Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

Research Paper

Determination of Heavy Metals in Ground Water by Icp-MS in Selected Coastal Areas of Spsr Nellore District, Andhra Pradesh, India

Chemistry

KEYWORDS : Ground Water– Heavy Metals – Coastal areas of SPSR Nellore – ICP-MS - WHO/IS

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ABSTRACT

Water Quality is one of the most important concern of the world. Ground water is one of the major drinking water sources in throughout the world. Owing the mineralogical background of the area there might be chances to have higher concentration levels of some of dissolved heavy metals in ground water. By ingestion of ground water as a drinking water with excess concentration levels of dissolved heavy metals may cause various short term and long term health effects to the human being. Determination of heavy metals up to trace levels with high accuracy and precision is one of the most important concern of the analytical methodology. Number of techniques (like ICP-MS, ICP-OES, AAS, Cyclic Voltammetery and UV-Visible Spectrophotometer) is employed for the determination of heavy metals in water. Inductively Coupled Plasma- Mass Spectrometer (ICP-MS) is one of the most sensitive and universally using techniques for determination of heavy metal up to trace levels. In this present study an attempt has been made to know the concentration of eight heavy metals in ground water of Coastal areas of SPSR Nellore District, Andhra Pradesh. For this study 35 villages are selected in coastal areas of SPSR Nellore district and ground water samples are collected in the selected villages in which the public are using for drinking purpose and subjected to analysis for eight heavy metals like Arsenic (As), Nickel (Ni), Chromium (Cr), Lead (Pb), Cobalt (Co), Selenium (Se), Mercury (Hg) and Cadmium (Cd) by using (ICP-MS). The minimum and maximum concentration levels of these eight heavy metals are summarized and discussed in the results and discussion and the concentrations of these eight heavy metal levels in the study area were compared with drinking water quality standards given by the Indian Standards (IS : 10500) and World Health Organization (WHO), 4th edition in 2011.

INTRODUCTION:

Ground Water is the most important resource for mankind existence and economical development. People around the world have been using groundwater as a source of drinking water, and even today more than half the world's population depends on groundwater for survival [1]. In India, due to the scarcity of surface water in many regions, ground water is becoming an important source of drinking water supply [2]. The overexploitation of ground water resources and discharge of untreated effluents induces degradation of ground water quality. Heavy metals enter in ground water from variety of sources and it can either be natural or anthropogenic [3-4].

Ground water forms a major source of drinking water. In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization. Human health is threatened by most of the agricultural development activities particularly in relation to excessive application of fertilizers and unsanitary conditions. Rapid urbanization especially in developing countries like India, has affected the availability and quality of ground water due to its overexploitation and improper waste disposal, especially in urban areas [5]. According to WHO (2004) about 80% of the diseases in human beings are caused by polluted water. As the water is the most important component of eco–system, any imbalance created either in terms of amount or the presence of impurities added to it can harm the whole eco–system [6].

Owing the mineralogical background of the area there might be chances to have higher concentration levels of some of dissolved metals in ground water. By taking of ground water as a drinking water with excess concentration levels of dissolved metals may cause serious health problems. The contamination of water is directly related to the water pollution. Many dangerous chemical elements released into the environment accumulate in the soil and sediments of water bodies [7]. Heavy metals enter the environment by natural and anthropogenic means. Such sources include: natural weathering of the earth's crust, mining, soil erosion, industrial discharge, urban runoff, sewage effluents and pest or disease control agents applied to plants, air pollution fallout, and a number of others [8].

Heavy metal toxicity is potentially dangerous because of bioaccumulation through the food chain and this can cause hazardous effects on livestock and human health [9]. Increased urbanization and industrialization are to be blamed for an increased level of trace metals, especially heavy metals, in our waterways [10]. There are over 50 elements that can be classified as heavy metals, 17 of which are considered to be very toxic and relatively accessible. Characteristically, also the anions have its important role in drinking water results also showed affecting the human health [11]. Toxicity level depends on the type of metal, its biological role and the type of organisms that are exposed to it.

Heavy metals have a marked effect on the aquatic flora &fauna which through biomagnifications enters the food chain and ultimately affect the human beings as well [12]. The heavy metals in drinking water linked most often to human poisoning are lead, iron, cadmium copper, zinc, chromium etc .They are required by the body in small amounts , but can also be toxic in large doses. They constitute one important group of environmentally hazardous substances if present. Usually in unaffected environments the concentration of most of the metals is very low and is mostly determined by the mineralogy and the weathering of that area [13-14].

Heavy metals like copper are the essential trace elements but show toxicity if in excess amounts in drinking water. Cadmium is extremely toxic even in low concentrations, and will bio-accumulate in organisms and ecosystems and it has a long biological half –life in the human body, ranging from 10 to 33years. Long term exposures to Cadmium also induces renal damage .So cadmium is considered as one of the priority pollutants form monitoring in most countries and international organizations.

Heavy metals have also gained much attention, since they are non–degradable persist in nature for a long period, toxic to living organisms at fairly low concentrations and tend to either biologically magnify or accumulate in plants or animal system [15]. A number of metallic ions cause metabolic disturbances in man by upsetting the production and function of certain enzymes, or to cause a variety of other toxic effects [16]. Lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are widely dispersed in the environment. These elements have no beneficial

Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

effects in humans, and there is no known homeostasis mechanism for them [17-18].

There needs to continuously assess the quality of ground and surface water sources [19]. The known fatal effects of heavy metal toxicity in drinking water include damaged or reduced mental and central nervous function and lower energy level. They also cause irregularity in blood composition, badly effect vital organs such as kidneys and liver. [20].

SPSR Nellore District, the Southernmost Coastal District of Andhra Pradesh lies between 13-30' and 15-6' of the Northern latitude and 70-5' and 80-15' of the Eastern Longitude and extending over an area of 13076 Sq.Kms, accounting for 4.75% of the total area of the state. Historically, the place has very importance. Culturally, Nellore city stands unique among the other towns of Andhra Pradesh as it is supposed to be the place where the greatest of the Telugu poets, Tikkana Somayaji, who translated the major part of Mahabharata into Telugu, lived. SPSR Nellore also has strategic commercial importance as it lies between the cities of Vijayawada and Chennai. SPSR Nellore district is famous for paddy which remarked as "Nellore Molagoluku".

In most of the villages of SPSR Nellore district the public is 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. In this present study an attempt has been made to evaluate the concentration levels of eight heavy metals in ground water in coastal surrounding villages of SPSR Nellore district, Andhra Pradesh using Inductively Coupled Plasma – Mass Spectrometer (ICP-MS).

A number of sophisticated instruments (like ICP-MS, ICP-OES, AAS, UV-VIS spectrometer, Cyclic Voltammetry, etc.) are using for the determination of heavy metals in water. Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) is one of the most widely and universally using technique for the determination of metals contaminants in water up to parts per billion (ppb) levels. By using ICP-MS, we can determine up to 0.1µg/L of metal concentration in water.

MATERIALS AND METHODS:

SAMPLE COLLECTION:

The ground water samples are collected by following of standard sample collection protocol and guidelines given in Indian Standards methods IS: 3025 part-1 and American Public Health Association (APHA) 22nd edition. Special precautions were taken during the collection of samples. Before collecting the samples, the sample containers are soaked overnight in 2% nitric acid and washed with double distilled water and dried in clean metal free area. At each sampling location, water samples were collected in two pre-cleaned containers for duplicate measurement. The bottles were rinsed three times with the ground water sample of the particular location and collected the final sample to avoid the contamination and 0.5 ml of Supra pure grade nitric acid is added to acidify the samples and also to prevent the loss of metals. All the collected ground water samples are preserved at $4^{O}C$ by using thermo-coal box with ice packs. The details of sampling locations have been summarized in **Table -1.**

DETAILS OF SAMPLING LOCATIONS:

TABLE -1

LOCATION CODE	LOCATION NAME	LOCATION CODE	LOCATION NAME
GW- 1	SULLURUPETA	GW- 19	JUVVALAPALEM
GW- 2	SRIHARIKOTA	GW-20	THUMMALAPENTA
GW- 3	MEEZURU	GW-21	RAMAYAPATNAM
GW- 4	KATTUVAPALLE	GW-22	AMUDALA PADU
GW- 5	KUMMARIPALLEM	GW-23	NELATURU CHERUVU
GW- 6	ELLORE	GW-24	PYNAPURAM
GW- 7	KOGILI	GW-25	KRISHNAPATNAM
GW- 8	JALAPEDDIPALEM	GW-26	NIDIGUNTAPALEM
GW- 9	MALLAM	GW- 27	MOLLURU
GW-10	VAKADU	GW-28	KAPPALATHERUVU
GW-11	SIDDAVARAM	GW-29	BRAHMADEVAM
GW-12	VENKANNAPALLEM	GW-30	MUTTUKURU
GW-13	GOVINDAPALLI	GW-31	EPURE
GW-14	MOMIDI	GW-32	VARAKAVIPUDI
GW-15	PUDIPARTHI	GW-33	PEDDAMAMBATTU
GW-16	INDUPURU	GW-34	KONDURU
GW-17	ALLURU	GW-35	GOPALAREDDIPALEM
GW-18	KOTHAPALEM		

ANALYTICAL METHODOLOGY:

Eight heavy metals were analyzed by direct aspiration of ground water samples in to Inductively Coupled Plasma – Mass Spectrometer (Agilent 7500) system and quantified against by Certified Reference Material (Multi elements-Merck). Five different linear concentration standards were prepared, ranging from 1.0 µg/L to 500 µg/L and aspirated into ICP-MS system before conducting sample analysis, and linear curve was prepared. All metals having good linear graph with correlation coefficient > 0.999 were observed in the preparation of standard curves. After the completion of standard curve preparation, one standard check and one QC check are analyzed.

SPIKE RECOVERY:

One Spiked sample is analyzed for every 10 sample study and recovery of spiked concentration has been studies. The spike recoveries are observed minimum of 85% for all metals. Hence the method is rugged to carry-out the ground water sample analysis for determination of metals by ICP-MS.

RESULTS AND DISCUSSION:

ICP-MS is the most widely using technique for the determination of heavy metals upto parts per billion levels. ICP-MS is very useful technique to determine trace levels of multielements in single aspiration.

The quantity of eight heavy metals (Arsenic, Nickel, Chromium, Lead, Cobalt, Selenium, Mercury and Cadmium) observed in the 35 village areas of coastal areas of SPSR Nellore district has been summarized in **Table -2** and the results are discussed below.

TABLE -2

S.NO	GROUND WATER	NAME OF LOCATION	Cr	Co	Ni	As	Se	Cd	Pb	Hg
	UNIT		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
1	GW-1	SULLURUPETA	1.8	<1.0	3.1	<1.0	6.8	<1.0	<1.0	0.9
2	GW-2	SRIHARIKOTA	<1.0	<1.0	1.3	2.2	1	<1.0	<1.0	0.5
3	GW-3	MEEZURU	<1.0	<1.0	1.0	<1.0	<1.0	2.2	27.5	0.4
4	GW-4	KATTUVAPALLE	<1.0	<1.0	1.0	<1.0	<1.0	2.1	9.8	0.4
5	GW-5	KUMMARIPALLEM	<1.0	<1.0	<1.0	2.6	2.4	<1.0	1.0	0.4

6	GW-6	ELLORE	2.5	3.2	5.8	4.2	4.1	1.9	9.9	0.2
7	GW-7	KOGILI	<1.0	<1.0	<1.0	3.1	2.4	<1.0	<1.0	0.4
8	GW-8	JALAPEDDIPALEM	<1.0	22.6	18.6	5.5	6.8	1.9	1.8	0.1
9	GW-9	MALLAM	<1.0	39.9	53	8.6	10.9	1.8	3.1	0.4
10	GW-10	VAKADU	<1.0	<1.0	<1.0	1.2	2.0	<1.0	<1.0	0.3
11	GW-11	SIDDAVARAM	<1.0	2.1	8.2	<1.0	8.1	<1.0	<1.0	0.2
12	GW-12	VENKANNAPALLEM	<1.0	1.7	5.1	<1.0	15.9	<1.0	<1.0	0.3
13	GW-13	GOVINDAPALLI	<1.0	<1.0	5.1	2.1	3.4	<1.0	<1.0	0.3
14	GW-14	MOMIDI	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	2.5	0.2
15	GW-15	PUDIPARTHI	3.7	2.8	5.8	2.2	<1.0	1.8	3.2	0.1
16	GW-16	INDUPURU	3.2	2.2	1.9	<1.0	<1.0	<1.0	8.1	0.1
17	GW-17	ALLURU	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	0.2
18	GW-18	KOTHAPALEM	3.1	2.2	5.4	<1.0	<1.0	<1.0	8.8	0.2
19	GW-19	JUVVALAPALEM	2.2	3.8	8.8	<1.0	1.0	<1.0	<1.0	0.1
20	GW-20	THUMMALAPENTA	<1.0	<1.0	<1.0	9.2	1.0	<1.0	<1.0	0.3
21	GW-21	RAMAYAPATNAM	6.9	5.2	8.8	5.1	2.2	<1.0	9.6	0.1
22	GW-22	AMUDALA PADU	<1.0	<1.0	<1.0	1.0	<1.0	<1.0	<1.0	0.3
23	GW-23	NELATURU CHERUVU	<1.0	<1.0	<1.0	1.9	1.4	<1.0	<1.0	0.2
24	GW-24	PYNAPURAM	4.1	3.2	4.1	2.8	1.5	<1.0	<1.0	0.1
25	GW-25	KRISHNAPATNAM	<1.0	<1.0	<1.0	1.8	1.5	<1.0	<1.0	0.1
26	GW-26	NIDIGUNTAPALEM	2.9	4.8	8.8	<1.0	<1.0	<1.0	<1.0	0.2
27	GW-27	MOLLURU	4.6	5.2	6.9	<1.0	<1.0	<1.0	<1.0	0.1
28	GW-28	KAPPALATHERUVU	<1.0	<1.0	<1.0	1.7	1.1	<1.0	<1.0	0.1
29	GW-29	BRAHMADEVAM	<1.0	<1.0	1.0	2.0	1.4	<1.0	<1.0	0.1
30	GW-30	MUTTUKURU	<1.0	<1.0	<1.0	1.7	1.3	<1.0	<1.0	<0.1
31	GW-31	EPURE	<1.0	<1.0	1.0	2.0	1.1	<1.0	<1.0	0.1
32	GW-32	VARAKAVIPUDI	<1.0	<1.0	<1.0	2.4	1.0	<1.0	<1.0	0.1
33	GW-33	PEDDAMAMBATTU	5.2	6.8	3.5	2.9	3.8	<1.0	<1.0	0.1
34	GW-34	KONDURU	4.9	3.3	7.1	1.8	<1.0	<1.0	<1.0	0.1
35	GW-35	GOPALAREDDIPALEM	5.9	4.8	3.3	<1.0	3.2	<1.0	<1.0	0.1

Arsenic concentrations vary from <1.0 µg/L to 9.2 µg/L in the overall study areas. The maximum concentration of Arsenic has been observed at Thummalapenta village. The maximum acceptable limit for arsenic as per IS: 10500 and World Health Organization is 10 µg/L. The observed concentration levels of arsenic in the study area are within the permissible limits of IS: 10500 and WHO guidelines.

Nickel concentrations vary from <1.0 µg/L to 53.0 µg/L in the overall study areas. The maximum concentration of Nickel has been observed at mallam village. The maximum acceptable limit for Nickel as per IS: 10500 is 20 µg/L and maximum acceptable limit as per World Health Organization is 70 µg/L. The observed concentration levels of nickel in the study area are within the permissible limits of IS: 10500 except mallam village and within the guide line value given in WHO guidelines.

Chromium concentrations vary from <1.0 µg/L to 6.9 µg/L in the overall study areas. The maximum concentration of chromium has been observed at ramayapatnam village. The maximum acceptable limit for chromium as per IS: 10500 is 50 µg/L and maximum acceptable limit as per World Health Organization is 70 µg/L. However the observed concentration levels of chromium are observed within the permissible limits of IS: 10500 and WHO guidelines.

Cobalt concentrations vary from <1.0 µg/L to 39.9 µg/L in the overall study areas. The maximum concentration of cobalt has been observed at mallam village. The maximum acceptable limit for cobalt as per IS: 10500 is 50 µg/L and maximum acceptable limit as per World Health Organization is 70 µg/L.

Selenium concentrations vary from <1.0 µg/L to 15.9 µg/L in the overall study areas. The maximum concentration of selenium has been observed at venkannapallem village. The maximum acceptable limit for selenium as per IS: 10500 is 10 µg/L and provisional guideline value as per World Health Organization is 40 µg/L. The observed concentration levels of selenium in the study area are within the permissible limits of IS: 10500 except venkannapallem village and however the concentration levels of selenium in the study area are within the limits of provisional guideline value given by WHO guidelines.

Cadmium concentrations vary from <1.0 µg/L to 2.2 µg/L in the overall study areas. The maximum concentration of cadmium has been observed at meezuru village. The maximum accept-

able limit for cadmium as per IS : 10500 and WHO guidelines is 3.0 µg/L However the observed concentration levels of cadmium in the study area are within the permissible limits specified in the IS: 10500 and WHO guidelines.

Lead concentrations vary from <1.0 µg/L to 27.5 µg/L in the overall study areas. The maximum concentration of Lead has been observed at meezuru village. The maximum acceptable limit for Lead as per IS: 10500 and WHO guidelines is 10.0 µg/L. However the observed concentration levels of Lead in the study area are within the permissible limits specified in the IS: 10500 and WHO guidelines except meezuru village.

Mercury concentrations vary from <0.1 µg/L to 0.9 µg/L in the overall study areas. The maximum concentration of Mercury has been observed at Sullurupeta village. The maximum acceptable limit for Mercury as per IS: 10500 is 1.0 µg/L and WHO guidelines are 6.0 µg/L. However the observed concentration levels of Mercury in the study area are within the permissible limits specified in the IS: 10500 and WHO guidelines.

CONCLUSION:

Ground water is one of the major important drinking water sources in throughout the world. Especially in most of the village areas the public are using ground water for drinking purpose. Heavy metals are most considerable contaminants in ground water. Excess levels of heavy metals might cause several short term and long term health effects to the human beings. Determination of these heavy metals with high accuracy and precision at trace levels is one of the major challenges in analytical chemistry. ICP-MS is one of the most widely and universally using technique for determination of heavy metals upto trace levels. The present study is focussed on determination of eight heavy metals like Arsenic (As), Nickel (Ni), Chromium (Cr), Lead (Pb), Cobalt (Co), Selenium (Se), Mercury (Hg) and Cadmium (Cd) in coastal surrounding villages of SPSR Nellore district. For this study 35 ground water samples are collected and subjected to analyze for As, Ni, Cr, Pb, Co, Se, Hg and Cd by using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) technique. The minimum and maximum concentration levels of these eight heavy metals are summarized and discussed in the results and discussion concentrations of these eight heavy metal levels in the study area were compared with drinking water quality standards given by the Indian Standards (IS : 10500) and World Health Organization (WHO), 4th edition in 2011. In the overall study area the concentration levels of Arsenic in Thummalapenta, Nickel in mallam village, selenium in venkannapallem, Lead in meezuru villages are observed higher levels acceptable limits of IS : 10500. However the concentration levels of these eight heavy metals observed within the permissible limits of IS: 10500 and WHO guidelines.

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