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Original Research

Monitoring of metal contaminations in groundwater in Northern Rajasthan, India

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ABSTRACT

Aim: The purpose of this study was to monitor concentrations of Zn, Cd, Pb, Cu and pH in groundwater of Hanumangarh, Sri Ganganagar, Churu and Sikar districts of in Northern Rajasthan, India; and to identify any relationships between metals. **Materials and Methods:** Heavy metals were analyzed by inductively coupled plasma mass spectrometry. **Results:** The measured concentrations of Zn, Cd, Pb and Cu varied from 14 to 23685 μg/l, 0.18 to 6.70 μg/l, 1 to 17 μg/l and 5 to 73 μg/l with overall mean values of 1595 $\pm$ 4094, 0.68 $\pm$ 1.02, 9 $\pm$ 4.44 and 23 $\pm$ 17 μg/l respectively. **Conclusions:** Copper level was found to be below the permissible limit of United States Environmental Protection Agency (1300 μg/l). In water sample code H-8 (Morjand Sikhan), the level of Cd was found (6.70 μg/l)to be above the permissible level (5 μg/l). In water samples codes H-7, H-9 and S-7 (Amarpura Jallu Khatt, Amar Singh Wala and Khandela-2), the level of Pb was found to be above the permissible level (15 μg/l). Significant correlations were found among the pH of water and different heavy metal concentrations.

KEY WORDS: Cadmium, contamination, groundwater, lead, water quality

INTRODUCTION

Water is one of the universal substances, which is used alike by all the kingdoms of life to sustain life. 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 directly as a result of drinking unsafe water and living in unhygienic conditions [1]. The water intended for human consumption must be free from harmful organisms and those chemical substances, which may be hazardous to health. The heavy metals are much toxic and have tendency to accumulate in the body and may result in chronic damage. The natural concentration of metals in fresh water varies depend upon the metal concentration in the soil and the underlying geological structures [2]. Pandey *et al.* [3] have reported the high concentration of lead in groundwater of Khajuwala area located in Bikaner division of Western Rajasthan. Raja *et al.* [4] have reported the elevated level of arsenic, fluoride, iron, nitrate, cadmium, copper, lead, nickel and zinc in drinking water of north-eastern states of India. Krishna and Govil [5] reported that the soils in the vicinity of the Pali Industrial Area, Rajasthan have been contaminated with heavy metals at levels far above the background concentrations in soil.

Consumption of large amounts of zinc can cause anemia, pancreas damage and lower levels of good forms of cholesterol. Cadmium is probably the most biotoxic element and is therefore regarded as a priority pollutant. When absorbed into the body, largely through food and water intake, cadmium can injure the renal, pulmonary, skeletal, testicular and nervous systems. Cadmium has been known to cause bone and joint aches and pains. The International Agency for Research on Cancer has concluded that cadmium is probably carcinogenic to humans (Group 2A, limited evidence of carcinogenicity in humans and sufficient evidence in animals)[6]. Lead in drinking water comes from lead pipes and lead based solder pipe joints. Lead is a cumulative poison and over exposure to lead cause both acute and chronic effects on a wide range of physiological systems

and organs. Young children, infants and fetuses are particularly vulnerable to lead poisoning. The International Agency for Research on Cancer has concluded that lead is possibly carcinogenic to humans (Group 2B, inadequate human data but sufficient evidence in animals for inorganic lead compounds) [6]. Lead has been identified in at least 1280 of the 1662 hazardous waste sites that have been proposed for inclusion on the Environmental Protection Agency National Priorities List [7]. Many studies have been conducted worldwide to determine the concentrations of heavy metals in water samples [8-12]. Sekhon and Singh [13] have concluded that the drinking water quality of Patiala district of Punjab varies from site to site depending upon the geological and ecological condition.

The natural water analysis for the detection of heavy metals is very important for public health studies. The present study aims to assess heavy metal contamination in groundwater of Northern Rajasthan, India; and to identify any relationships between metals.

MATERIALS AND METHODS

Study Area

Rajasthan is located in Northwest of India. Figure 1 shows the geographic location of the state of Rajasthan in India, as well as the location of the sampling sites in Rajasthan. The Sikar district is located in the North Eastern part of Rajasthan State. The climate of this district is characterized by a hot summer, scanty rainfall, chilly winter season and a general dryness of air except in brief monsoon. The minimum and maximum temperature is 3°C and 46°C. The average temperature is 23°C. The average annual rainfall is 466 mm. The district is divided into two parts by Aravalli range, Eastern part is represented by Alwar group of rocks which comprises quartzite marble, schist, and gneiss, among metallic mineral copper ore is the most important found. The Khandela and Kotri villages of Sikar district in studied area is known for radioactive mineralization. The soils of the district are predominantly light textured, weak structured, well drained alluvial and eolian in nature.

The Churu district lies in the north east of the Rajasthan State. The climate of the district is absolutely dry with scanty rainfall. It is very hot during summer and very cold during winter. The maximum and minimum temperature is 48.2°C and freezing point respectively. District Churu is a part of the Thar Desert. Soils of Churu district are pale brown, single grained, deep and well drained. The climate of the Hanumangarh and Sri Ganganagar districts are marked by the large variation of temperature, extreme dryness and scanty rainfall. November-March is cold season, followed by summer April-June, from July-mid to September is monsoon while mid-September to October is post monsoon period. Minimum and maximum temperature is 1°C and 45°C respectively, while the mean temperature remained 23°C. The study area is plain and with thick layer of alluvium and windblown sand. The oldest rocks of the area belong to Aravalli super groups which includes phyllite, shale and quartz veins. The studied area is bounded on the Western side by Pakistan, on the Northeast side by Haryana and Punjab to the north. Residents of these areas are poor, mostly illiterate farmers, who use the groundwater for irrigation and for domestic consumption without prior treatment [14].

Sample Collection and Preparation

In the present study, concentrations of heavy metals have been measured in groundwater samples from four districts of Northern Rajasthan, India. The water samples were collected from individual home wells normally operated with hand pumps. The water directly from the tap is used by the residents.

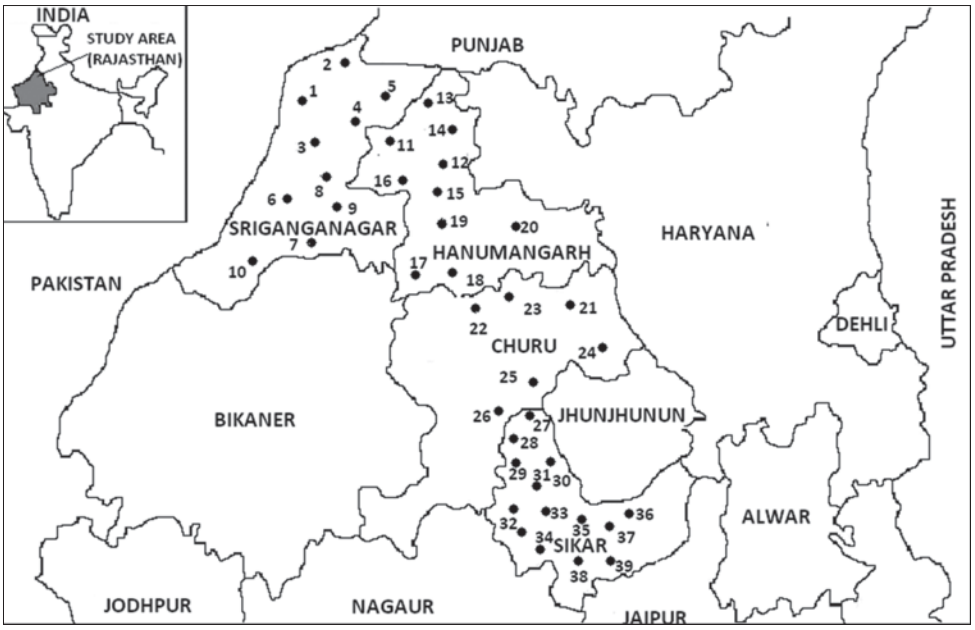

Figure 1: Map of Rajasthan showing the area surveyed during the present investigations

Before the samples were taken, the water was pumped out 5-10 min until fresh water comes from deep in the well. New polyethylene sample bottles were washed out with filtered water to be sampled. All these samples were collected and analyzed during the month of January-February 2012 (winter season) and the weather conditions during the sampling period were fairly stable. The pH value has been determined in collected groundwater samples using analytical kit-362D. The sampled water was acidified immediately with nitric acid, and heavy metal analyses were carried out in the geochemistry division inductively coupled plasma mass spectrometry (ICP-MS)lab, National Geophysical Research Institute (NGRI), Hyderabad, India.

Inductively Couples Plasma Mass Spectrometry

Inductively coupled plasma-MS technique is full multi-elemental over a mass range of 3-238, a rapidly emerging technique, typically requiring only 2 min for the whole run of each sample and lower detection limit is even <0.15 ng/l for aqueous samples [15]. Calibration was performed using National Institute of Standards and Technology 1640a (USA), which is a reference material for trace elements in a natural water, to minimize matrix and other associated interference effects and to check the precision and accuracy of the analysis. The analytical procedure utilized is described in detail by Balaram *et al*. [16]. The precisions achieved were <5% relative standard deviation with comparable levels of accuracy; in most cases suggesting that the data obtained by ICP-MS are best suited for high precision geochemical studies. The important features of ICP-MS technique are high sample throughput, small sample quantity and the lower detection limits. ICP-MS is a simple, rapid and inexpensive method for the determination of heavy metals in groundwater.

RESULTS AND DISCUSSION

Results of heavy metal concentration in groundwater are shown in Table 1. The permissible levels for the concentration of Zn, Cd, Pb and Cu in water proposed by the United States Environmental Protection Agency (USEPA)are 5000, 5, 15 and 1300 μg/l respectively [17]. These levels are set to represent a concentration that does not result in any significant risk to human over lifetime's drinking water. Heavy metal concentrations in groundwater of Sri Ganganagar district ranged from 56 to 5204 μg/l Zn; 0.24 to 1.32 μg/l Cd; 2 to 14 μg/l Pb and 11 to 35 μg/l Cu and the average values were found to be 1254 ± 1514, 0.60 ± 0.39, 9 ± 3.7 and 18 ± 8.67 μg/l, respectively. In water sample code G-7 (site-Radewala), the level of Zn was found (5204 μg/l)to be above the permissible level (5000 μg/l). Cd, Pb and Cu levels were found to be below the permissible limits of USEPA.

Heavy metal concentrations in groundwater of Hanumangarh district ranged from 152 to 2430 μg/l Zn; 0.20 to 6.70 μg/l Cd; 4 to 17 μg/l Pb and 9 to 56 μg/l Cu and the average values were found to be 504 ± 652, 1.19 ± 1.85, 11 ± 4.2 and 28 ± 15.7 μg/l, respectively. In water sample code H-8 (site-Morjand Sikhan), the level of Cd was found (6.70 μg/l)to be above the permissible level (5 μg/l). In water samples codes H-7 and H-9 (sites-Amarpura Jallu Khatt and Amar Singh Wala), the level of Pb was found to be above the permissible level (15 μg/l). Zn and Cu levels were found to be below the permissible limits of USEPA.

Heavy metal concentrations in groundwater of Churu district ranged from 63 to 11242 μg/l Zn; 0.20 to 0.95 μg/l Cd; 4 to 13 μg/l Pb and 6 to 73 μg/l Cu and the average values were found to be 2496 ± 4067, 0.63 ± 0.26, 9 ± 3 and 38 ± 23.7 μg/l, respectively. Cd, Pb and Cu levels were found to be below the permissible limits of USEPA. In water sample code C-5 (site-Taranagar), the level of Zn was found (11242 μg/l)to be above the permissible level (5000 μg/l). Heavy metal concentrations in groundwater of Sikar district ranged from 14 to 23685 μg/l Zn; 0.18 to 0.85 μg/l Cd; 1 to 17 μg/l Pb and 5 to 43 μg/l Cu and the average values were found to be 2280 ± 6222, 0.39 ± 0.22, 8 ± 5 and 17 ± 13 μg/l, respectively. In water sample code S-6 (site-Khandela-1), the level of Zn was found (23685 μg/l)to be above the permissible level (5000 μg/l). Cd and Cu levels were found to be below the permissible limits of USEPA. In water samples codes S-7 (sites-Khandela-2), the level of Pb was found (17 μg/l)to be above the permissible level (15 μg/l).

For whole of the studied area, heavy metal concentrations in groundwater samples ranged from 14 to 23685 μg/l Zn; 0.18 to 6.70 μg/l Cd; 1 to 17 μg/l Pb and 5 to 73 μg/l Cu and the average values were found to be 1595 ± 4094, 0.68 ± 1.02, 9 ± 4.4 and 23 ± 17 μg/l, respectively. The pH of the water samples ranges between 6.90 and 8.76. The safe limit for the pH as recommended by USEPA [17] is 6.5-8.5. All the water samples except one (from sampling site-Fatehpur, pH value 8.76)have a pH value within the safe limit.

There is not any major industry found in Northern Rajasthan that may cause an increase in the concentrations of heavy metals in groundwater. The measured average concentrations of Zn and Cu were found to be higher in Churu district in comparison with Sri Ganganagar, Hanumangarh and Sikar districts of Northern Rajasthan may be due to the geological structure such that the Churu district is a part of the Thar Desert. The measured average concentration of Cd was found to be higher in Hanumangarh district in comparison with Sri Ganganagar, Churu and Sikar districts of Northern Rajasthan may be due to the use of mineral phosphate fertilizer, which typically contains high Cd concentrations in addition to other elements.

The present values of Pb in water samples are comparatively lower than those reported for Amritsar District of Punjab State by Singh *et al*. [8] and for Bathinda district of Punjab by Kumar *et al*., [9] The measured concentrations of Zn, Cd, Pb and Cu obtained in the present investigations are comparatively higher than those reported for Delhi region of India by Raj *et al*. [18] The present values of Pb and Cd in water samples are comparatively higher than those reported for Patiala district of Punjab, India by Sekhon and Singh [13].

Table 1: The concentration of heavy metals *viz*. Zn, Cd, Pb and Cu in groundwater samples from some areas of Northern Rajasthan, India

Sample code	Sample location	Latitude and longitude	Depth (m)	pH	Zn (μg/l)	Cd (μg/l)	Pb (μg/l)	Cu (μg/l)
District Sri Ganganagar								
G-1	3H	29.88 N 73.75 E	22.8	7.64	1331	0.28	9	11
G-2	Gulabawala	29.87 N 73.69 E	22.5	7.75	1584	0.65	11	34
G-3	14Q	29.96 N 73.71 E	22.5	6.91	235	0.40	10	15
G-4	Sangatpura	30.02 N 73.70 E	20.4	7.04	855	0.24	2	21
G-5	Sri Gnganagar city	29.92 N 73.88 E	24.0	7.56	181	0.30	12	11
G-6	Karanpur	29.84 N 73.46 E	24.0	7.21	2502	0.40	14	12
G-7	Radewala	28.83 N 73.42 E	30.0	7.19	5204	1.32	12	11
G-8	Kalian	30.00 N 73.86 E	24.6	8.40	56	0.30	9	17
G-9	23Z	29.91 N 73.72 E	25.5	7.00	434	0.80	11	35
G-10	Malkana Kalan	29.97 N 73.69 E	23.4	7.33	159	1.30	3	16
District Hanumangarh								
H-1	Rawatsar	29.28 N 74.38 E	19.5	8.15	216	0.48	15	17
H-2	Nukera	29.88 N 74.37 E	28.5	7.27	455	0.90	6	14
H-3	Rasuwala	29.90 N 74.32 E	21.6	7.56	164	0.40	10	17
H-4	Shahpini	29.81 N 74.29 E	33.0	7.40	152	0.90	10	28
H-5	Pilibanga	29.49 N 74.09 E	24.0	7.41	475	0.38	9	16
H-6	Sangaryia	29.47 N 74.28 E	21.0	7.45	2430	0.42	14	56
H-7	Amarpura jallu Khatt	29.79 N 74.33 E	23.4	7.25	208	0.75	17	38
H-8	Morjand Sikhan	29.80 N 74.39 E	22.5	7.57	303	6.70	11	31
H-9	Amar Singh Wala	29.64 N 74.07 E	24.0	7.95	238	0.75	17	53
H-10	Hanumangarh city	29.58 N 74.31 E	22.5	6.97	396	0.20	4	9
District Churu								
C-1	Rajgarh	28.64 N 75.38 E	21.6	7.10	3191	0.95	8	73
C-2	Ratangarh	28.07 N 74.62 E	21.0	8.45	78	0.20	7	6
C-3	Seowa	28.63 N 75.16 E	22.5	7.32	319	0.80	11	39
C-4	Chimanpura	28.67 N 75.15 E	21.0	7.82	93	0.80	11	64
C-5	Taranagar	28.40 N 75.20 E	27.0	8.02	11242	0.64	13	27
C-6	Churu city	28.28 N 74.96 E	25.5	7.85	63	0.40	4	20
District Sikar								
S-1	Goria	27.55 N 75.25 E	51.0	7.74	1316	0.18	10	41
S-2	Fatehpur	27.99 N 74.95 E	60.1	8.76	14	0.20	1	7
S-3	Palthana	27.74 N 75.09 E	57.1	8.08	116	0.22	3	5
S-4	Sikar city	27.62 N 75.14 E	60.1	8.11	111	0.38	11	12
S-5	Ranoli	27.52 N 75.30 E	54.0	8.10	108	0.18	3	9
S-6	Khandela-1	27.60 N 75.50 E	45.0	6.90	23685	0.85	2	43
S-7	Khandela-2	27.60 N 75.50 E	48.0	8.24	85	0.82	17	26
S-8	Raseedpura	27.71 N 75.08 E	75.1	7.21	101	0.42	8	11
S-9	Kotri	27.69 N 75.56 E	48.0	7.19	408	0.36	11	13
S-10	Khandela Gokul	27.62 N 75.52 E	42.0	7.47	2666	0.34	1	5
S-11	Laxmangarh	27.82 N 75.02 E	54.0	8.68	126	0.28	10	11
S-12	Kotri Lalasar	27.66 N 75.55 E	51.0	7.14	851	0.56	14	29
S-13	Dadhia	27.72 N 75.22 E	67.6	7.88	51	0.28	8	10
Minimum				6.90	14	0.18	1	5
Maximum				8.76	23685	6.70	17	73
Mean				7.62	1595	0.68	9	23
Standard deviation				0.49	4094	1.02	4.4	17

The correlation among the pH of water and different heavy metal concentrations were also studied and the results are presented in Table 2. There was no significant correlation observed in the change of Pb concentration with the pH of water. But Zn, Cd and Cu exhibited a significant positive correlation with pH of water. Among the heavy metals themselves, a significant negative correlation was observed between Zn and Pb, whereas Zn exhibited a significant positive correlation with Cu. There was no significant correlation was observed between Zn and Cd. Cd exhibited a significant positive correlation with Pb and Cu. A significant positive correlation was observed between Pb and Cu. This will help to understand the nature of these metals and to determine the level of inter-metal association.

Table 2: Correlation coefficient matrix (*r*) for heavy metal contents and pH of water

	Zn	Cd	Pb	Cu	pH
Zn	1.00				
Cd	0.03	1.00			
Pb	−0.16	0.13	1.00		
Cu	0.23	0.20	0.36	1.00	
pH	−0.25	−0.12	0.01	−0.23	1.00

CONCLUSION

In the present study, concentrations of Zn, Cd, Pb Cu and pH have been measured in groundwater samples from four districts

of Northern Rajasthan using ICP-MS. In water samples codes G-7, C-5 and S-6 (sites-Radewala, Taranagar and Khandela-1), the level of Zn was found to be above the permissible level (5000 μg/l). Cu level was found to be below the permissible limits of USEPA (1300 μg/l). In water sample code H-8 (site-Morjand Sikhan), the level of Cd was found (6.70 μg/l)to be above the permissible level (5 μg/l). In water samples codes H-7, H-9 and S-7 (sites-Amarpura jallu Khatt, Amar Singh Wala and Khandela-2), the level of Pb was found to be above the permissible level (15 μg/l). Significant correlations were found among the pH of water and different heavy metal concentrations. The results showed that the groundwater quality of Northern Rajasthan varies from site to site depending upon the geological condition.

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