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# Determination of heavy metals in surface and groundwater in and around Tirupati, Chittoor (Di), Andhra Pradesh, India

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**ABSTRACT**

*Water Quality is one of the most important concerns. The heavy metals levels up to ppb levels in drinking water quality may cause seviour health problems and also cause cancer. In this study we made an attempt to know the concentration of eight heavy metals in ground water and surface water in different locations of Tirupati, Chittoor District, Andhra Pradesh up to ppb levels. For this study 10 water samples (both ground water samples and surface water samples) were collected in February 2012 and preserved by adding of 2-3 drops of nitric acid. These samples were subjected to analysis for eight elements like As, Ni, Cr, Pb, Co, Se, Hg and Cd by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is most advanced technique for determination of trace metal concentration up to 1 part per billion (ppb). The concentrations of these metals in the study area were compared with drinking water quality limits given by the World Health Organization (WHO), 4$^{th}$ edition in 2011.*

**Key Words:** Water Quality – Trace Metals – ICP-MS -Tirupati-WHO.

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## INTRODUCTION

Ground Water and Surface Water is an important and major source of drinking water in both urban and rural areas in India. Determination of water quality is one of the most important aspects in groundwater studies. Groundwater is highly valued because of certain properties not possessed by surface water [1-2]. People around the world have used groundwater as a source of drinking water, and even today more than half the world's population depends on groundwater for survival. The value of groundwater lies not only in its widespread occurrence and availability, but also in its consistent good quality, which makes it an ideal source of drinking water. In recent times, increasing focus is being given to studies on groundwater contamination. Since groundwater is directly in contact with soil, rocks, and plants, the constituents of these sources might contaminate the groundwater [3-4].

Trace elements constitute a natural component of the earth crust and they are not biodegradable, hence persist in the environment. Trace elements may come from natural sources, leached from rocks and soils according to their geochemical mobility or come from anthropogenic sources, as the result of human land occupation and industrial pollution [5]. Depending on their solubility, these metals may eventually become associated with suspended particulate matter and accumulate in the bottom sediments. The increase of industrial activities has intensified environmental pollution problems and the deterioration of several aquatic ecosystems with the accumulation of metals in biota and flora. Although trace metals at low concentrations are essential to life, at high concentrations, may become hazardous.

High concentrations of trace elements are dangerous because they tend to bio-accumulate resulting in heavy metal poisoning. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Many trace metals are regarded as serious pollutants of aquatic ecosystems

because of their environmental persistence, toxicity and ability to be incorporated into food chains. Various metals from industrial, agricultural, domestic and urban wastes may enter river and lake waters through leaching, runoff, effluents and dry deposition.

Heavy metals pollution represents a serious problem as these metals leach into ground water or soil, which is detrimental to human health. Ground water pollution is a consequence of several activities like chemical manufacturing, painting and coating and mining. Metals exert a deleterious effect on fauna and flora of lakes and streams.

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 water. The most effective technique for the determination of trace level contamination of heavy metals in water is ICP-MS and GFAAS. By using ICP-MS (Inductively Coupled Plasma Mass Spectrometry) we can determine up to 0.1µg/L of metal concentration in water. In this paper an attempt has been made to evaluate the quality and concentration of trace elements in surface and ground water in the area of Tirupati, Chittoor district, Andhra Pradesh using Inductively Coupled Plasma – Mass Spectrometer.

## MATERIALS AND METHODS

**2. Sample Collection:**
10 water samples were collected in the above said area. Standard methods were adapted for the analysis of various water qualities. 1 liter 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. Two Liters of each sample was collected and homogeneous sample is prepared for analysis of physicochemical parameters. Separately 100ml of each water sample is collected and acidified with Con.$HNO_3$ heavy metal and toxic metal analysis.

Samples were collected in various places.
Sample – 1 : Outside of amara raja factory ( Near Karakambadi)
Sample – 2 : Near Neutron Pharma labaroutary
Sample – 3 : Karakambadi Tank (cheruvu)
Sample – 4 : Mangalam
Sample – 5 : S. V. University campus
Sample – 6: SVIMS Hospital
Sample – 7 : Kapilathirtham
Sample – 8 : S. V. Muncipal high School
Sample – 9 : M. R. Palli
Sample – 10 : Vidya Nagar

**3. Qualityassurance Rocedure:**
Special precautions were taken during sampling and analysis of trace elements. Before collecting the samples, the sample containers are soaked overnight in 2% nitric acid and washed with double distilled water. All the samples were collected in polythene containers and stored at 4 $^{o}$C by using ice packs. Supra pure grade nitric acid was used to acidify the samples.

**4. Analytical Methodology:**
Trace metals were analyzed by using ICP-MS (Agilent 7300) Standard reference material of 1,000mg/L (Multi elements-Merck). Seven different linear concentration standards were prepared, ranging from 0.001 mg/L to 0.1 mg/L. Before conducting sample analysis, different concentrations of standards were analyzed and linear curve was prepared. All metals having good linear graph with correlation coefficient of > 0.999 were observed in the preparation of standard curves.

***Instrumentation***

***ICP- MS***

The instrument used was a Perkin-Elmer Sciex Elan 5000 ICP-mass spectrometer (Perkin-Elmer, U¨ berlingen, Germany) equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining a 1 ml min−1 sample uptake rate), a cross-flow type pneumatic nebulizer and a double pass Scott-type spray chamber. Operating conditions are summarized in Table.

***ICP- MS operating conditions***

**ICP-MS Batch Agilent 7500**

| | |
|---|---|
| Rf power | 1500W |
| Nebulizer Ar flow | 1.0 L min−1 |
| Plasma Ar flow | 15.0 L min−1 |
| Auxiliary Ar flow | 1.0 L min−1 |
| Nebulizer | Concentric |
| Nebulizer chamber | Scott double-pass |
| Aspiration rate | 1.0 mL min−1 |
| Acquisition mode | Scanning |
| Dwell time | 20–30 ms |
| Calibration | Analyte addition |
| Replicates | 3 |
| Readings per replicates | 300 |

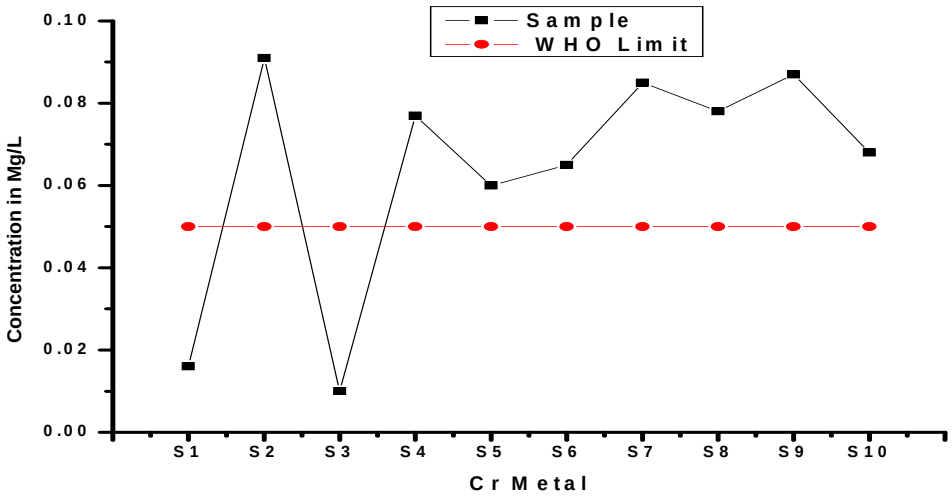
## RESULTS AND DISCUSSION

ICP-MS and AAS-GFA are the most useful techniques for the determination of trace metals up to parts per billion levels. AAS-GFA is a single element analyzer and it will take more time to analyze multi elements. The conductivity in the most of the study locations found less than 548µs/cm. But WHO referral value is 400µs/cm. Whereas ICP-MS is very useful technique to determine trace levels of metals in single aspiration. Therefore we suspect that there may be metals contamination in the selected samples of ground water and surface water.

### 5.1. Chromium (Cr):

The minimum and maximum concentrations of Chromium were 0.010 to 0.091 mg/L respectively. Whereas the maximum allowable limit for chromium as per WHO guidelines is 0.05 mg/L. Chromium concentration levels in all studied samples except S-1 and S-3 are exceeding then compared WHO Standards. The concentration levels of chromium in all the samples are shown in Table 1 & 2 and the comparison levels of chromium in study area is shown in Graph-I.

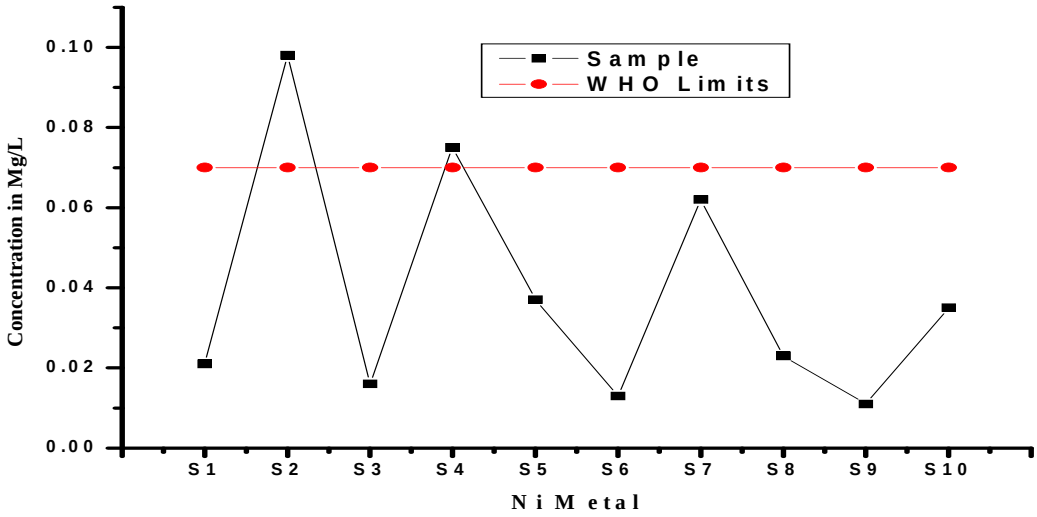
**Graph – I**




### 5.2. Nickel (Ni):

The minimum, and maximum concentrations of Nickel were 0.011 to 0.098 Mg/L respectively. Samples showed measurable concentrations of Nickel, expect of only S-2 and S-4 samples exceeded the maximum contaminant limits for WHO drinking water. The concentration levels of Nickel in all the samples are shown in Table 1 & 2 and the comparison levels of Nickel in study area is shown in Graph- II.

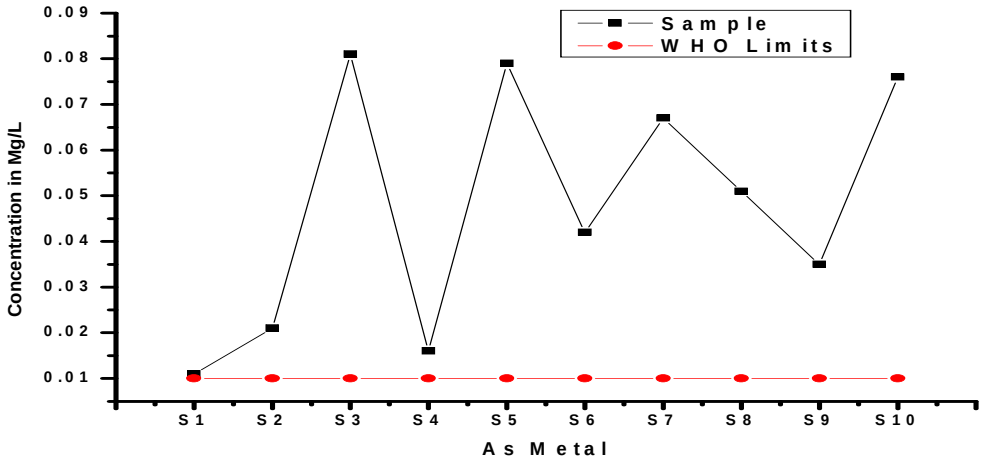
**Graph – II**




**5.3. Arsenic (As):**

The minimum and maximum Arsenic concentrations varied between 0.011 and 0.081 Mg/L. Measurable concentrations of the metal were found in all 10 samples exceeded the maximum contaminant limits as per WHO drinking water. The concentration levels of Arsenic in all the samples are shown in Table 1 & 2 and the comparison levels of Arsenic in study area is shown in Graph-III.

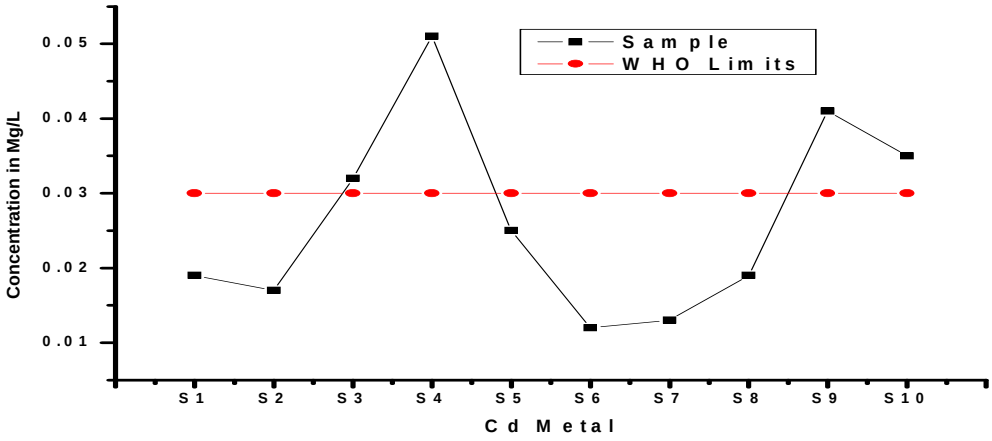
**Graph – III**




**5.4. Cadmium (Cd) :**

The minimum and maximum concentrations of Cadmium were 0.012 to 0.051 mg/L respectively. Whereas the maximum allowable limit for chromium as per WHO guidelines is 0.03 mg/L. Chromium concentration levels in all studied samples only S-4, S-9 and S-10 are exceeding then compared WHO Standards. The concentration levels of chromium in all the samples are shown in Table 1 & 2 and the comparison levels of cadmium in study area is shown in Graph-IV.

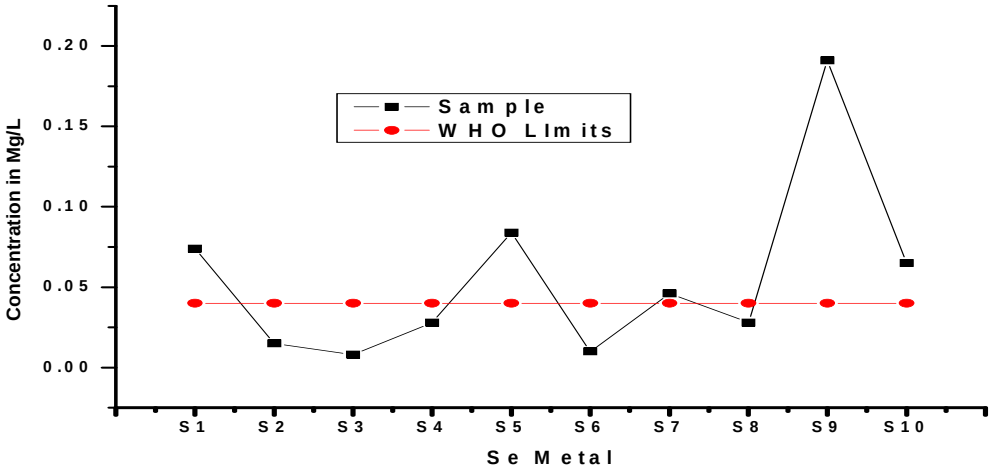
**Graph – IV**



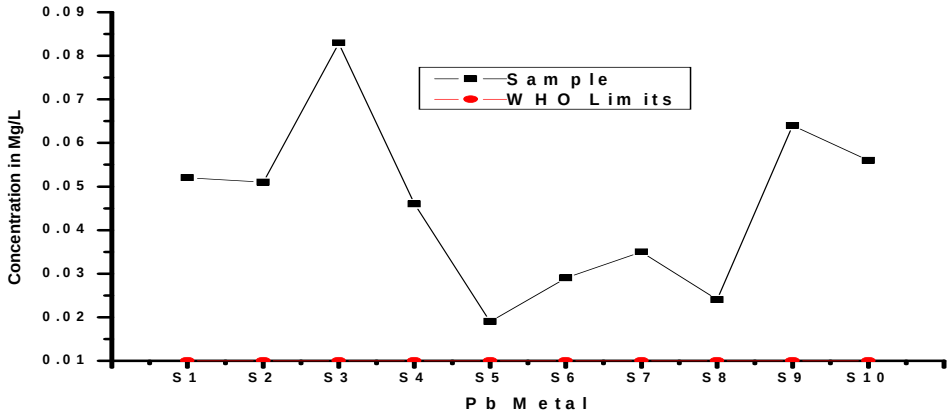

**5.5. Selenium (Se):**

All water samples had measurable concentrations of Selenium. However, only four like S-1, S-5, S-9 and S-10 samples are slightly higher the WHO maximum contaminant limits prescribed for Selenium in water samples. Remaining all samples are low the WHO Guidelines for drinking water quality. The concentration levels of Selenium in all the samples are shown in Table 1 & 2 and the comparison levels of Selenium in study area is shown in Graph- V.

**Graph – V**




**Graph – VI**



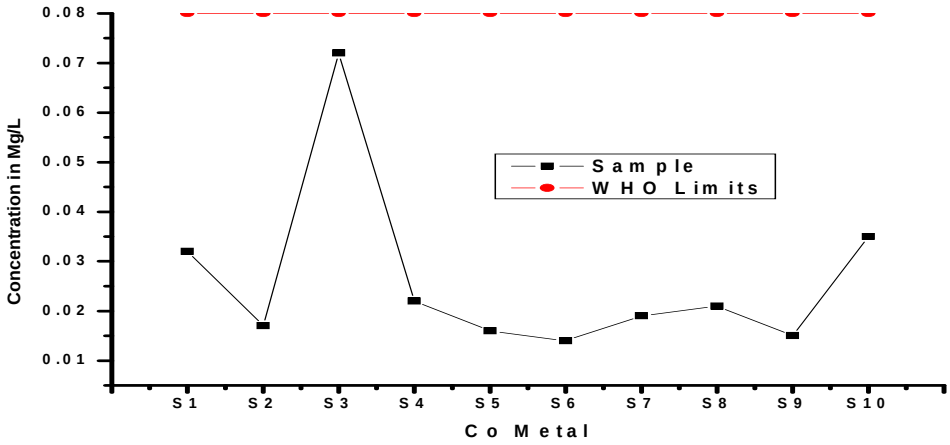
**5.6. Lead (Pb):**

The minimum and maximum Lead concentrations varied between 0.019 and 0.083 Mg/L. All selected sample concentration is higher of the maximum (0.01 Mg/L) WHO quality. Measurable concentrations values are shows in Table 1 & 2, the comparison levels of Lead in study area is shown in Graph- VI.

**5.7. Cobalt (Co):**

Cobalt is commonly found at low concentrations in most of the ground water and is generally well below the WHO Guidelines for drinking water quality. Measurable values shows in Table 1 & 2, the comparison levels of Cobalt in study area is shown in Graph- VII.

**Graph – VII**




But from the data we found that almost all samples are having high levels of trace metals. Higher concentrations of metals like As, Ni, Cr, Pb, Co, Se, Hg and Cd are found in some samples. The concentrations of metals are shown in tables 1 and 2.

**Table – 1: SAMPLES WATER**

| S.NO | TRACE ELEMENTS | SAMPLE-1 Mg/L | SAMPLE-2 Mg/L | SAMPLE-3 Mg/L | SAMPLE-4 Mg/L | SAMPLE-5 Mg/L | WHO Guidelines for drinking water quality(2011)-mg/L |
|---|---|---|---|---|---|---|---|
| 1 | Cr | 0.016 | 0.091 | 0.010 | 0.077 | 0.060 | 0.05 |
| 2 | Ni | 0.021 | 0.098 | 0.016 | 0.075 | 0.037 | 0.07 |
| 3 | As | 0.011 | 0.021 | 0.081 | 0.016 | 0.079 | 0.01 |
| 4 | Cd | 0.019 | 0.017 | 0.032 | 0.051 | 0.025 | 0.03 |
| 5 | Pb | 0.052 | 0.051 | 0.083 | 0.046 | 0.019 | 0.01 |
| 6 | Se | 0.074 | 0.015 | 0.0080 | 0.028 | 0.084 | 0.04 |
| 7 | Co | 0.032 | 0.017 | 0.072 | 0.022 | 0.016 | 0.08 |
| 8 | Hg | <0.001 | <0.001 | <0.001 | 0.001 | <0.001 | 0.006 |

**Table – 2: SAMPLES WATER**

| S.NO | TRACE ELEMENTS | SAMPLE-6 Mg/L | SAMPLE-7 Mg/L | SAMPLE-8 Mg/L | SAMPLE-9 Mg/L | SAMPLE-10 Mg/L | WHO Guidelines for drinking water quality(2011)-mg/L |
|---|---|---|---|---|---|---|---|
| 1 | Cr | 0.065 | 0.085 | 0.078 | 0.087 | 0.068 | 0.05 |
| 2 | Ni | 0.013 | 0.062 | 0.023 | 0.011 | 0.035 | 0.07 |
| 3 | As | 0.042 | 0.067 | 0.051 | 0.035 | 0.076 | 0.01 |
| 4 | Cd | 0.012 | 0.013 | 0.019 | 0.041 | 0.035 | 0.03 |
| 5 | Pb | 0.029 | 0.035 | 0.024 | 0.064 | 0.056 | 0.01 |
| 6 | Se | 0.010 | 0.046 | 0.028 | 0.191 | 0.065 | 0.04 |
| 7 | Co | 0.014 | 0.019 | 0.021 | 0.015 | 0.035 | 0.08 |
| 8 | Hg | <0.001 | <0.001 | 0.002 | <0.001 | <0.001 | 0.006 |

## CONCLUSION

The Ground Water and surface water samples were collected from various locations of Tirupati, Chittor District, A.P., India in February 2012 for the determination of Cr, Ni, As, Cd, PB, Se, Co and Hg by using ICP-MS. The

concentrations of the above listed elements were found to be ranged between 0.016-0.091, 0.011-0.098, 0.011-0.081, 0.012-0.051, 0.019-0.083, 0.010-0.0191, 0.015-0.072,and <0.001-0.002 Mg/L. Heavy metals like As, Pb in all sample are exceeded WHO limits for drinking water. Some metals like Cr except samples S-1 and S-3, Ni metal in samples S-2 and S-4, Cd metal in samples S-3,S-4,S-9 and S-10, and Se metal in S-1, S-5,S-9 and S-10 sample are exceeded WHO limits for drinking water. Remaining metals like Co, Hg Sample are low level of WHO limits for drinking water.

The excess presence of Arsenic in water may cause cancerous and skin lesions. Higher value of mercury is toxic and causes neurological damage, paralysis and blindness. Excess concentration of Lead causes damages the nervous system and causes brain disorder. Excessive lead also causes blood disorders in mammals. Among the Ten sample only S-1 sample were of good quality, seven were of fair quality and the samples S-7 and S-10 was of poor quality for drinking purpose. Therefore sixty percent of the samples were found to heavy fair quality. From the results of the present study, we can suggest that the Government should be adopted some treatment technologies in the following study areas to minimize these heavy metals in Ground water and surface water for safe drinking water to the public.

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