Determination of Heavy Metals and Their Correlation with Uranium in Water of Baran District of Rajasthan, India

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Abstract—The heavy metal analysis of ground water samples was done by collecting 40 samples including pre and post monsoon sampling from 40 villages of 8 tehsil of the area under investigation. The concentrations of heavy metals copper, iron, zinc, cobalt and lead were determined using the direct air- acetylene and the concentrations of aluminium were determined using the direct air- acetylene- nitrous oxide atomic absorption spectrometer and determination of uranium in groundwater by the LED Fluorimetry. The heavy metals have been studied for their health hazards and the concentration is correlated with uranium and recommended safe limits as suggested by various protection agencies. All groundwater samples have resulted in Cu, Zn, Fe under the permissible limits by BIS, 2012 in the study area which makes it fit for drinking and other domestic purposes but 70% the ground water samples exceeded the desirable limit for Pb in pre monsoon and 37% samples have exceeded the limit for Pb content in post monsoon as per BIS, 2012. 50% the ground water samples exceeded the desirable limit for Al in pre monsoon and 42% the ground water samples exceeded the desirable limit for Al in post monsoon and 29% samples have exceeded the limit for Co content in post monsoon as per BIS, 2012 due to the area falls in the baran district of Rajasthan and there is widespread use of pesticides such as atrazine, chlordane, dibromochloropropane, endrin, heptachlore, lindane etc and fertilizers such as urea, superphosphate, diammonium phosphate and NPK etc. A weak positive correlation has been observed between U and Fe, Pb in pre monsoon and U and Pb, Al in post monsoon so significant positive correlation between the heavy metal indicated that the metals are from the same source of origin but there is weak negative correlation between U and Cu, Zn, Co, Al in pre monsoon and U and Cu, Zn, Fe, Coin post monsoon which may be due to the different origin of both the metals in the area groundwater. Uranium is mostly from the natural earth crust while Pb, Al is through vehicular activities, pesticides, fertilizers, industrials effluents and manmade activities. Therefore, continuous monitoring of heavy metals in soils must be ensured to aware the consumers to mitigate the health-related problems occurring due to uranium and other heavy metals. The results carouse that drinking water defiled with heavy essence is prone to radiological and chemical pitfalls for occupants. A large population is using ground water as drinking purpose; hence they're at the high threat of heavy essence toxin.

Index Terms—Heavy metals, Quantitative analysis, Uranium, LED Fluorimetry, AAS.

I. INTRODUCTION

Heavy Essence are generally defined as essence needed in trace quantities and considered as poisonous. Heavy essence pollution is a serious global environmental problem as it negatively affects factory growth and inheritable variation (1-2). The sources for heavy essence impurity in terrain include geogenic, agrarian, pharmaceutical, artificial, domestic backwaters, and atmospheric rush (3-4). The attention of essence is adding at an intimidating rate due to boost of unplanned industrialization and urbanization. Mobility of this heavy essence by exertion of several atmospheric events e.g., runoff water and blowing winds enhanced their accumulation in the cold, contaminating air and water that leads to habitual diseases in living bodies inhabiting these points (5). Street dust, roadside soil and shops growing in these defiled areas are subordinated to admit high quantum of heavy essence both from dangerous feasts emitting from motor vehicle and transported poisonous accoutrements (6). Vehicular conditioning on roads by motors also promote essence situations especially lead and nickel, in our ecosystem through burning fossil energies and vehicle wear i.e., thickets, vehicle body, tyres and vehicular fluids (7-9). Some heavy essence viz. Pb, Cd, As, Hg is toxic to shops and creatures indeed at veritably low attention, while other heavy essence

viz. Cu, Zn, Fe, Mo may accumulate in factory apkins to relatively abnormal countries with no egregious side goods (10- 14). Heavy essence impurity of water is honored as one of major environmental problem and dangerous for mortal consumption, thus the study related to water impurity has come important. Essence is of non-degradable Nature and can accumulate in mortal body system which causes damage to the nervous system and other internal organs of mortal body (15- 17). The heavy essence like bobby, zinc, cobalt, boron, iron, molybdenum are the introductory requirements for the growth of the shops but these heavy essences are dangerous to the brutes and shops when their attention go beyond the admissible limits (18- 19). Other many heavy essences similar as lead, mercury, cadmium, and arsenic are n't essential for the growth of shops and creatures (20-21). From the health point of view the input of large quantum of zinc can beget anemia. The input of cadmium by food and water can injure the renal, pulmonary, cadaverous, testicular and nervous system (22- 25). Redundant of lead in the mortal body may lead to beget headache, perversity, abdominal pain and colorful symptoms related to the nervous system (26-27). Large consumption of arsenic via water may lead to gastrointestinal symptoms, severe disturbances of the cardiovascular and central nervous systems, and ultimately death (28-30). Large input of bobby may beget stomach and intestinal torture similar as nausea, puking, diarrhea and stomach cramps. Cobalt may affect the heart, thyroid, liver, bronchitis, anemia and feathers (31-35)). Al accumulates in feathers, lungs, liver, brain and thyroid where it competes with calcium for immersion and can affect the cadaverous mineralization (35-36). Iron insufficiency leads to anemia, headache, frazzle, loss of attention and weak vulnerable system (36-39). This exploration includes the analysis of 40 groundwater sample collected from designated slice spots in baran quarter for water answerable uranium and heavy essence content and their correlation to understand possibility of groundwater pollution from filtering of soil.

II. MATERIALS AND METHODS

Study Area

The study area is one of the major quarters of Rajasthan named baran quarter with an area of 6992 sq km, located between latitude 24°25'00" and 25°27'00" east and longitude 76°12'00" and 77°25'00" north. The quarter forms a part of Kota Division. It's bounded by Kota quarter in the west and Madhya Pradesh in the northeast and in south by Jhalawar quarter. Administratively, the quarter is divided into eight tehsils and six development blocks. The quarter has eight tehsils picking as Anta, Baran, Kishanganj, Shabad, Atru, Chabra, Mangrol and Chhipabarod.

Method of Heavy Metal Analysis

Heavy metals concentrations (Cu, Zn, Co, Ni, Cd, As, Fe, Pb and Al) in groundwater samples were measured using Atomic Absorption Spectrophotometer (thermo scientific iCE 3000 Series) with a precision better than 5%. Atomic Absorption Spectrometer (AAS) is an instrument for estimating the ingestion of follow components introduce in water by estimating the radiation consumed by the compound component of intrigue. This is finished by investigation the spectra created when the sample is energized by radiation. It depends on the Beer-Lambert law standard in which atomic absorption technique measures the vitality as photons of light that are consumed by the sample. A detector measures the wavelengths of light transmitted by the sample, and compares them to the wavelengths which originally passed through the sample. A signal processor then integrates the changes in wavelength absorbed, which appear in the readout as peaks of energy absorption at discrete wavelengths.

Estimation of Uranium in samples

Uranium analysis was done in LED fluorimeter LF-2 (Quantalase Enterprises Pvt. Ltd., India). Calibrate the fluorimeter with four uranium standards to check the instrument performance and the linear dynamic range. One uranium standard of 500 ppb can be prepared; each time 50 microliter can be added to 5 ml ultrapure water and 0.5 ml buffer, to avoid the error in the preparation of lower ppb level standards. Also, the ppb level standards require fresh preparation before analysis. If the TDS level is low (less than 1500 ppm) in clear drinking water samples, then the water sample can be directly analysed for uranium using a fluorimeter, no chemical processing is required. Take 5 ml of water sample in a cleaned and dry suprasil quarts cuvette, add 0.5 ml of buffer

(fluorescence enhancing agent that is 5 % sodium pyrophosphate solution, pH is almost 7 adjusted using phosphoric acid). Record the fluorescence response of the sample only, in terms of counts, minimum 4 repetitions. Add 50 microliter of 500 ppb uranium standard onto the cuvette that contains the sample and buffer, record the fluorescence response of the first standard added (amount of standard additions depends on the sample fluorescence counts). Again add 50 microliters of 500 ppb uranium standard onto the cuvette and record the fluorescence response. Uranium level in the sample can be analysed using standard addition method using excel sheet, to avoid matrix effect.

III. RESULTS AND DISCUSSION

This paper consists of results of measurements together with statistics (spatial distribution and Pearson's correlations) and the evaluation of results under the influence of observations and discussions based on general evidence related with this research.

Copper (Cu)

Copper content in ground water collected in study area varied between 0.0003 (village bamori kalan, tehsil mangrol) to 0.0641mg/L (village amalsara, tehsil anta) with mean, median, mode, standard deviation value 0.0113, 0.0086, 0.0023, 0.011 during pre mansoon and varied between 0.004 (village sorsan, tehsil baran) to 0.1529 (village chipabarod, tehsil chipabarod) with mean, median, mode, standard deviation value 0.02553, 0.017, 0.0193, 0.02525mg/L during post mansoon. Copper are not detected in many ground water samples of pre and post monsoon in the study area. Most of ground water samples were within desirable limit of copper which makes it fit for drinking and other domestic purposes. From 40 ground water samples, one samples village amalsara, tehsil anta in pre monsoon and village chipabarod, tehsil chipabarod in post monsoon were above desirable limit which reported that ground water is unfit for drinking purpose in this area. Post monsoon average of copper is more than pre monsoon average which reflects possibility of leaching of salts during rainy season.

Zinc (Zn)

The zinc content in ground water collected in study area ranged between 0.0036 (village dobra, tehsil chipabarod) and 0.1208mg/L (village chipabarod, tehsil chipabarod) with mean, median, mode, standard deviation value 0.0561, 0.0088, 0046, 0.0504mg/L in pre mansoon and ranged between 0.0427 (village mungawali, tehsil shabad) to 0.6698 (village khushiyara, tehsil shabad) with mean, median, mode, standard deviation value 0.1628, 0.1388, 0.0765, 0.09170mg/L in post mansoon. Most of ground water samples were within desirable limit and permissible limits of Zn which makes it fit for drinking and other domestic purposes. Zinc is not detected in many ground water samples of pre and post monsoon in the study area. Post monsoon average of zinc is more than pre monsoon average which reflects possibility of dilution of salts during rainy season.

Iron (Fe)

The iron content measured in all ground water collected samples varied from 0.0004mg/L (village kelwada, tehsil kishanganj) to 0.0871 mg/L (village kachra, tehsil atru) with mean, median, mode, standard deviation value 0.02215, 0.0195, 0.0223, 0.0135 in pre mansoon and varied from 0.0006 mg/L(village gajanpura, tehsil baran) to 0.1031mg/L (village mangrol, tehsil mangrol) with mean, median, mode, standard deviation value 0.0426, 0.03935, 0.0028, 0.02847 in post mansoon in the study area. Iron is not detected in some village viz. bamorikalan of tehsil mangrol, mugawali of tehsil shabad, iklera of tehsil baran in ground water samples of pre monsoon in the study area. Post monsoon average of iron is more than pre monsoon average which reflects possibility of leaching of salts during rainy season.

Lead (Pb)

Lead content in the ground water collected samples varied from 0.0042mg/L (village balharpur, tehsil chabra) to 0.2216mg/L (village bengani, tehsil baran) with average, median, mode, standard deviation value 0.0929, 0.0828, 0.0206, 0.0564mg/L in pre monsoon and varied from 0.0029 (village dilod, tehsil chabra) to 0.0412 (village manpura, tehsil anta) with average, median, mode, standard deviation value 0.02196, 0.0219, 0.0191, 0.01275 in the post monsoon. 70% and 37% ground water samples during pre and post mansoon were above the desirable limits/ permissible limits as per BIS, 2012 in the study area. It is evident from results that ground water is not suitable for the drinking purposes because of presence of higher lead content. Pre monsoon average of lead is more than post monsoon average which reflects possibility of

not dilution of concentrated substances in pre monsoon.

Cobalt (Co)

Cobalt content in the ground water collected samples in study area varied from 0.002 (village mjrauta, tehsil kishanganj) to 0.0665mg/L (village bhaterian, tehsil mangrol) with mean, median, mode, standard deviation value 0.02675, 0.02695, 0.0261, 0.01298 in pre monsoon and varied from 0.0401 (village dilod, tehsil chabra) to 0.1424 (village mangrol, tehsil mangrol) with mean, median, mode, standard deviation value 0.09213, 0.0922, 0.0941, 0.01415 in post monsoon. From the analyzed result, all ground water samples of pre monsoon were within desirable limit and permissible limits as per BIS, 2012 in the study area and Co which makes it fit for drinking and other domestic purposes in the pre monsoon. 29% ground water samples during post mansoon were above the desirable limits/ permissible limits as per BIS, 2012 in the study area due to the cobalt containing substance dissolve in post monsoon by the rainy season so leaching of cobalt in pre monsoon to post monsoon. Post monsoon average of cobalt is more than pre monsoon average which reflects possibility of leaching of salts during rainy season.

Aluminium (Al)

The aluminium content in ground water collected samples varied from 0.0653 (village mundla, tehsil atru) to 3.7583mg/L (village setkolu, tehsil chipabarod) with the average, median, mode, standard deviation value of 3.3208, 3.8246, 2.246, 1.900mg/L in pre monsoon and varied from 0.013 (village dilod, tehsil chabra) to 1.56mg/L (village mangrol, tehsil mangrol) with mean, median, mode, standard deviation value 0.39, 0.30, 0.04, 0.32 in post monsoon. 50% ground water samples during pre mansoon were above the desirable limits as per BIS, 2012 and 49% samples during pre mansoon were above the permissible limits as per BIS, 2012 in the study area. It is evident from results that ground water is not suitable for the drinking purposes because of presence of higher aluminium content. Pre monsoon average aluminium is more than post monsoon average which reflects possibility of not dilution of concentrated substances in pre monsoon.

Correlation Analysis

The Pearson's correlation coefficient (r) is calculated from the elemental concentrations as described in article in order to predict the possibility of a common source. The correlation matrix was prepared to check relation between the Uranium and different heavy metals in ground water samples during both pre monsoon and post monsoon season in the study area which are presented below in Tables 1 and 2 respectively. The correlation coefficients and the nature of correlation for uranium with different heavy metal in ground water are given in Table 3 in the study area.

Table.1: Correlations values of different parameters during pre monsoon

Parameters	U(mg/l)	Cu(mg/l)	Zn(mg/l)	Fe(mg/l)	Pb(mg/l)	Co(mg/l)	Al(mg/l)
U(mg/l)	1	-0.0352	-0.1979	0.0527	0.1181	-0.1257	-0.0907
Cu(mg/l)		1	1	0.1045	0.6224	-0.0786	0.3063
Zn(mg/l)			1	-0.3914	-0.6875	0.0113	1
Fe(mg/l)				1	0.0145	0.07833	-0.0158
Pb(mg/l)					1	-0.3608	-0.653
Co(mg/l)						1	0.3427
Al(mg/l)							1

Table.2: Correlations values of different parameters during post monsoon

Parameters	U(mg/l)	Cu(mg/l)	Zn(mg/l)	Fe(mg/l)	Pb(mg/l)	Co(mg/l)	Al(mg/l)
U(mg/l)	1	-0.1898	-0.1449	-0.1324	0.1417	-0.0965	0.0822
Cu(mg/l)		1	-0.0962	0.0054	-0.1858	-0.2785	0.2278
Zn(mg/l)			1	0.3986	0.2382	0.299	-0.2
Fe(mg/l)				1	-0.0111	-0.0913	0.0
Pb(mg/l)					1	-0.0318	-0.1
Co(mg/l)						1	0.0
Al(mg/l)							1

Table.3: Correlation coefficients and the nature of correlation for uranium with different heavy metal in ground water during pre and post monsoon.

S.No.	Heavy metal	Correlation coefficient (pre monsoon)	Nature of correlation (pre monsoon)	Correlation coefficient (post monsoon)	Nature of correlation (post monsoon)
1	Copper	-0.03	Negative correlation	-0.18	Negative correlation
2	Zinc	-0.19	Negative correlation	-0.14	Negative correlation
3	Iron	0.05	Weak positive	-0.13	Negative correlation
4	Lead	0.11	Weak correlation	0.14	Weak positive
5	Cobalt	-0.12	Negative correlation	-0.09	Negative correlation
6	Aluminium	-0.09	Negative correlation	0.08	Weak positive

IV. CONCLUSION

In the present work, an attempt has been made to provide complete studies the assessment of heavy metals viz. Cu, Zn, Fe, Co, Pb and Al in ground water and their correlation with uranium and related a significant environmental hazard, heavy metal pollution in Baran district in view of the influence of prevailing water parameters in the transport and dispersion of heavy metal pollutants and other industries to the study area. It is concluded from the results that water parameters factors such as temperature, TDS, EC, TH etc special play important roles in spreading heavy metal pollutants. This contamination is an important concern for food safety and human health and highlights the need for establishing water quality standards for heavy metals to predict human induced water pollution. The present study is an effort to investigate concentrations of heavy metals viz. Cu, Zn, Fe, Co, Pb and Al in ground water samples in order to determine the influence of the main anthropogenic sources in Baran district at various sampling sites situated in many villages as point sources in 2020-21, 2021-22 and 2022-23. All groundwater samples have resulted in Cu, Zn, Fe under the permissible limits by BIS, 2012 in the study area which makes it fit for drinking and other domestic purposes but 70% the ground water samples exceeded the desirable limit for Pb in pre monsoon and 37% samples have exceeded the limit for Pb content in post monsoon as per BIS, 2012. 50% the ground water samples exceeded the desirable limit for Al in pre monsoon and 42% the ground water samples exceeded the desirable limit for Al in post monsoon and 29% samples have exceeded the limit for Co content in post monsoon as per BIS, 2012 due to the area falls in the baran district of Rajasthan and there is widespread use of pesticides such as atrazine, chlordane, dibromochloropropane, endrin, heptachlore, lindane etc and fertilizers such as urea, superphosphate, diammonium phosphate and NPK etc. These pesticide and fertilizers also contribute Pb, Al, Co to the water system. Regular use of phosphate fertilizer in waterlogged and calcareous soil conditions is one of the main reasons for contributing significantly to contamination of ground water so ground water is not suitable for drinking purposes. Vegetables growing around heavy metal threatened areas are at higher risk of accumulating toxic levels of heavy metals. Through bio-magnification, consumption of rooted vegetables adversely affects the synthesis of haem in the blood of human beings. Increasing content of heavy metal will become threat for aquatic life for the vegetation and mankind, because heavy metals in groundwater may further contaminate agriculture, which then enters the food chain and results in biomagnifications. Finally, steps must be taken to treat effluent before discharging it in water bodies. A weak positive correlation has been observed between U and Fe, Pb in pre monsoon and U and Pb, Al in post monsoon so significant positive correlation between the heavy metal indicated that the metals are from the same source of origin but there is weak negative correlation between U and Cu, Zn, Co, Al in pre monsoon and U and Cu, Zn, Fe, Co in post monsoon which may be due to the different origin of both the metals in the area groundwater. Uranium is mostly from the natural earth crust while Pb, Al is through vehicular activities, pesticides, fertilizers, industrials effluents and manmade activities. It appears instructive to regularly monitor water quality to determine alterations in uranium and heavy metals in groundwater of baran district of hadoti region in Rajasthan for a unique variation with time. Since copper, iron, zinc have not found in higher values but

lead, aluminium, cobalt are found higher values so a detailed work of monitoring of trace elements in groundwater may be carried out in future. Post monsoon average of copper, zinc, iron, cobalt are more than pre monsoon average which reflects possibility of leaching of salts during rainy season increasing their correlation in ground water but pre monsoon average of lead, aluminium are more than post monsoon average which reflects possibility of not dilution of concentrated substances in pre monsoon. It is recommended on the basis of the analytical results that to mitigate the entry of heavy metals, to minimize the use of chemical fertilizers and pesticides which are also finally added to shallow ground water and encourage tree plantations which results in lowering of temperature in shades and significantly less evaporation of water and other toxic elements in the food chain, the municipal and industrial waste must not be drained into the rivers and other areas such as farmlands without the prior treatment.

V. ACKNOWLEDGEMENT

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