 30` E longitudes in the southern part of Tamilnadu, India (Fig. 1). Mamundiyar River originates at an altitude of 315 m above Irungadu group of hills and joins Ariyavur River near Maravanur about 25 Km south-west of Tiruchirapalli. The western, north-western and south-western parts are characterized by the presence of residual hills. The basin is generally hot and dry except during winter season. The mean maximum monthly temperature varies from 37°C in May to 29°C in December. While as mean minimum monthly temperature ranges from 27°C in June and 20°C in January. The area receives an average annual rainfall of about 464 mm. The surface runoff goes to stream as instant flow. Rainfall is the direct recharge source and the irrigation return flow is the indirect source of groundwater in the Mamundiyar hydrographic basin. The study area depends mainly on the North-east monsoon rains which are brought by the troughs of low pressure established in the South Bay of Bengal.

Several digital image processing techniques, including standard color composites, intensityhue-saturation (IHS) transformation and decorrelation stretch (DS) were applied to map rock types. The statistical technique adopted by Sheffield (1985) was employed to select the most effective Three-band color composite image. The band combination 1, 4 and 5 is the best triplet and was used to create color composites with Landsat TM bands 5, 4 and 1 in red, green and blue, respectively. IHS transformation and DS were also applied to the selected band combination in order to enhance the difference between rock types. Better contrast was obtained due to color enhancement and this facilitated visual discrimination of various rock types. Eleven lithologic units were mapped and could be distinguished by distinct colors in the processed images. These are: Ultramafics, Hornblende biotite gneiss, Basic rocks, Charnockite, Pyroxene granulite, Pink magmatite, Quartzite, Pegmatite vein, Quartz vein, Granite, and Calc granulite and limestone. Fig. 2 is a map of the interpreted distribution of rock types Mamundiyar basin (Dar et. el, 2010).

3. Sampling

Most samples reported here were taken from drinking water wells in small villages and settlements scattered throughout the Mamundiyar basin, India. Factory new, unwashed 100-ml high-density polyethylene (HDPE) bottles were used for sampling. Different brands of plastic bottles had previously been thoroughly checked for possible contamination (Reimann et al., 1999a). No risk of contamination from such bottles was found for the





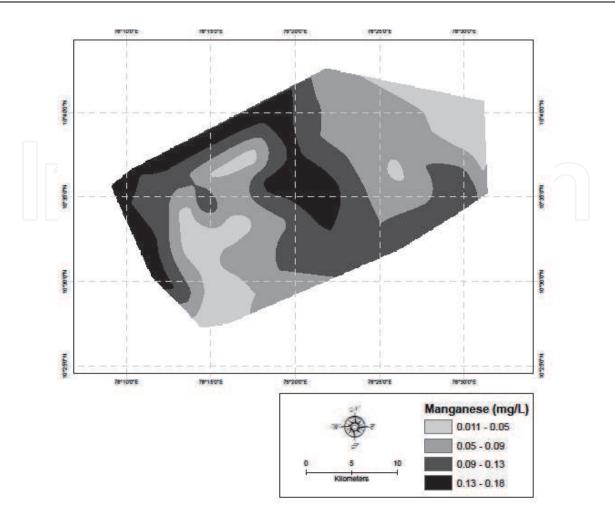


Fig. 2.

parameters reported here, as long as the bottles are thoroughly rinsed with water prior to sampling. In the field the bottles were rinsed three times with running water and then filled to the top.

Sampling took place directly at the tap or the wellhead. In order to collect fresh well water, the water was left running for at least 5 min or until temperature and conductivity remained stable. In most cases, each of these wells supplies more than 100 people with their daily drinking water. The water, therefore, never accumulates over longer periods in the well.

Two 100-ml bottles were collected at each site. The first sample, which was intended for anion analyses, was left unfiltered and unacidified. The unfiltered water of the second sample was acidified with 2 ml of concentrated nitric acid (Merck, Ultrapure). This second sample was used later for cation analysis. The acid was tested for its trace element content using the same analytical procedure as for the water samples. In the field, the samples were stored in a cool box and in the evening transferred to a refrigerator, where they were stored until shipment to the laboratory.

4. Analysis

The trace elements analyzed included manganese (Mn), iron (Fe), chromium (Cr), copper (Cu), zinc (Zn) and boron (B).

5. Results and discussion

The result of the analysis of 50 groundwater sampling stations is shown in tables 1 and 2.

Sample station	Zinc	Copper	Iron	Manganese	Chromium	Boron
1	0.01	0.02	0.03	0.011	0.001	0.38
2	0.01	0.2	0.02	0.012	0.001	0.35
3	0.04	0.03	0.03	0.07	0.002	0.31
4	0.03	0.03	0.04	0.13	0.001	0.31
5	0.04	0.03	0.03	0.12	0.001	0.4
6	0.01	0.02	0.01	0.09	0.001	0.55
7	0.07	0.03	0.02	0.05	0.002	0.56
8	0.07	0.02	0.02	0.06	0.001	0.25
9	0.006	0.03	0.04	0.08	0.001	0.38
10	0.07	0.02	0.06	0.05	0.001	0.55
11	0.03	0.03	0.06	0.04	0.001	0.31
12	0.04	0.04	0.02	0.07	0.001	0.31
13	0.02	0.03	0.2	0.13	0.002	0.4
14	0.05	0.01	0.03	0.12	0.002	0.41
15	0.002	0.02	0.03	0.09	0.002	0.32
16	0.1	0.02	0.04	0.09	0.001	0.48
17	0.1	0.02	0.04	0.09	0.001	0.55
18	0.1	0.02	0.04	0.09	0.001	0.41
19	0.1	0.02	0.04	0.09	0.001	0.31
20	0.01	0.01	0.03	0.06	0.001	0.4
21	0.07	0.02	0.04	0.18	0.001	0.12
22	0.08	0.03	0.03	0.15	0.002	0.18
23	0.002	0.03	0.03	0.14	0.001	0.38
24	0.07	0.01	0.02	0.17	0.001	0.55
25	0.08	0.01	0.03	0.13	0.001	0.31
26	0.05	0.02	0.01	0.12	0.002	0.31
27	0.002	0.03	0.03	0.08	0.001	0.4
28	0.07	0.01	0.02	0.15	0.001	0.23
29	0.05	0.03	0.03	0.02	0.002	0.31
30	0.08	0.01	0.04	0.04	0.001	0.38
31	0.07	0.02	0.06	0.13	0.001	0.55
32	0.08	0.01	0.01	0.02	0.001	0.41
33	0.07	0.03	0.01	0.07	0.002	0.31
34	0.01	0.02	0.02	0.05	0.001	0.4
35	0.07	0.02	0.02	0.04	0.002	0.32
36	0.02	0.03	0.03	0.03	0.001	0.38
37	0.08	0.01	0.12	0.02	0.002	0.42
38 39	0.1		0.02	0.02	0.001	0.44
40	0.1 0.09	0.01 0.03	0.03	0.1 0.15	0.001 0.001	0.47 0.38
40 41	0.09	0.03	0.21 0.02	0.13	0.001	0.58
41 42	0.07	0.01	0.02	0.14	0.002	0.35
42	0.09	0.02	0.21	0.17	0.001	0.31
43 44	0.1	0.01	0.03	0.12	0.001	0.51
44 45	0.09	0.03	0.03	0.13	0.001	0.4
45 46	0.07	0.03	0.04	0.15	0.002	0.55
40	0.03	0.01	0.02	0.15	0.001	0.31
48	0.02	0.02	0.02	0.17	0.001	0.31
40	0.07	0.01	0.03	0.02	0.001	0.51
49 50	0.05	0.03	0.03	0.02	0.001	0.42
•••	5.00	2.00		0.0-	0.001	

Table 1.

Parameters	Z	Cu	Fe	Mn	Cr	В
Minimum	0	0.01	0.01	0.01	0	0.12
Maximum	0.1	0.2	0.21	0.18	0	0.56
Range	0.1	0.19	0.2	0.17	0	0.44
Mean	0.06	0.03	0.04	0.09	0	0.38
Median	0.07	0.02	0.03	0.09	0	0.38
First quartile	0.03	0.01	0.02	0.05	0	0.31
Third quartile	0.08	0.03	0.04	0.13	0	0.42
Standard error	0	0	0.01	0.01	0 4	0.01
95% confidence interval	0.01	0.01	0.01	0.01	0	0.03
99% confidence interval	0.01	0.01	0.02	0.02	0	0.04
Variance	0	0	0	0	0	0.01
Average deviation	0.03	0.01	0.03	0.04	0	0.07
Standard deviation	0.03	0.03	0.05	0.05	0	0.1
Coefficient of variation	0.57	1.06	1.09	0.55	0.35	0.26
Skew	-0.4	6.01	3.09	0	1.13	0.06
Kurtosis	-1.2	40.1	9.06	-1.2	-0.8	0.2
Kolmogorov-Smirnov stat	0.22	0.39	0.38	0.13	0.46	0.15
Critical K-S stat, alpha=.10	0.17	0.17	0.17	0.17	0.17	0.17
Critical K-S stat, alpha=.05	0.19	0.19	0.19	0.19	0.19	0.19
Critical K-S stat, alpha=.01	0.23	0.23	0.23	0.23	0.23	0.23

Table 2.

6. Manganese

The U.S. Public Health Service Drinking Water Standards of 1925, 1942, and 1946 included manganese with iron for a combined maximum level of 0.30 mg/L, but in 1962 the regulations included, in addition, a maximum concentration of 0.05 mg/L for manganese. The USEPA adopted the 0.05 mg/L of the USPHS as recommendation, and issued a secondary standard in 1989. The WHO recommended 0.05 mg/L (maximum acceptable) and 0.50 mg/L as maximum allowable. The European Community (1980) used a guide value of 0.02 mg/L and a maximum of 0.05 mg/L.

Figure 2 shows the spatial distribution of manganese through Natural Nearst Neighbor interpolation technique. It's quite obvious from the map that manganese tends to dominate the central part of the Mamundiyar basin, and its concentration diminishes radially outwards from the centre. The highest concentration of manganese found was 0.18; which means all the samples fall within the permissible limit set by WHO.

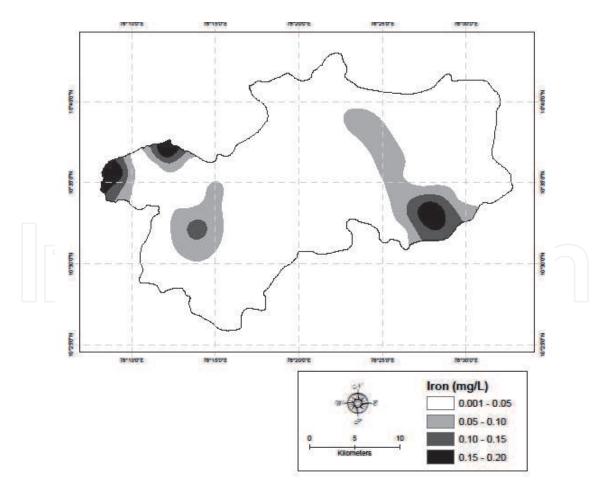
7. Iron

Since the standards for iron have been set for less than 0.3 mg/L, acceptability of water sources was a condition for meeting this concentration. Groundwater exceeding this limit may need a treatment to meet the standard at the distribution system. Groundwater containing soluble iron may remain clear when pumped out, but exposure to air will cause precipitation of iron due to oxidation, with a consequence of rusty color. The presence of iron bacteria may clog well screens particularly when sulphate compounds in addition to iron may be subjected to chemical reduction. Solubility of iron is increased by a low pH (<5).

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High turbidity may help to keep acid- soluble iron in suspension. Iron in raw or potable water may be either ferrous or ferric or both and categorized as in solution, in colloidal state, in organic or inorganic compounds or in the form of coarse suspended or settled particles. The 1925, 1942, 1946 and 1962 regulations of the U.S Public Health Service always reported the maximum concentration for iron as 0.30 mg/L. the USEPA did not include iron in the National Drinking Water Quality Regulations, but maintained in the secondary Drinking Water Regulations of 1989 the limit of 0.3 mg/L based on aesthetic and taste consideration. WHO (1963) also adopted a 0.3 mg/L as a maximum acceptable level and 1.0 as maximum allowable. The European Community adopted in 1980 a guide of 0.05 mg/L and a maximum of 0.20 mg/L; WHO (1984 and 1993) recorded a guideline of 0.30 mg/L. USEPA (1979 and 1991) confirmed the original ruling for iron as a contaminant to be included in the Secondary Drinking Water Standards with a level of 0.3 mg/L as the final rule.

Figure 3 shows the spatial distribution of iron using interpolation method in GIS environment. It's quite evident from the map that iron contaminations occur at few locations, mainly around the Kadavur (western) region of the Mamundiyar basin. In each patch, the concentration of iron was found to decrease/diminish radially outwards from centre. That means, at the point of rock (iron bearing) - water interaction, the concentration of Iron is maximum; and as the distance increases from the interface of rock (bearing iron element) and water, the concentration also gets decreased because of dilution factor. The values of iron were within the permissible limit of drinking water standards.

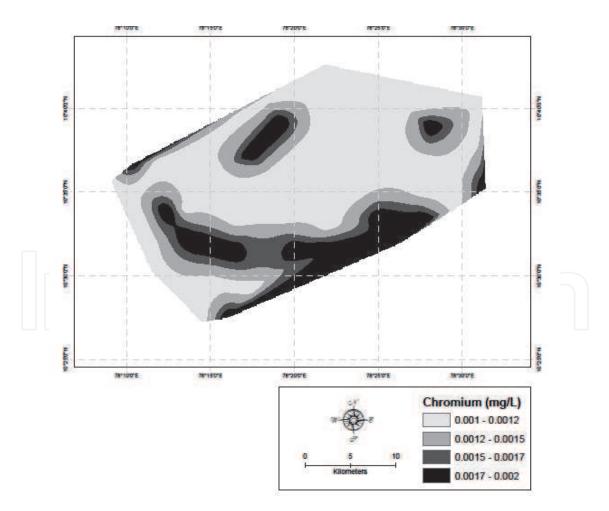




8. Chromium

It's a naturally occurring metal in drinking water. **USPHS 1925** = not stated **USPHS 1942** = 0 mg/L as hexavalent **USPHS 1946** = 0.05 mg/L**USPHS 1962** = 0.05 as hexavalent WHO guidelines = 0.05 mg/L (as Cr⁶⁺ and total chromium) European Community =0.05 mg/L (as Cr^{6+} and total chromium) MCLG and MCL (USEPA, 1989) = 0.1 mg/L (proposed)MCLG and MCL = 0.1 mg/L (final; effective 7/30/1992) (USEPA, 1991)

The spatial distribution map of chromium is shown in figure 4; which is created using Nearest Neighbors interpolation technique. It's clear from the figure that the maximum concentration (0.002 mg/L) of chromium occurs in the southern region of Mamundiyar basin; and its concentration decreases towards the north-west, due to dilution. The concentration of chromium wherever recorded is well within the limits of drinking water standards prescribed by WHO.





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9. Copper

USPHS 1925	= 0.2 mg/L
USPHS 1942	= 3 mg/L
USPHS 1962	= 1 mg/L
WHO guidelines	= 1 mg/L (1.5 mg/L excessive)
European Community	=0.1 mg/L
MCLG and MCL	
(USEPA, 1988)	= 1.3 mg/L (proposed)
MCLG and MCL	
(USEPA, 1991)	= 1.3 mg/L at the consumer's

(USEPA, 1991) = 1.3 mg/L at the consumer's tap (final revised regulations for lead and copper according to the New Lead and Copper Rule as requested by the Safe Drinking Water Act- Revision of 1986).

Copper can exist in aquatic environment in three forms namely soluble, colloidal and particulate. It is found in less quantity as an essential element for organisms. Excess of copper in human body is toxic and causes hypertension and produces pathological changes in brain tissues. Excessive ingestion of copper is responsible for specific disease of the bone (Krishnamurthy, C.R. and V. Pushpa. 1995). The spatial distribution map of copper (figure 5) is prepared using interpolation technique in GIS environment. It's quite obvious from the map that the maximum concentration of copper is present at eastern edge of Mamundiyar basin. In the present study, the values of copper are showed within the limit of drinking water standards.

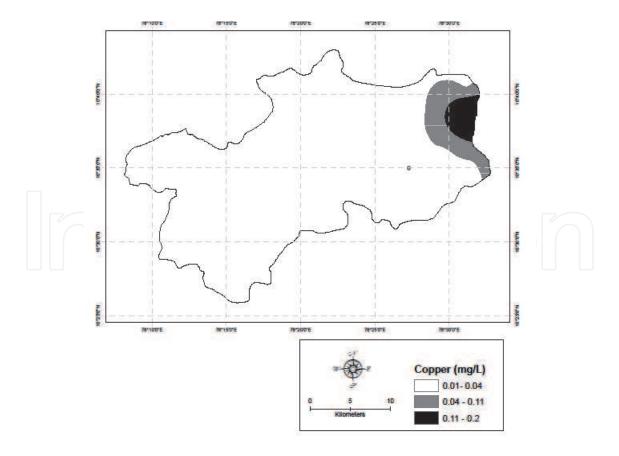
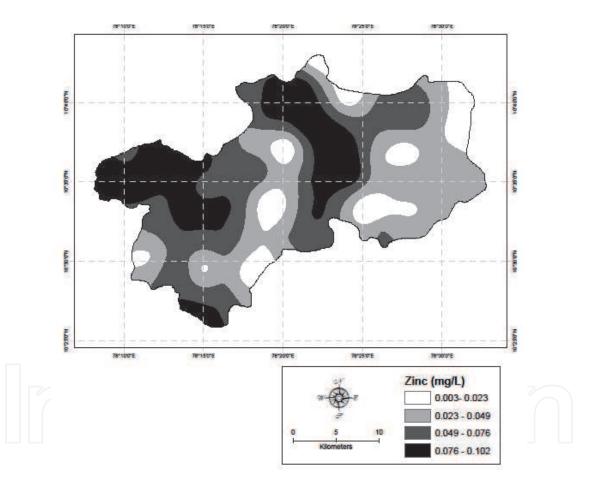


Fig. 5.

10. Zinc

The USPHS recommended a maximum zinc concentration of 15.0 mg/L in 1942 and 1946 standards, and 5.0 mg/L in the 1962 standards.USEPA recommended 5 mg/L in 1980 and a SMCL of 5 mg/L in 1989. WHO (1971) recommended 5 mg/L with a maximum of 15mg/L. the European Community advised 0.1 mg/L, with a maximum of 1.5 mg/L. the WHO (1984) adopted a guideline of 5 mg/L based on the taste consideration. USEPA (1991) issued a final status for Zinc as a Secondary Drinking Water Standard (SDWS) of 5 mg/L, confirming the final rule of 5 mg/L issued in 1980.

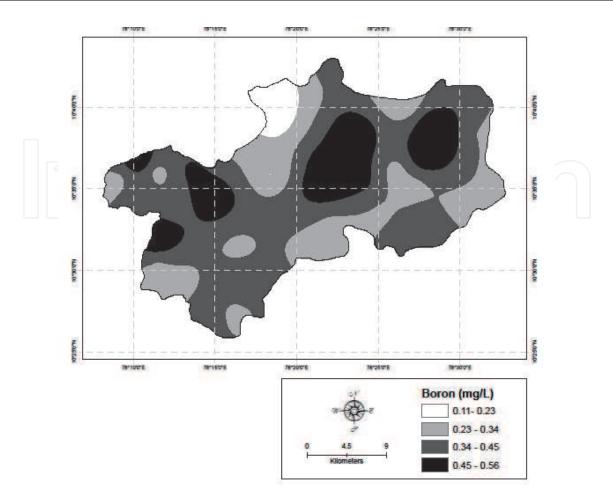
The spatial distribution map of zinc (figure 6) is prepared using interpolation technique in GIS environment. It's quite obvious from the map that the maximum concentration of zinc (0.5 MG/L) is present at the Kadavur (western) and central part of Mamundiyar basin. In the present study the values of zinc are showed within the limit of drinking water standard.



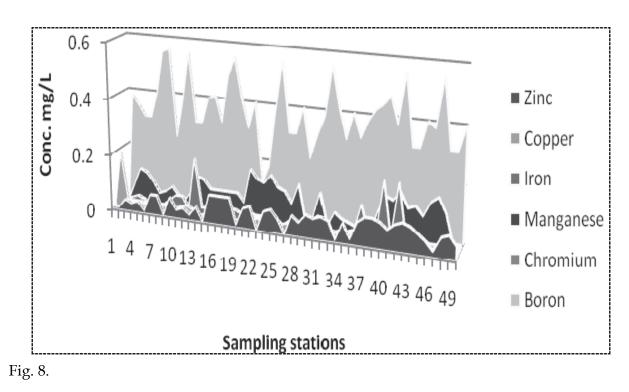


11. Boron

Spatial distribution map of boron (figure 7) depicts that maximum concentration of boron in patches at Central, Eastern and western part of Mamundiyar basin. Boron concentration varied between 0.11 to 0.56, indicating that the samples fall within the permissible limit set by WHO. Overall, boron dominates the trace metal pool of the Mamundiyar basin as shown graphically in figure 8.







The correlation between these parameters is shown in table 3. The highest positive correlation (0.244) was found between iron and manganese, followed by iron and zinc (0.138). The lowest positive correlation (0.047) was found between iron and chromium. While as the highest negative correlation (- 0.293) was found between zinc and copper. Moreover, boron was found to show the negative correlation with all the parameters except zinc.

	1 0.8 0.6 0.4 0.2 0 -0.2						
_	-0.4	Z	Cu	Fe	Mn	Cr	В
	■Z	1	-0.29338	0.138309	0.136238	-0.0242	0.062718
	■ Cu	0.29338	1	-0.02784	-0.26347	-0.0433	-0.10313
	■ Fe	0.138309	-0.02784	1	0.244276	0.047197	-0.01913
	∎ Mn	0.136238	-0.26347	0.244276	1	-0.0448	-0.1304
	Cr	-0.0242	-0.0433	0.047197	-0.0448	1	-0.08985
- F	B			-0.01913			1

Table 3.

12. Conclusion

The concentrations of the investigated heavy metals (Mn, Fe, Cr, Cu, Zn and B) in the drinking water samples from Mamundiyar basin, India were found below the guidelines for drinking waters given by the WHO (World Health Organization), EC (Europe Community), EPA (Environment Protection Agency). It was concluded that drinking waters in Mamundiyar contain low heavy metal levels.

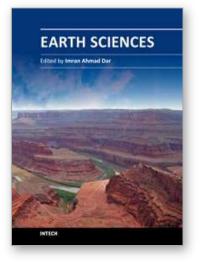
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