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DETERMINATION OF HEAVY METALS IN GROUND WATER BY USING ICP-MS IN SURROUNDING AREAS OF IDA PYDIBHEEMAVARAM,SRIKAKULAM AND VIZIANAGARAM DISTRICT, ANDHRA PRADESH, INDIA

Priyanka, G., Byragi Reddy, T., Prasada Rao, P.V.V., Ajay B. & Ch. Venkata Ramana
Department of Environmental Sciences, Andhra University, Visakhapatnam – 530 003.

ABSTRACT
A study was conducted to assess the quality of ground water surrounding IDA (Industrial development area) Pydibheemavaram. In the present study 25 ground water samples are collected from 21 villages of Srikakulam and Vizianagaram districts. The 25 samples are subjected to analysis for heavy metals like Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Ag, Cd, Ba, Pb by using ICP-MS.ICP-MS is most advanced technique for determination of heavy metal concentration up to 1part per billion(ppb). The heavy metals were found in ground water in the study area except cobalt and arsenic. The concentration of these metals were compared with drinking water quality limits given by IS: 10500 and World Health Organization (WHO),4th edition in 2011.

KEYWORDS: *Ground water, Heavy metals, IDA pydibheemavaram, ICP-MS, IS, WHO.*

INTRODUCTION

Ground water is one of the major sources of drinking water in the study area hence it was important to assess the ground water quality with respect to heavy metal contamination (Rao and Mamatha, 2004). In recent times, increasing focus is being given to studies on groundwater contamination. The water quality of borehole is generally neglected based on the general belief that it is pure through the natural purification process (Agbaire and Oyibo, 2009). Contamination of the groundwater by domestic, industrial effluents and agricultural activity is a serious problem facing by the developing countries. Importance of trace metal concentrations evidence in natural waters and/or environment is growing for the pollution monitoring studies. Traces of metal ions have important roles in a wide spectrum of functions of life. Some of these toxic trace metal levels are high, such as poisoning by Fe, Pb and Ni affects the central nervous system. Heavy metals presence in nature usually is not dangerous for the environment because they are present only in very small quantities (Stihi *et al*., 2001). Heavy metals are pollutants in the environment only if it's present in large quantities (this fact is usually attributed to industrial activities) (Voica, 2012). Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Storelli, 2014). The known fatal effects of heavy metal toxicity in drinking water include damaged or reduced mental and central nervous function and lower energy level. The industrial waste water, sewage sludge and solid waste materials are currently being discharged into the environment indiscriminately. These materials enter subsurface aquifers, resulting in the pollution of irrigation and drinking water (Forstner and Wittman,, 1981). Potentially toxic metals resulting from anthropogenic activities cause severe disturbance of ecosystems (Martorell *et al.*, 2009; Abdallah, 2008). It is necessary to preserve the quality of the environment mainly throughout reducing negative effects of human activities.

Study Area

Pydibhimavaram is a village located in Ranastalam mandal in Srikakulam district, Andhra Pradesh, India (shown in Figure. 1). The study area covers 21 villages of Srikakulam and Vizianagaram districts around industrial development area (IDA) of pydibheemavaram. The public in these villages using ground water for drinking and house hold purpose. There might be chances to get contamination of ground water with different elements and ions at higher concentration levels.

MATERIALS & METHODS

In this present study an attempt has been made to evaluate the concentration levels of heavy metals in ground water in surrounding villages of IDA, pydibheemavaram, Srikakulam district, Andhra Pradesh using inductively coupled plasma mass spectrometry (ICP-MS). A number of sophisticated instruments (like ICP-MS, ICP-OES, AAS, UV-VIS spectrometer, cyclic voltammetry, *etc*.) were used for the determination of heavy metals in the water. The most effective technique for the determination of trace level contamination of heavy metals in water is ICP-MS and GFAAS. ICP-MS is a type of mass spectrometry based on coupling together inductively coupled plasma as a method of producing ions (ionizations) with a mass spectrometer as a method of separating and detecting ions. It is highly sensitive and can determine up to 0.1µg/L.

Sample Collection

25 samples were collected in the above said 21 villages by following Indian standards method IS: 3025(Part-1) and American Public Health Association (APHA) 22nd edition (APHA, 2005) (Shown in table. 1). 1 litre polythene bottles were used for water quality parameter analysis and all bottles were washed with dilute acid followed by

distilled water and were dried. At each sampling location, water samples were collected in two poly ethylene bottles. Before taking final water samples, the bottles were rinsed three times with the water to be collected. 100ml of sample is collected for heavy and toxic metal analysis and the sample is acidified with 0.5ml of Con. HNO_3 to prevent the loss of metals.

Analytical Methodology

Trace metals were analysed using ICP-MS (Agilent 7700) standard reference material of 1000mg/L (Multi elements-Merk) (Shown in table 2). Different concentration standards are prepared 0.001mg/L to 0.5mg/. Before doing sampling analysis different concentrations of standards were analysed and prepared linear curve. All the metals having good linear graph with correlation coefficient of >0.999 is observed in standard curves preparation.

RESULTS & DISCUSSION

ICP-MS is the most widely using technique for the determination of trace metals up to parts per billion levels. ICP-MS is very useful technique to determine trace levels of multi elements in single aspiration. The quantity of 14 metals (Aluminium, Chromium, Manganese, Ferrous, Nickle, Copper, Zinc, Arsenic, Silver, Cadmium, Lead, Barium, Cobalt, Strontium) observed in 25 sampling locations around IDA pydibheemavaram, Srikakulam district has been summarized in Table-3 and the results are discussed below. Aluminium concentrations vary from 0.0785 mg/L to 1.2490mg/L in the overall study areas. The maximum concentration of aluminium has been observed at Akkayyapalem (2) village. The maximum acceptable limit for aluminium as per IS: 10500 is 0.2mg/L and as per World Health Organization is 0.9mg/L. The observed concentration levels of aluminium in the study area are above the permissible limits of IS: 10500. However the observed concentration levels of aluminium observed within the acceptable limits of WHO guidelines except Akkayyapalem (2) village.

Chromium concentrations vary from 0.001mg/L to 0.054mg/L. The maximum concentration of chromium observed at Boyapalem village. The permissible limit for chromium as per IS: 10500 and WHO is 0.05mg/L. However the observed concentration of chromium is within the acceptable and permissible limits of IS: 10500 and WHO guidelines except Boyapalem village. Manganese concentrations vary from 0.0638mg/L to 0.8265mg/L. The maximum concentration of manganese observed at Alladapalem. The maximum acceptable limit for manganese as per IS: 10500 and WHO is 0.1mg/L. However the observed concentration levels of manganese is above the acceptable limit given by IS: 10500 and WHO except Akkayyapalem and Mukkupalavalsa.

Ferrous concentrations vary from 0.1738mg/L to 18.8092mg/L. The maximum concentration of ferrous observed at Kanimella. The maximum acceptable limit for ferrous as per IS: 10500 and WHO is 0.3mg/L. However the observed concentration levels of ferrous is above the acceptable limit in the study area given by IS: 10500 and WHO except Mukkupalavalasa, Akkayyapalem (1), Pydibheemavaram (1).

Cobalt concentration varies from 0.0002mg/L to 0.008mg/L. The maximum concentration of cobalt observed at Mentada. The maximum acceptable limit for ferrous as per IS: 10500 and WHO is 0.08mg/L. However the observed concentration levels of cobalt is within the acceptable limit in the study area given by IS: 10500 and WHO.

Nickle concentration varies from 0.003mg/L to 0.072mg/L. The maximum concentration of cobalt observed at Boyapalem. The maximum acceptable limit for nickel as per IS: 10500 and WHO is 0.02mg/L and 0.07mg/L. The observed concentration levels are above the permissible limits given by IS: 10500 in Naruva, Akkayyapalem (2), Mentada, Surampeta, Alladapalem, Devunipalavalasa (2), Kamavaram and Kanimella. However the observed concentration levels are within the permissible limits given by WHO except Boyapalem.

Copper concentration varies from 0.08685mg/L to 3.4035mg/L. The maximum concentration of copper observed at Devunipalavalasa (1).The maximum acceptable limit for copper as per IS: 10500 and WHO is 0.05mg/L and 2mg/L. In all villages the observed concentration levels are above the permissible limits given by IS: 10500.

Zinc concentrations vary from 1.6239mg/L to 20.8073mg/L. The maximum concentration of zinc observed at Peddatharimi. The maximum acceptable limit for zinc as per IS: 10500 is 5mg/L and permissible limit is 15mg/L and no guideline value given by WHO. However the observed concentration levels of zinc observed within the permissible limits of IS: 10500 except Peddatharimi.

Arsenic concentrations vary from 0.001mg/L to 0.0046mg/L. The maximum concentration of arsenic observed at Vommi. The maximum acceptable limit for arsenic as per IS: 10500 and WHO is 0.05mg/L and 0.01mg/L. However the observed concentration levels of arsenic observed within the permissible limits given by IS: 10500 and WHO.

Strontium concentrations vary from 0.0155mg/L to 10.532mg/L. The maximum concentration of strontium observed at devunipalavalasa. No guideline value given by IS: 10500 and WHO.

Silver concentrations vary from 0.004mg/L to 2.3841mg/L. The maximum concentration of silver observed at Saragudapeta. The maximum acceptable limit for silver as per IS: 10500 and WHO is 0.1mg/L and 0.05mg/L. However the observed concentration levels of silver observed within the permissible limits of IS: 10500 and WHO except Saragudapeta. Cadmium concentrations vary from 0.0018mg/L to 0.0348mg/L. The maximum concentration of cadmium observed at Boyapalem. The maximum acceptable limit as per IS: 10500 and WHO is 0.003mg/L. However the observed concentration levels are above permissible limits given by IS: 10500 and WHO except in Akkayyapalem (1), Alladapalem, Mukkupalavalsa, Vommi, Sathivada. Barium concentrations vary from 0.1735mg/L to 1.7004mg/L. The maximum concentration of barium observed at Naruva. The maximum acceptable limit as per IS: 10500 and WHO is 0.7mg/L. However the observed concentration levels are above the permissible limits in pydibheemavaram (1), Peddatharimi, Boyapalem, Vommi, Malayada, Patharapalli, Sathivada, Surampeta, Kamavaram.

Lead concentrations vary from 6.0997mg/L to 8.4344mg/L. The maximum concentration of lead observed at saragudapeta. The maximum acceptable limit

as per IS: 10500 and WHO is 0.01mg/L. However the observed concentration levels are above the permissible limits in all villages.

TABLE 1: Details of Sampling Locations

Location Code	Location Name	Location Code	Location Name
GW-1	Pydibheemavaram	GW-14	Alladapalem
GW-2	Saragadapeta	GW-15	Mukkupalavalasa
GW-3	Boyapalem	GW-16	Devunipalavalasa
GW-4	Naruva	GW-17	Devunipalavalasa
GW-5	Akkayyapalem	GW-18	Kamavaram
GW-6	Akkayyapalem	GW-19	Kanimella
GW-7	Mentada	GW-20	Malyada
GW-8	Surampeta	GW-21	Vommi
GW-9	Patharapalli	GW-22	Sathivada
GW-10	Patharapalli	GW-23	Venkannapalem
GW-11	Varisam	GW-24	Peddatharimi
GW-12	Pydibheemavaram	GW-25	Boddapeta
GW-13	Sancham	----	

TABLE 2: ICP-MS operating conditions

Rf power	1500w	Aspiration rate	1mL/min
Carrier air flow	1L/min	Acquisition mode	Analytical
Plasma air flow	15L/min	Dwell time	0.01sec/element
Auxilliary air flow	1L/min	Replicates	3
Nebulizer	concentric	NIST 1643e	natural water
Spray chamber	Scott double pass		

CONCLUSION

Ground water is one of the major important drinking water sources in throughout the world. Ground water is the major drinking source in villages. Contamination of ground water by heavy metals causes several short term and long term health effects to the human beings. ICP-MS is the most widely used technique for determination of heavy metals in trace levels. The present study is focused on determination of 14 metals like Aluminium(Al), Chromium (Cr), Manganese (Mn), Ferrous (Fe), Cobalt (Co), Nickle (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Strontium (Sr), Silver (Ag), Cadmium (Cd), Barium (Ba), Lead (Pb) in IDA pydibheemavaram surrounding villages of Srikakulam and Vizianagaram districts. For this study 25 ground samples were collected and analysed using ICP-MS. The minimum and maximum concentration levels of these 14 metals are discussed in results and discussion. Except Cobalt and Arsenic all heavy metals are above the permissible limits given by IS: 10500 and WHO limits for drinking water in the study area. Excess presence of these heavy metals causes several health problems; hence the study should suggest that Government should adopt controlling and treatment technologies to minimize heavy metal contamination of Ground water to provide safe and pure drinking water to the villages.

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TABLE 3: heavy metal parameters ICP-MS results for ground water

S.No.	Name of Location	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Ag	Cd	Ba	Pd
1	Pydibheemavaram(1)	0.0785	0.0106	0.1019	0.2757	0.0006	0.0137	0.9907	1.6864	0.0019	9.6091	0.0222	0.0181	1.3457	6.0997
2	Saragadapeta	0.2161	0.0074	0.1657	0.6573	0.0013	0.0074	1.5000	3.5257	0.0011	0.0155	2.3841	0.0054	0.000	8.4344
3	Boyapalem	0.7061	0.0540	0.2785	1.3551	0.0019	0.0729	1.7401	3.3298	0.0022	3.7812	0.0342	0.0348	1.2074	6.8805
4	Naruva	0.8309	0.0141	0.2115	3.7716	0.0015	0.0544	1.3278	6.0218	0.0019	5.3881	0.0099	0.0055	1.7004	7.0084
5	Akkayyapalem(1)	0.00	0.0075	0.0638	0.1738	0.0002	0.0078	0.9289	1.6638	0.001	0.8581	0.0043	0.0018	0.1735	7.6444
6	Akkayyapalem(2)	1.2490	0.0113	0.2594	2.2834	0.0014	0.0248	1.3432	2.4602	0.0022	3.5596	0.0059	0.0040	0.5799	7.7454
7	Mentada	0.1853	0.0161	0.3019	3.7179	0.008	0.02155	1.1124	4.0459	0.0019	2.4497	0.0291	0.0321	0.28065	6.7963
8	Surampeta	0.4159	0.0218	0.3845	0.8169	0.0013	0.0366	1.5953	2.8306	0.0017	1.9582	0.0323	0.0176	0.7372	6.9017
9	Patharapalli(1)	0.8268	0.0118	0.1715	1.5155	0.0012	0.0199	1.3499	2.3418	0.0014	3.7173	0.0117	0.0036	0.7854	7.4503
10	Patharapalli(2)	0.2467	0.0066	0.1852	2.5240	0.0008	0.0099	1.4809	2.6495	0.0011	1.7117	0.0130	0.0029	0.2843	7.7281
11	Varisam	0.5916	0.0056	0.1354	0.8710	0.0009	0.0073	1.2623	2.3852	0.0009	3.9156	0.0057	0.0029	0.5966	7.6221
12	Pydibheemavaram(2)	0.7231	0.0088	0.5521	2.2074	0.0019	0.0178	1.4708	2.5854	0.0013	2.4079	0.0071	0.0041	0.4564	7.8143
13	Sancham	0.1027	0.0036	0.4345	1.5644	0.0016	0.0171	0.9601	7.5219	0.0011	2.8497	0.0054	0.0035	0.2862	7.4950
14	Alladapalem	0.5197	0.0084	0.8265	6.3311	0.0027	0.0219	1.280	2.737	0.0016	3.5044	0.0049	0.00	0.00	7.62
15	Mukkupalavalasa	0.00	0.0030	0.0864	0.2097	0.0002	0.0039	0.8618	1.6239	0.001	1.8046	0.010	0.0023	0.2621	6.7830
16	Devunipalavalasa(1)	0.5845	0.0247	0.4529	12.7292	0.0027	0.04815	3.4035	4.0782	0.0034	10.532	0.0124	0.0140	0.5150	6.8389
17	Devunipalavalasa(2)	0.5622	0.0117	0.3282	1.8902	0.0011	0.0224	0.8685	2.1614	0.0026	5.1940	0.0085	0.0178	0.5791	6.7802
18	Kamavaram	0.7839	0.01755	0.3255	10.4402	0.0014	0.0204	1.3952	5.160	0.0016	1.8438	0.0106	0.0112	0.6082	7.6039
19	Kanimella	0.6652	0.0128	0.3200	18.8098	0.0011	0.0221	1.5349	2.5437	0.0019	3.4450	0.01075	0.0064	0.7026	7.1280
20	Malayada	0.3765	0.0148	0.2770	2.6754	0.0021	0.0157	1.2051	2.4750	0.0033	10.0676	0.0100	0.0054	0.9857	6.9291
21	Vommi	0.2289	0.0159	0.1287	1.7424	0.0009	0.0086	1.5335	2.7624	0.0046	1.9537	0.0054	0.0025	1.0715	7.8972
22	Sathivada	0.2543	0.0053	0.1129	1.3208	0.0000	0.0061	1.4798	2.5862	0.0014	3.8774	0.0061	0.0020	0.7502	8.0213
23	Venkannapalem	0.00	0.0012	0.1706	1.2518	0.0016	0.0031	0.9532	1.7407	0.0014	2.9068	0.0095	0.0031	0.2893	7.1902
24	Peddatharimi	0.5162	0.0124	0.5506	6.6588	0.0025	0.0319	1.5401	20.8073	0.0019	4.5974	0.0111	0.0063	1.3369	7.4190
25	Boddapeta	0.3030	0.0116	0.1904	6.3545	0.00	0.0130	1.4084	2.1643	0.0012	2.157	0.0084	0.0057	0.5872	8.2824

Note: All parameters are expressed in mg/l

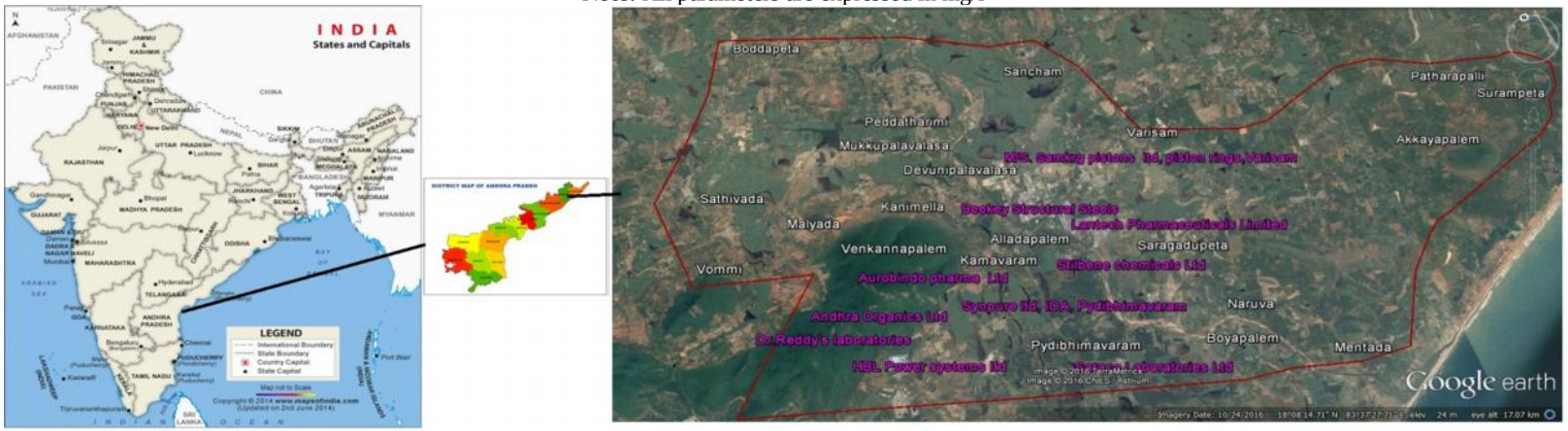

FIGURE 1: Showing study area with sampling locations