

ASSESSMENT OF HEAVY METALS IN CORRELATION WITH PHYSICO-CHEMICAL PROPERTIES OF DRINKING WATER OF NORTHERN RAJASTHAN, INDIA.

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Abstract—In the present communication, analysis of various heavy metal (Cr, Fe, Cu, Zn, As, Se, Cd, Pb and Th) concentrations in 10 drinking water samples collected from the diverse locations from different depths of Nagaur district of Rajasthan, India has been carried out by using high resolution inductively coupled plasma mass spectroscopy (HR-ICP-MS) technique. The water samples were taken from hand pumps and tube wells. The measured concentrations of Cr, Fe, Cu, Zn, As, Se, Cd, Pb and Th varies from 4.27 to 10.12 $\mu\text{g l}^{-1}$, 75.62 to 1163.38 $\mu\text{g l}^{-1}$, 1.8 to 7.67 $\mu\text{g l}^{-1}$, 17.02 to 170.27 $\mu\text{g l}^{-1}$, 1.6 to 11.79 $\mu\text{g l}^{-1}$, 6.48 to 25.92 $\mu\text{g l}^{-1}$, 0.3 to 1.7 $\mu\text{g l}^{-1}$, 4.96 to 18.11 $\mu\text{g l}^{-1}$ and 0.57 to 2.94 $\mu\text{g l}^{-1}$ with the mean value of 6.38 $\mu\text{g l}^{-1}$, 303.06 $\mu\text{g l}^{-1}$, 3.90 $\mu\text{g l}^{-1}$, 79.46 $\mu\text{g l}^{-1}$, 4.14 $\mu\text{g l}^{-1}$, 12.85 $\mu\text{g l}^{-1}$, 0.80 $\mu\text{g l}^{-1}$, 10.97 $\mu\text{g l}^{-1}$ and 1.80 $\mu\text{g l}^{-1}$, respectively. The heavy metals have been studied for their health hazards and the concentration is correlated with recommended safe limits as suggested by various protection agencies. The concentration of above mentioned heavy metals in all the investigated water samples lies within the safe limit as approved by USEPA (2011). According to WHO (2008) recommended limit the heavy metal concentrations of all investigated water samples lies below than the permissible limit except from Fe, Se and Pb. Moreover, significant correlation has been observed among the physico-chemical properties of water and heavy metal concentration. The results reveal that drinking water contaminated with heavy metals is prone to radiological and chemical threats for inhabitants.

I. INTRODUCTION

In the 20th century obtaining drinking water has become a very big problem due to the contamination of ground water by the addition of toxic substance. According to UNICEF's report "Fresh Water for India's Children and Nature," nearly 1 million children in India die of diarrheal diseases each year due to the drinking of contaminated water and living in unhygienic conditions [1]. A large number of studies have been conducted in the whole world to determine the concentration of heavy metals in water samples [2-6]. Among these heavy metals Zn, As, Cu, Cd and Pb are present throughout the earth crust and are much toxic than other metals. These toxic heavy metals have a tendency to accumulate in the body and may result chronic damage. So, the drinking water must be free from these toxic substances.

From the health point of view Zinc toxicity can occur in both acute and chronic forms. Acute health effect of high intake of zinc includes vomiting, nausea, abdominal cramps, loss of appetite, headaches and diarrhea [7]. Chronic exposure of arsenic in drinking water can cause cancer in the kidney, bladder, lungs and skin. WHO states that there is a probability of poses a lifetime skin cancer risk of 6 people in 10000 from the arsenic exposure of 0.01 mg l^{-1} and recommends that it is acceptable risk [8]. Large intake of copper can cause tissue damage, nausea, stomach problem and diarrhea. The intake concentration of copper for a large amount of the population is lower than suggested levels according to U.S. Institute of Medicine report (2001) [9]. The Cadmium (Cd) is an extremely toxic industrial and environmental pollutant classified as a human carcinogen. Immediate poisoning and damage to the kidneys and liver occurs due to ingestion of large amount of cadmium [10]. Acute exposure of lead causes the constipation, nausea, abdominal pain, diarrhea, weakness of muscles and vomiting [11]. Neurological, Gastrointestinal and neuromuscular are three multiple systems which are affected due to Chronic poisoning of lead [12]. Neuromuscular and Central nervous system are affected due to intense exposure, while gastrointestinal system affect usually result from long term exposure [11]. Chronic exposure of the lead causes depression, loss of short-term memory or concentration, nausea, fatigue, abdominal pain, headaches, problems with sleep, stupor, anemia and slurred speech [13].

In the Nagaur district of Northern Rajasthan, India the high activity concentration of natural radionuclides in the soil samples has been reported [14]. The natural concentration of heavy metals in fresh water depends upon the concentration of these natural radionuclides in the soil. In the investigated region the main sources of drinking water is mainly tube well. The water obtained from the tube well may be unsafe for drinking purpose due the contamination of toxic substances. Hence the measurement of heavy metal concentration in water sample of Nagaur district of Marwar region of Northern Rajasthan, India assumes significance. Such study will be

helpful in determining whether the water of this district can be used for drinking purposes without posing any health hazard to the inhabitants. However literature survey shows no attempt has been made towards the measurement of heavy metal concentration in water in Nagaur district of Northern Rajasthan, India. In the present study, heavy metal concentration in water from Nagaur district of Marwar region of Northern Rajasthan, India has been investigated systematically. A correlation has been found between heavy metals and physicochemical parameters of groundwater samples.

II. GEOLOGY OF THE AREA

Rajasthan is located in North-West part of India. Its location varies between 23°30' to 30°11' north latitude and 69°29' to 78°17' east longitude. Figure 1 shows the geographical location of Rajasthan in India as well the locations of sampling sites are also marked in it.

The Nagaur district falls almost in the central part of Rajasthan. The district is expanded between latitudes 26°02' to 27°37' and longitudes 73°05' to 75°24' and comprises a major part of Thar Desert, India. The boundary of this region is shared by seven districts of Rajasthan viz.-Jaipur, Ajmer, Pali, Jodhpur, Bikaner, Churu and Sikar. This district is well known over the world map owing to producing the Makrana marble. It is covered by the Delhi super group rocks, Erinpura granite, Malani igneous suite, Marwar super group rocks and Jogira fuller's Earth/Kuchera Khajuwana series rocks. Moreover, the lake containing highest content of salt; the Sambhar Lake is also located in Nagaur district. The

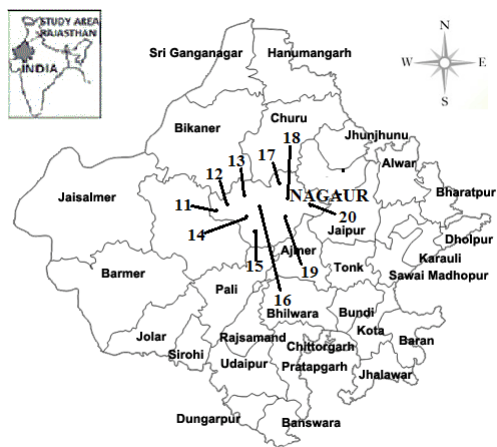


Fig. 1 The map showing the sample locations of Nagaur District

minerals abundantly found in this region are limestone, lignite, gypsum and marble. The soil found in these two districts is mostly comprised of clay, clay loam, sandy loam and sandy soil [15].

III. MATERIALS AND METHODS

A. Sample Collection and Preparation

In order to measure the heavy metal concentration, water samples were collected from 10 different locations of Nagaur district of Rajasthan, India on random bases. The samples were collected from tube wells and hand pumps. The tube wells and hand pumps were pumped for at least 10 minutes before the samples were taken so as to get fresh water. For each location 100 ml of water sample was taken and there after filtered by using Whatman filter paper No. 1.

B. Physico-Chemical Analysis

Half of the filter water for each sample was used for physico-chemical analysis namely pH, conductance and total dissolved solids (TDS) by using pH/EC bench top meter using standard procedures (ALPHA, 1985).

C. HR-ICP-MS Analysis

In order to measure the concentration of heavy metal in water samples, remaining half of water samples from each location was acidified with 3% nitric acid (HNO₃). The heavy metal analysis has been carried out by using high resolution inductively coupled plasma mass spectroscopy (ICP-MS) (Perkin-Elmer Sciex Elan DRC II) technique at National Geophysical Research Institute (NGRI), Hyderabad, India. In this technique chemical analysis of the samples is based on the inductively coupled plasma for producing ions and mass spectroscopy for separating and detecting ions. For heavy metal analysis, NIST 1640a (National Institute of Standards and Technology) was used as a calibration standard and reference material NIST 1643e was analyzed by ICP-MS as unknown samples. ¹⁰³Rh was used as an internal standard material for accurate determination of heavy metals in water samples. HR-ICP-MS technique takes only 2 to 6 minutes for the analysis of each sample and has excellent precision of about 5% relative standard deviation (RSD).

IV. RESULTS AND DISCUSSION

A. Analysis of Heavy Metal Concentration in Drinking Water Samples

The data for various concentrations of heavy metal (Cr, Fe, As, Pb, Cu, Cd, Zn, Se and Th) in 10 groundwater samples collected from the diverse locations from different depths of Nagaur district of Rajasthan, India are tabulated in table 1. From which it can be seen that in groundwater samples the heavy metal concentration ranges from 4.27 to 10.12 µg l⁻¹ (Cr), 75.62 to 1163.38 µg l⁻¹ (Fe), 1.8 to 7.67 µg l⁻¹ (Cu), 17.02 to 170.27 µg l⁻¹ (Zn), 1.6 to 11.79 µg l⁻¹ (As), 6.48 to 25.92 µg l⁻¹ (Se), 0.3 to 1.7 µg l⁻¹ (Cd), 4.96 to 18.11 µg l⁻¹ (Pb) and 0.57 to 2.94 µg l⁻¹ (Th) with the mean value of 6.38 µg l⁻¹, 303.06 µg l⁻¹, 3.90 µg l⁻¹, 79.46 µg l⁻¹, 4.14 µg l⁻¹, 12.85 µg l⁻¹, 0.80 µg l⁻¹, 10.97 µg l⁻¹ and 1.80 µg l⁻¹, respectively. Various protection organizations have recommended the different permissible limits of concentration of heavy metal in drinking water for inhabitants.

Table1. The concentration of different heavy mates in groundwater samples from some areas of Nagaur District.

Sr. No.	Sample Location (Village)	Source	Depth (meter)	Cr $\mu\text{g l}^{-1}$	Fe $\mu\text{g l}^{-1}$	Cu $\mu\text{g l}^{-1}$	Zn $\mu\text{g l}^{-1}$	As $\mu\text{g l}^{-1}$	Se $\mu\text{g l}^{-1}$	Cd $\mu\text{g l}^{-1}$	Pb $\mu\text{g l}^{-1}$	Th $\mu\text{g l}^{-1}$
Nagaur												
1	Kuchera	Tube well	105	5.41	221.54	2.75	47.00	1.60	9.77	0.91	11.99	2.94
2	Gogelave	Tube well	75	10.12	757.73	7.16	133.40	11.79	25.92	0.48	8.07	2.82
3	Nagaur	Hand Pump	35	4.27	170.78	2.58	87.00	3.18	10.33	0.65	11.59	1.35
4	Mundawa	Tube well	30	6.52	75.62	2.46	17.94	3.52	6.48	0.75	8.47	1.95
5	Mehrta Road	Tube well	110	7.10	99.49	1.80	17.02	2.09	9.07	0.88	10.77	1.68
6	Somana	Tube well	90	4.87	86.46	5.02	101.83	6.76	17.28	1.44	18.11	2.26
7	Ladnun	Tube well	185	5.18	92.66	3.73	81.86	3.38	12.70	1.70	15.22	0.66
8	Didwana	Tube well	35	5.64	1163.38	7.67	84.36	4.07	12.10	0.30	4.96	1.72
9	Makrana	Tube well	245	8.82	100.75	3.22	53.93	2.86	14.43	0.42	12.84	0.57
10	Nawa City	Tube well	10	5.90	262.25	2.64	170.27	2.18	10.44	0.43	7.76	2.01
Range			30-245	4.27-10.12	75.62-1163.38	1.8-7.67	17.02-170.27	1.6-11.79	6.48-25.92	0.3-1.7	4.96-18.11	0.57-2.94
Average			95.4	6.38	303.06	3.90	79.46	4.14	12.85	0.80	10.97	1.80

Table 2. Physico-Chemical properties at various locations in Nagaur district of Northern region of Rajasthan.

Sr. No	Sample Location (Village)	TDS (mg l^{-1})	Conductance ($\text{m}\Omega^{-1}$)	Ph
1	Kuchera	680	1.80	7.24
2	Gogelave	1395	3.46	7.15
3	Nagaur	1125	2.86	7.61
4	Mundawa	535	1.39	8.73
5	Mehrta Road	760	2.20	7.19
6	Somana	1590	4.12	7.17
7	Ladnun	1165	2.88	7.03
8	Didwana	2460	5.78	7.87
9	Makrana	1125	2.74	7.10
10	Nawa City	1090	2.81	7.46
Range		535-2460	1.39-5.78	7.03-8.73
Average		1192.5	3.0	7.45

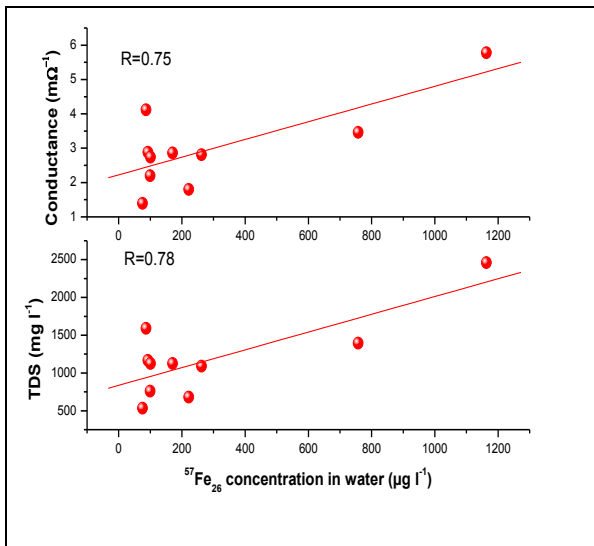


Fig. 2 Iron concentration vs TDS and Conductance in water samples.

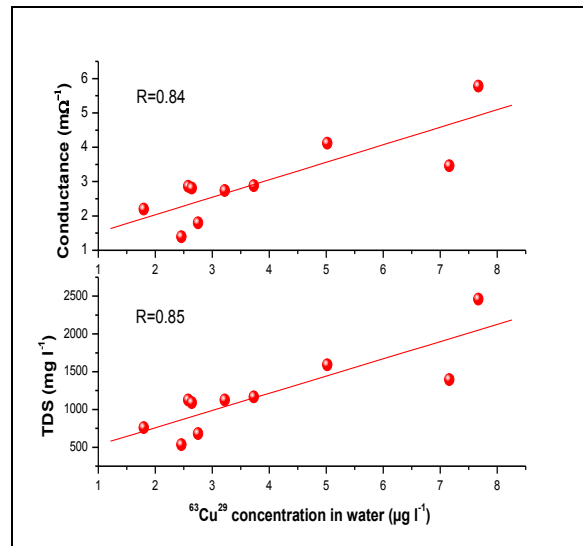


Fig. 3 Copper concentration vs TDS and Conductance in water samples.

The US Environmental Protection Agency (USEPA, 2011) has recommended 1300, 5, 50, 10 and 100 $\mu\text{g l}^{-1}$ of Cu, Cd, Se, As and Cr respectively in drinking water as a permissible limit [16]. The concentration of these heavy metals in all the investigated water samples lies within the safe limit approved by USEPA (2011) except arsenic in one sample [16]. Moreover the safe limits of heavy metal concentration of Fe, Cu, Cd, Se, As, Pb and Zn in groundwater samples are 100, 1000, 5, 10, 10, 10 and 5000 $\mu\text{g l}^{-1}$ respectively as approved by WHO (2008) [17]. The observed values of Cu and Cd concentration in our investigated water samples are well below the allowed maximum contamination limit as approved by WHO (2008) [17]. The concentration of iron in 60% , As in one sample, Se in 70% and lead in 60% groundwater samples is found to be higher than the permissible limit as recommended by WHO (2008) [17]. The high concentration of heavy metal has been found in Nagaur district of Rajasthan, India district may be due to the geological structure of the district and intensive mining of marble in investigated districts. Moreover in drinking water samples high concentration of heavy metals may be due to the use of minerals such as jasper, dolomite, limestone, granite, phosphate, which contains high concentration of heavy metals in investigated district. On the other hand, the investigated area are adjoined by Churu, Sri Ganganagar, Sikar and Hanumangarh districts where concentration of heavy metals are quite higher, which to large influence on the water quality of our investigated area [18]. The Zn and Cu concentration in present groundwater samples are higher where as Cd and Pb are lower than the published values for Amritsar, Punjab [2].

B. Physico-Chemical Risk Assessment and Correlation

The total dissolved solids (TDS) in groundwater samples varies from 535 to 2460 mg l^{-1} with the mean value of 1192.5 mg l^{-1} as shown in table 2 The value of TDS in seven groundwater samples was found more than the permissible limit 1000 mg l^{-1} given by WHO (2008) [17]. According to the general rule, if TDS value (or conductance values) is lower, the value of radioactivity is also lower in all the water samples [19]. This theoretical result is proved by a good positive correlation of heavy metals (Fe ($R=0.78$) and Cu ($R=0.75$) (figure 2 and 3, respectively) with TDS.

The conductance of the water samples varies from 1.39 to 5.78 $\text{m}\Omega^{-1}$ with the mean value of 3.00 $\text{m}\Omega^{-1}$ as tabulated in table 2. The conductance in eight groundwater samples is found higher than the recommended level of 2 $\text{m}\Omega^{-1}$ given by WHO (1971) [20]. Like TDS a good positive correlation of heavy metals (Fe ($R=0.85$) and Cu ($R=0.84$) (figure 2 and 3, respectively) with conductance has been observed. Higher values of TDS and conductance may be due to the natural minerals dissolved in the studied water samples.

The pH of groundwater samples varies from 7.03 to 8.73 with the mean value of 7.45 as given in table 2. The pH value measured in all water samples of the investigated region is found within the recommended safe limit 7.0-8.5 as reported by WHO (1971), expect one (Mundawa, pH value 8.73) [20].

Also it has been observed that there is no correlation of heavy metal content with pH value in drinking water samples.

V. CONCLUSION

The measured levels of heavy metals (Cu, Cd, Se, As and Cr) in all the investigated groundwater samples are less than the safe limit approved by USEPA (2011) except arsenic in one sample. The observed concentrations of Cu, Cd and As in our investigated groundwater samples are less, but concentration of Fe in six samples, As in one sample, Se in seven samples and lead in six samples is found to be higher than the permissible limit as recommended by WHO (2008). A good positive correlation between heavy metals (Se and Cu) with TDS and conductance in investigated water samples has been observed. The overall result shows that heavy metal concentration in nine drinking water samples cross the MCL as recommended by various protection agencies and therefore unsafe for drinking purposes which is harmful for health point of view.

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