

HEAVY METAL CONTAMINATION OF GROUNDWATER IN GUWAHATI CITY, ASSAM, INDIA

Manoshi Lahkar¹, K.G. Bhattacharyya²

¹Department of Chemistry, Gauhati University, Guwahati, Assam, India.

²Retired Professor, Department of Chemistry, Gauhati University, Guwahati, Assam, India.

Abstract - Heavy metal contamination of the groundwater in Guwahati city was assessed for their Cd, Pb, Fe and As contents. 27 groundwater samples were analysed using Atomic Absorption Spectrophotometer and the levels of the four heavy metals were compared to the WHO specified maximum contaminant levels. According to WHO, the Maximum Contaminant Level (MCL) for Cd is 0.003 mg/L, while for Pb and As are both 0.01 mg/L (or 10 µg/L), and for Fe permissible limit is 0.3 mg/L. From the results obtained, it was found that out of the 81.48% samples where Cd was present, all of them had Cd content above MCL. Out of the 100% samples where Pb was present, only 22.22% samples had Pb content just within MCL in the wet season, and only 7.4% within MCL in the dry season. Only one sample had Pb content below MCL in the dry season. 62.96% samples had Fe content above the WHO permissible limit in wet season, while 92.59% had it above the limit in dry season. Out of the 70.37% samples that had As content present in wet season and 81.48% in dry season, all of the values were found to be below MCL in both seasons. The results obtained from this study indicate a significant risk to the population given how long term exposure to these metals even in low quantities can affect their health, and since for majority, groundwater is the most widely used and reliable source of water supply in the area.

Key Words: Heavy metals, Groundwater contamination, Maximum Contaminant Level, Atomic Absorption Spectrophotometry, WHO.

1. INTRODUCTION

97% of the water on Earth is salt water and only 3% is fresh water. Slightly over 67% of this fresh water is frozen in glaciers and polar ice caps. The remaining unfrozen fresh water is found mainly as groundwater, which constitutes 30% of the freshwater on Earth. Only a small fraction is present above ground or in the air. Though fresh water is a renewable resource, yet the world's supply of groundwater is steadily decreasing, with depletion considered to be occurring most prominently in Asia and North America. Moreover, groundwater quality is constantly decreasing due to various anthropogenic as well as geogenic causes, and water quality crisis is a rampant problem the world over.

Groundwater is a vital natural resource. There is a natural belief that groundwater is safer and purer than surface water because of the protective quality of the soil cover. The

quality of groundwater is often referenced in comparison to drinking water standards specified by the World Health Organisation (WHO). Behaviour of groundwater is often complicated in case of urban regions especially, because of occurrence of pollution and various such other anthropogenic causes, in addition to diversified geological formations and complex tectonic formations.

Groundwater is held in the pore space of sediments such as sands or gravels or in the fissures of fractured rock such as crystalline rock and limestone. The body of rock or sediments containing the water is termed an aquifer and the upper water level in the saturated body is termed the water table. Typically, ground waters have a steady flow pattern. Velocity is governed mainly by the porosity and permeability of the material through which the water flows, and is often up to several orders of magnitude less than that of surface waters. The media in an aquifer are characterized by porosity and permeability. Porosity is the ratio of pore and fissure volume to the total volume of the media. It is measured as percentage voids and denotes the storage or water volume of the media. Permeability is a measure of the ease with which fluids in general may pass through the media under a potential gradient and indicates the relative rate of travel of water or fluids through media under given conditions. The movement of percolating water through larger pores is much more rapid than through the finer pores.

The overall effect of all these factors is that the composition of ground water varies from time to time and from place to place. Consequently, the chemical composition of ground water will vary depending upon several factors like frequency of rain, which will leach out the salts, time of stay of rain water in the root-zone and intermediate zone, presence of organic matter, etc. The groundwater chemistry is dependent on the following factors as well: reactions of carbonic acid with calcite/limestone, oxidation of pyrite in the presence of calcite under alternate wet - dry conditions, dissolution of gypsum to produce calcium ions and sulphate ions, etc. The weathering of silicate mineral is believed to be the key process in the chemical evolution of ground water. The key weathering reactions involve the formation of hydrogen ions in subsurface water through dissolution of carbon dioxide.

Apart from these reactions, there are several other reactions including microbiological mediated reactions, which tend to alter the chemical composition of the percolating water. For example, the bicarbonate present in most waters is derived mostly from CO₂ that has been extracted from the air and liberated in the soil through biochemical activity. Some rocks serve as sources of chloride and sulphate through direct solution. Apart from geogenic causes, many of the anthropogenic disturbances through industrial and agricultural pollution degrade the groundwater quality.

Among the many contaminants in groundwater, heavy metals receive particular concern considering their strong toxicity even at low concentrations [1]. Heavy metals are elements having atomic weights between 63.546 and 200.590 and a specific gravity greater than 4.0 (at least five times that of water) [2]. They exist in water in colloidal, particulate and dissolved phases [3] with their occurrence in water bodies being either of natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents etc [1]. The domestic wastewater effluents (source especially of Cr, Cu, Mn and Ni), effluents from coal-burning power plants (Hg and Se in particular), non-ferrous metal smelters (Cd, Ni, Pb), iron and steel plants (Cr, Mo, Sb and Zn) and dumping of sewage sludge (Mn and Pb) could eventually lead to metal pollution of shallow aquifers [4].

Heavy metals produce their toxicity by forming complexes with proteins, in which carboxylic acid (-COOH), amine (-NH₂), and thiol (-SH) groups are involved. These modified biological molecules lose their ability to function properly and result in the malfunction or death of the cells [2]. WHO has specified Maximum Contaminant Levels (MCL) for the presence of heavy metals in water. The most common heavy metals humans get exposed to that are very toxic to them are Cd, Pb and As; while Fe is one of the most common heavy metal found in high concentrations in the groundwater of the study area.

Cd is known to have a high toxic potential and occurs naturally in igneous rocks and some sedimentary rocks, which is generally associated with Zn ore minerals like sphalerite and with a range of Cu ore minerals [5,6]. Cd is often present in artificial fertilizers and elevated Cd levels in water have been associated with runoff from agricultural land where fertilizers are used (WHO). Cd exposure can produce kidney damage and hypertension.

Pb is a commutative poison and a possible human carcinogen. Pb is present in tap water to some extent as a result of its dissolution from natural sources. It is primarily found in drinking water from household plumbing systems in which the pipes, solder, fittings contain lead. Polyvinyl chloride (PVC) pipes also contain Pb compounds that can be leached from them and result in high Pb concentrations in drinking water (WHO). Pb may cause the development of autoimmunity in which a person's immune system attacks its

own cells. This can lead to joint diseases and ailment of the kidneys, circulatory system and neurons. At higher concentrations, Pb can cause irreversible brain damage [2].

Fe is an essential element in human nutrition. Estimates of the minimum daily requirement for Fe depend on age, sex, physiological status and iron bioavailability, and range from about 10 to 50 mg/day (WHO). However, high levels of Fe in groundwater can cause irritability in the gastrointestinal tract and can affect water's taste by enhancing the growth of iron bacteria, which is an undesirable bacterial growth within waterworks, resulting in the deposition of a slimy coating on the piping. Although Fe does not cause major health problems in humans, but excess Fe in water can stain utensils and clothes, and has aesthetic problems. In drinking-water supplies, iron(II) salts are unstable and are precipitated as insoluble iron(III) hydroxide, which settles out as a rust coloured silt. Aeration of iron-containing layers in the soil can affect the quality of groundwater if the groundwater table is lowered or nitrate leaching takes place. Dissolution of iron can occur as a result of oxidation and decrease in pH (WHO).

As is introduced into water through the dissolution of rocks, minerals and ores, from industrial effluents, including mining wastes, and via atmospheric deposition. In well oxygenated surface waters, arsenic(V) is generally the most common As species present; under reducing conditions, such as those often found in deep lake sediments or groundwater, the predominant form is arsenic(III). An increase in pH may increase the concentration of dissolved As in water [7]. It has been reported that As and Fe concentrations in groundwater gradually increase from lower depth to higher depth up to 39.4 m, and then decrease with increasing depth [8]. The acute toxicity of As compounds in humans is predominantly a function of their rate of removal from the body. Arsine is considered to be the most toxic form, followed by the arsenites (arsenic(III)), the arsenates (arsenic(V)) and organic As compounds (WHO). According to WHO, the main adverse effects reported to be associated with long-term ingestion of inorganic As by humans are cancer, skin lesions, developmental effects, cardiovascular disease, neurotoxicity and diabetes.

2. METHODOLOGY

2.1 Selection of sites and sampling

A total of 27 water samples were collected from dug wells and hand pumps from various locations of the city based on their GPS co-ordinates. The samples were collected twice in a year during the wet (June-July) and dry (January-February) seasons. Determination of some parameters is affected by sample storage and these need to be estimated immediately after collection. Pre-washed polythene bottles were used for sample collection, and the samples were then pretreated and stored following standard procedures. One part was acidified with conc. HNO₃ to pH<2 and stored at 4°C for metal analysis,

and the unacidified part was used for analyzing the dissolved anions. It is impossible to state exactly how much elapsed time may be allowed between sample collection and analysis; this depends on the character of the sample, the analysis to be made, and the conditions of storage. Changes caused by growth of microorganisms may be greatly retarded by keeping the samples in dark and at low temperature.

2.2 Sample analysis

The groundwater samples were analyzed for heavy metals following standard methods (APHA 2005) [9]. For metal estimation, the water samples have to be digested first to remove organic impurities so as to prevent interference during analysis. For this, a volume of 100 mL of each acid-preserved, well-mixed water sample was taken in a beaker, 5 mL of conc. HNO₃ was added and the mixture was slowly evaporated on a hot plate in a fume-hood to a volume of 10 – 20 mL of clear solution. The beaker walls were then washed with distilled water and the volume was remade to 100 mL in a volumetric flask. This was then used for analysis of the metals with Atomic Absorption Spectrophotometer (AAS). The heavy metals Cd, Pb, Fe and As were measured in each water sample with Atomic Absorption Spectrometry (Perkin Elmer AAnalyst 200) using air-acetylene flame. Calibration was done for each metal with certified AAS standards of 1000 mg/L (Merck, Germany). Calibration solutions for each metal ion was prepared by serial dilution of the standard stock solution. Operational conditions were adjusted in accordance with the manufacturer's guidelines to yield optimal determination. All chemicals used were of analytical grade (Merck, India).

3. RESULTS AND DISCUSSION

The calibration curves for each of the four metals were obtained using a series of varying concentrations of the standards for the four metals. Table 1 shows the levels of Cd and Pb found present in the studied water samples in wet and dry seasons, while Table 2 shows the levels of Fe and As in both seasons. Since several international organisations like WHO, USEPA, EPA, etc. have set guidelines for the presence of heavy metals in water for the protection of human health, thus heavy metals have maximum permissible levels in water as specified by these organisations called maximum contaminant level (MCL), which is the highest level of a contaminant that is allowed in a water system. The four heavy metals analysed in this study Cd, Pb, Fe and As have maximum contaminant levels of 0.003 mg/L, 0.01 mg/L, 0.3 mg/L and 0.01 mg/L respectively.

Table -1: Seasonal variation of Cd content and Pb content for wet and dry seasons:
(BDL= below detection level)

Sample No.	Cd content (mg/L)		Pb content (mg/L)	
	Wet season	Dry season	Wet season	Dry season
1	BDL	BDL	0.014	0.024
2	BDL	0.008	0.025	0.034
3	BDL	BDL	0.026	0.032
4	BDL	BDL	0.021	0.024
5	BDL	BDL	0.024	0.041
6	0.043	0.046	0.030	0.024
7	0.014	0.018	0.028	0.009
8	0.045	0.074	0.036	0.057
9	0.027	BDL	0.016	0.034
10	0.065	0.102	0.024	0.053
11	0.107	0.123	0.048	0.034
12	0.098	0.047	0.037	0.066
13	0.054	0.084	0.021	0.029
14	0.098	0.156	0.033	0.059
15	0.081	0.084	0.019	0.024
16	0.124	0.127	0.034	0.049
17	0.095	0.091	0.010	0.014
18	0.148	0.145	0.022	0.030
19	0.130	0.138	0.017	0.051
20	0.112	0.142	0.045	0.053
21	0.103	0.132	0.032	0.028
22	0.138	0.147	0.059	0.066
23	0.094	0.156	0.037	0.032
24	0.091	0.112	0.032	0.041
25	0.088	0.074	0.025	0.057
26	0.054	0.039	0.040	0.051
27	0.076	0.084	0.010	0.015

Concentrations of Cd in water are only likely to be of concern to health in environments where pH is less than 4.5 [10]. The WHO standard for Cd in drinking water is 0.003 mg/L. In the present study, the range of values for Cd content were found to be BDL - 0.148 mg/L in the wet season, and, BDL - 0.156 mg/L in the dry season. 81.48% of the samples had Cd content above MCL. The high level of Cd concentration may be due to discharge from industrial wastes or by leaching from sewage laden landfills. It is seen that the values are higher in the dry season than in the wet season with one or two exceptions. This may be due to reduction in the water volume during the long dry spell.

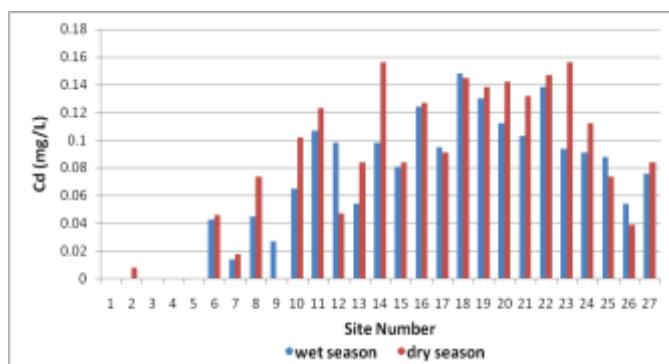


Chart -1: Cd content between wet and dry seasons

Pb is a very toxic heavy metal and a possible carcinogen, which is primarily found in drinking water from household plumbing systems. The WHO limit of Pb for drinking water is 0.01 mg/L. In the present study, Pb content was found to be in the range of 0.010 – 0.059 mg/L in the wet season, and, 0.009 – 0.066 mg/L in the dry season. Only 22.22% samples had Pb content just within MCL in the wet season, and only 7.4% within MCL in the dry season. Only one sample had Pb content below MCL in the dry season. The highest Pb content in both the seasons was observed in the site 22. Pb was present in all the aquifers in both the seasons and it is likely that its adsorption on organic and inorganic sediment surfaces [11] may have enhanced its concentration in the ground water. The low concentration of Pb in natural waters is normally ascribed to less solubility of Pb containing minerals in water, while high concentration of Pb in natural water occurs mainly through anthropogenic activities.

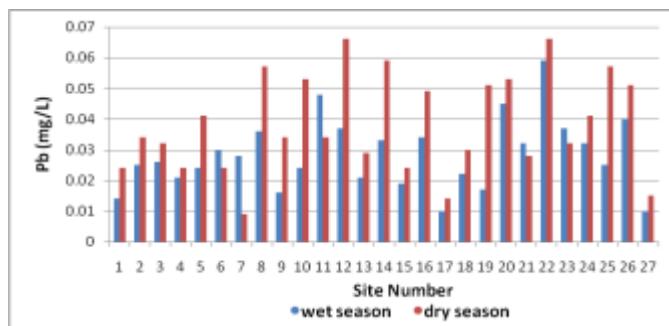


Chart -2: Pb content between wet and dry seasons

Table -2: Seasonal variation of Fe content and As content for wet and dry seasons:
(BDL= below detection level)

Sample No.	Fe content (mg/L)		As content (µg/L)	
	Wet season	Dry season	Wet season	Dry season
1	0.229	0.834	1.73	2.50
2	0.984	2.847	BDL	0.98
3	1.013	2.629	BDL	BDL
4	0.651	0.744	2.22	3.33
5	6.666	7.854	2.03	BDL
6	0.688	0.707	1.82	2.37
7	1.525	3.5	BDL	0.95
8	0.151	0.766	1.70	2.5
9	0.098	0.363	1.26	1.84
10	0.462	0.599	1.03	0.93
11	3.088	3.725	2.22	0.84
12	1.015	2.698	BDL	BDL
13	0.132	0.250	1.17	2.80
14	0.222	0.349	1.52	2.45
15	0.998	2.196	BDL	1.10
16	2.372	5.427	BDL	BDL
17	0.254	0.828	2.45	2.73
18	0.355	0.836	BDL	1.31
19	0.118	0.415	1.73	2.50
20	1.015	0.958	0.73	1.02
21	0.889	2.682	0.42	1.31
22	0.649	0.778	1.24	2.72
23	0.452	0.474	0.82	BDL
24	0.126	0.319	1.32	2.10
25	0.090	0.305	2.48	3.20
26	0.965	1.218	BDL	0.75
27	0.077	0.476	2.82	3.60

Fe is seldom found in drinking water at concentrations greater than 10 mg/L. However, as little as 0.3 mg/L can cause water to turn a reddish brown color. According to WHO, no health-based guideline value for Fe is proposed, but

the permissible limit is considered as 0.3 mg/L. Fe concentrations of 1–3 mg/L can be acceptable for people drinking anaerobic well-water. Taste is not usually noticeable at Fe concentrations below 0.3 mg/L, although turbidity and color may develop in piped systems at levels above 0.05–0.1 mg/L. Laundry and sanitary ware will stain at Fe concentrations above 0.3 mg/L. In anaerobic groundwater where Fe is in the form of Fe (II), concentrations will usually be from 0.5–10 mg/L, but values as high as 50 mg/L has also been observed (WHO).

In the present study, Fe content was found to be in the range of 0.077 – 6.666 mg/L in the wet season, and, 0.250 – 7.854 mg/L in the dry season. 62.96% samples had Fe content above the WHO permissible limit in wet season, while 92.59% had it above the limit in dry season. The highest Fe content in both the seasons was observed in the site 5. The comparably higher Fe content in the aquifers in dry season than in wet season may be due to reduction in water levels in the season.

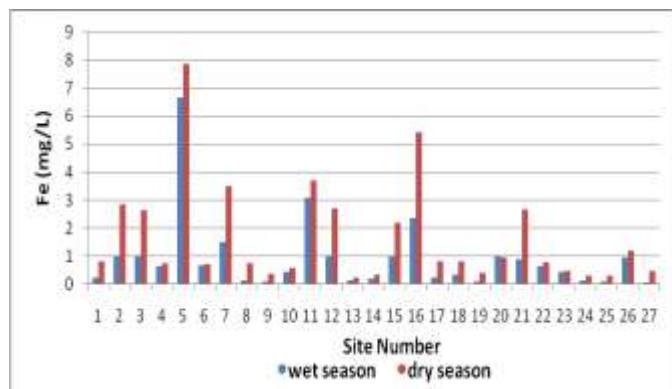


Chart -3: Fe content between wet and dry seasons

The extent to which Fe dissolves in groundwater depends on the amount of oxygen in the water. Fe can occur in two forms: as Fe^{2+} and as Fe^{3+} . When levels of dissolved oxygen in groundwater are greater, Fe occurs as Fe^{3+} , while at lower dissolved oxygen levels, Fe occurs as Fe^{2+} . Although Fe^{2+} is very soluble, Fe^{3+} will not dissolve appreciably. In the rainy season, there is an influx of oxygenated water from the surface during periods of high recharge. This oxygenated water will prevent the Fe from dissolving and the water will have low concentrations of the metal. After the oxygen in the recharge water has been consumed, Fe will again be dissolved.

In case of As, arsine is considered to be the most toxic form, followed by the arsenites (arsenic(III)), the arsenates (arsenic(V)) and organic arsenic compounds (WHO). The WHO standard for As is 0.01 mg/L or 10 $\mu\text{g}/\text{L}$. However, in some countries, most affected by As contamination, like Bangladesh, India, and Nepal, the As standard has remained at 50 $\mu\text{g}/\text{L}$ due to the technical and economic challenges associated with achieving the stringent standard [12].

In the present study, As content was found to be in the range of BDL – 2.82 mg/L in the wet season, and, BDL – 3.60 mg/L in the dry season. All the samples had As content below MCL in both seasons. The highest As content in both the seasons was observed in the site 27.

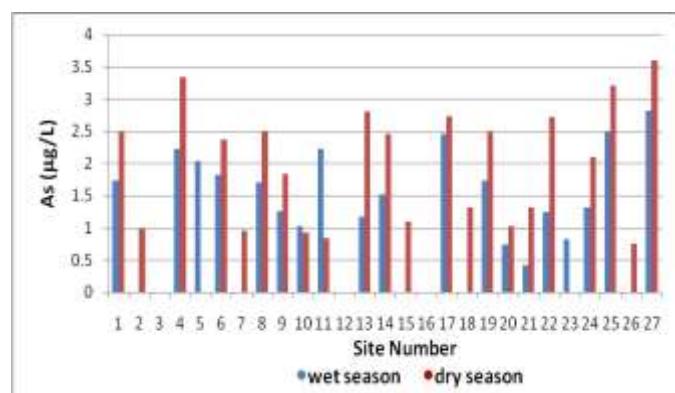


Chart -4: As content between wet and dry seasons

The aquifers in the present study are considerably rich in Fe, and this perhaps is responsible for the low values of As in the water samples. Desorption or dissolution of As from Fe oxides is sometimes considered to be the process on regional distributions of As in water [13]. The anionic, As(III) and As(V), species were not speciated in this work and it is likely that the water contains only As(V) species (in the form of arsenate) due to atmospheric oxidation of As(III), if any. When the storm water runoff percolates down, it is likely that it has accumulated as from the surrounding soil. This also explains the higher as content of some samples during the wet season.

4. CONCLUSION

The results obtained from this study show significant risk to the health of the population in the area. Out of the 81.48% samples where Cd was present, all of them had Cd content above MCL with marked variations in values in the different sites. Pb was present in all of the samples, out of which only 22.22% samples had Pb content just within MCL in the wet season, and only 7.4% within MCL in the dry season. 62.96% samples had Fe content above the permissible limit in the wet season, while 92.59% had it above the limit in the dry season, with wide variations observed among the sites in both seasons. For the samples where As was present, all of the values were found to be below MCL in both seasons.

REFERENCES

- [1] J.E. Marcovecchio, S.E. Botte and R.H. Freije, "Heavy metals, major metals, trace elements," Handbook of Water Analysis, L.M. Nollet (Ed.), 2nd Edn., 2007, pp. 275-311, CRC Press.

- [2] M.A. Momodu and C.A. Anyakora, "Heavy metal contamination of ground water: the Surulere case study," *Environmental and Earth Sciences*, vol. 2(1), 2010, pp. 39-43.
- [3] A.A. Adepoju-Bello, O.O. Ojomolade, G.A. Ayoola and H.A.B. Coker, "Quantitative analysis of some toxic metals in domestic water obtained from Lagos metropolis," *The Nig. J. Pharm*, vol. 42(1), 2009, pp. 57-60.
- [4] J.O. Nriago and J.M. Pacyna, "Quantitative assessment of worldwide contamination of air, water and soils by trace metals," *Nature*, vol. 333, 1988, pp. 134-140.
- [5] C.H. Picker, L.S. Hawkins, J.E. Pehrson and N.V. O'Connell, "Irrigation practices, herbicide use and groundwater contamination in citrus production: a case study in California," *Agric. Ecosyst. Environ.*, vol. 41(1), 1992, pp. 1-17.
- [6] C. Poggetto, N. Remy, M. Legret and P. Le Cloirec, "Heavy metal pollution of road dust and roadside soil near a major rural highway," *Environ. Tech.*, vol. 22, 2001, pp. 307-319.
- [7] W. Slooff et al., Integrated criteria document arsenic, National Institute of Public Health and Environmental Protection, Bilthoven, 1990.
- [8] T. Roychowdhury, "Groundwater arsenic contamination in one of the 107 arsenic-affected blocks in West Bengal, India: status, distribution, health effects and factors responsible for arsenic poisoning," *International Journal of Hygiene and Environmental Health*, vol. 213, 2010, pp. 414-427.
- [9] APHA, Standard Methods for the Examination of Water and Waste Water, American Public Health Association, Washington DC, 2005.
- [10] J. Nouri, A.H. Mahvi, G.R. Jahed and A.A. Babaei, "Regional distribution pattern of groundwater heavy metals resulting from agricultural activities," *Environ. Geol.*, vol. 55, 2008, pp. 1337-1343.
- [11] J. Hem, "Inorganic chemistry of lead in water: lead in the environment," U.S. Geological Survey Professional Paper, 957, 1976, pp. 5-11.
- [12] D.P. Shukla, C.S. Dubey, N.P. Singh, M. Tajbakhsh and M. Chaudhry, "Sources and controls of arsenic contamination in groundwater of Rajnandgaon and Kanker district, Chattisgarh, central India," *Journal of Hydrology*, vol. 395, 2010, pp. 49-66.
- [13] P.L. Smedley and D.G. Kinniburgh, "A review of the source, behaviour and distribution of arsenic in natural waters," *Appl. Geochem.*, vol. 17, 2002, pp. 517-568.
- [14] WHO, Guidelines for Drinking Water Quality, World Health Organization, 2011.