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ICP-OES Determination of Trace Metals in Groundwater of Proddatur area, YSR Kadapa dist., AP-India

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Abstract:

Groundwater is the only drinking water source in the study area. Heavy metals may be considered as contaminants in the groundwater of this area due to dyeing and electroplating industries. Extreme amounts of heavy metals within drinkable waters may have a variety of short- and long-term health consequences for humans. There are no reports of heavy metals in any previous studies of this area. Ten groundwater samples were collected from different locations of Proddatur and analyzed for twelve trace metals namely arsenic, cadmium, manganese, copper, iron, mercury, chromium, nickel, lead, molybdenum, zinc and selenium using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) method at trace levels. The proportion of elements in the examined sample determines the strength of the energy released. The results showed that 70% of samples contained Molybdenum, 30% of samples contained lead and copper which were reported within allowable bounds of WHO. The cadmium concentration in 40% samples was detected above World Health Organization - WHO guidelines. Cadmium is a very hazardous environmental and industrial waste adulterant. Consumable water containing high amounts of cadmium causes severe stomach irritation, resulting in vomiting, diarrhea, renal damage, osteoporosis, & osteomalacia. So, periodical monitoring and elaborate study on heavy metal pollution in groundwater are suggested.

Keywords: Groundwater, Heavy metals, Contamination, ICP-OES method, Plasma flow, Toxicity of cadmium.

Introduction

Water is among the most valuable resources on the planet, as it is required for life's existence and sustenance. As the world's population expands, so does the demand for water, putting more pressure on the groundwater supplies. Groundwater is currently overused in many parts of the world. As a result, water levels are dropping, ground subsidence is occurring, and ecological degradation is occurring, such as wetland drying out.

Because of its polarity & hydrogen bond, water has distinct chemical characteristics that allow it to disintegrate, absorb, adsorb, and hang a wide range of compounds. As a result, water in nature is not clean since it picks up pollutants from its environs as well as those human activities, animals, as well as other bioactivities. Ground water pollution is among the most pressing environmental issues today, and among the wide range of pollutants influence the water resources, dense metals are of significant concern due to their high toxicity perhaps at reduced concentrations as well as their proclivity to bioaccumulate within tissues of life forms overtimes.^{1,2}

Heavy metals are defined as elements with atomic weights ranging from 63.546 to 200.590 with a specific gravity more than 4.0, or at least 5 times than that water. They can be found in colloidal, particle, and dissolved forms in water³. Heavy metals reach the atmosphere via both natural and human-caused sources⁴. Natural weathering of the earth's crust, mining, soil depletion, industrial emissions, runoffs, sewage effluents, pest or disease management chemicals applied to plants, and air pollution fallout are all examples of potential sources⁵. Because heavy metals are permanent and indestructible, and many of them have harmful effects on species, aquifer contamination with heavy metals has become a global concern in contemporary years⁶. Metals are a specific issue amongst environmental contaminants because of the potential for toxicity and tendency to bioaccumulate in aquatic environments⁷. Concentrations of heavy metals in aquatic environments are often monitored by detecting their amounts in water, sediments, and biota that are found in low quantities in water but reach significant quantities in sediments and biota. Heavy metals, which include necessary & non-essential elements, are particularly important in ecotoxicology as they're very enduring and most have the capacity to be toxic of living organisms due to the bioaccumulation propensity⁸. Groundwater quality is degraded as a result of overexploitation of groundwater recharge and release of unchecked effluents. Heavy metals may infiltrate groundwater out of a number of sources, both natural & anthropogenic⁹. It is claimed that one-third of the worldwide people rely on groundwater to consumption.

Trace heavy metal analysis is an essential element of public health studies¹⁰ because of the impact of heavy metals on human metabolism. Certain transition elements are necessary for optimal health at trace amounts in human metabolism. Heavy metals found in nature are not hazardous to our environment just as they are prevalent in such tiny quantities. However, if quantities of such metals exceed that required for a healthy existence, their functions take on a negative aspect. Water and food are the primary direct sources of heavy metal ions, whilst industrial activities and transportation are indirect sources¹¹.

The public consumes groundwater both drinking as well as domestic uses in all of the research area's sites. Some areas of the study region are home to businesses such as dyeing, electroplating, & battery manufacturing. As a result, there may be a risk of pollution of the water table with various elements including ions at various quantities. The current study employed the Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) technique to assess the saturation levels of heavy metals in groundwater¹². The emission method is used in the Inductively Coupled Plasma – Optical Emission Spectrometer - ICP-OES. In regard of limit of detection and also analysis speed, ICP – OES has an edge over other methods^{13,14}. We can detect trace element concentrations up to ppb levels by using ICP-OES method.

Materials and methods

Study Area

Proddatur (Figure-1c) is the second largest municipal town in the district of YSR Kadapa -Figure-1b, Andhra Pradesh - Figure-1a, India, lying in latitude 14°73' N and longitude 78°55'E respectively. The area of the town is 7.125 square kilometers with an elevation of 158 meters. As of 2011 census, the town had 1, 62,816 population with 23000 inhabitants per square kilometer population density.

Sample Collection

10 sources of groundwater with conventional sample gathering protocol & guidelines handed in Indian Standards Methods IS: 3025 (Part-1) also American Public Health Association - APHA 22nd edition, samples were gathered from tube wells by arbitrary choice in clean as well as sterile one liter polythene empty containers that were meticulously washed with 1:1 HNO₃, rinsed multiple times with distilled water, & left to dry in an electric oven. To avert or reduce contamination, every accessible safety procedure were followed at each and every stage, beginning with sample collection, storing, transportation, including the sample's final analysis.



Fig.1a-Andhra Pradesh



Fig.1b-YSR Kadapa Dt.



Fig.1c-Proddatur

Methodology

Heavy metals within the water are analyzed using a variety of sophisticated devices such as ICP-OES, ICP-MS, AAS, UV-VIS spectrophotometer, Cyclic Voltammetry, and others¹⁵⁻¹⁸. Direct aspiration of groundwater sources into an ICP-OES multi analyzer system (Perkin Elmer, 7300DV) with radio frequency (RF) 1400 watts, plasma flow 15 L/min, Nebulizer flow 0.5 L/min, and plasma view in axial mode was used to analyze 12 heavy metals. Thru the thin tube within center of the torch tube, solution samples are atomized and fed into the plasma. To make plasma, argon gas is delivered into the torch coil, and then a high-frequency electric current is sent through the work coil so at the torch tube's tip. Argon gas gets ionized and plasma is formed by using an electromagnetic field established with in torch tube by that of the high frequency current. This plasma does have a high electron density plus temperature (10000K), which is employed in the sample's excitation / emission. As the electrons revert to the ground state, the excited atoms release energy at a certain wavelength. A particular element releases radiation at wavelengths that are unique to its chemical makeup. The amount of element in the tested sample determines the intensity of the radiation released at around that wavelength. In aspects of specificity, precision, linearity, accuracy, & limit of quantification, this technique has now been validated. Most of the components in this technique have quantitative values of parts per million and perhaps even parts per billion. The metal contents in the research region were matched to World Health Organization drinking water quality guidelines¹⁹.

Results and discussion

10 groundwater samples were chosen to take from various areas of the Proddatur region and examined using the ICP-OES technique. Table-1 shows the amount of different metals found in the tested samples. All results were statistically evaluated using Microsoft Excel to assess the significance of differences between the variables (Table-2).

Table-1: Concentration of trace metals in samples of groundwater, Proddatur

S. No.	Sample Location	As	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Se	Zn
1	Modampalle	<BDL	0.003	0.002	<BDL	0.002	<BDL	0.001	<BDL	0.001	<BDL	0.015	0.006
2	SastryNagar	<BDL	0.003	0.002	0.001	1.201	<BDL	0.053	0.004	0.004	0.007	0.019	1.336
3	Industrial area	<BDL	0.004	0.003	<BDL	0.005	<BDL	0.007	0.009	0.002	0.002	0.044	0.213
4	YMR Colony	<BDL	0.004	0.002	<BDL	0.018	<BDL	0.322	0.002	0.003	<BDL	0.034	0.034
5	HB Colony	<BDL	0.003	0.002	<BDL	0.226	<BDL	0.545	<BDL	0.003	<BDL	0.048	0.032

6	Bollaram	<BDL	0.003	0.002	0.007	0.942	<BDL	0.055	0.014	0.006	<BDL	0.034	0.026
7	Rameswaram	<BDL	0.003	0.002	<BDL	0.001	<BDL	0.993	0.004	0.004	<BDL	0.037	0.021
8	One Town	<BDL	0.004	0.002	0.015	0.009	<BDL	0.183	<BDL	0.003	<BDL	0.036	0.025
9	Two Taps	<BDL	0.004	0.002	<BDL	0.009	<BDL	0.584	0.004	0.002	0.003	0.027	0.029
10	Dorasanipalle	<BDL	0.003	0.005	<BDL	0.004	<BDL	0.002	0.004	0.002	<BDL	0.032	0.010

BDL=Below Detection Limit

* Concentration of all metals in mg/L

Table-2: Comparison of statistical data of different metals in groundwater of proddatur

Conc.(mg/L)	As	Cd	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Se	Zn
Min	---	0.0030	0.0020	0.0010	0.0010	---	0.0010	0.0020	0.0010	0.0020	0.0150	0.0060
Max	---	0.0040	0.0050	0.0150	1.2010	---	0.9930	0.0140	0.0060	0.0070	0.0480	1.3360
Average	---	0.0034	0.0024	0.0076	0.2417	---	0.2745	0.0059	0.0030	0.0040	0.0326	0.1732
SD	---	0.0005	0.0010	0.0070	0.4468	---	0.3356	0.0042	0.0014	0.0026	0.0102	0.4130
Skewness	---	0.4841	2.6616	0.4232	1.7672	---	1.2434	1.5584	0.8838	1.4578	-0.3816	3.0450
Kurtosis	---	-2.276	7.1938	---	1.7293	---	0.8576	1.8777	1.2261	---	-0.139	9.4056
Percentage of samples containing heavy metals	0.0	100	100	30	100	0.0	100	70	100	30	100	100
WHO limit	0.01	0.003	0.05	2	NE	0.006	NE	NE	0.07	0.01	0.04	NE

Not Established (NE)

Arsenic

The quantity of arsenic in groundwater samples was determined to be below the detectable level (BDL). According to the World Health Organization, the maximum permissible level for arsenic is 0.01 mg/L. The arsenic concentrations in the research region are well within the WHO allowed limits.

Cadmium

The cadmium concentration in the groundwater samples was observed between 0.003mg/L and 0.004mg/L. Per the World Health Organization, the maximal allowable level of cadmium is 0.003 mg/L. The mean cadmium content in the research region exceeds WHO standards' acceptable limits. Cadmium concentrations were observed to be over the WHO acceptable limit in 40% of the research area's samples (S-3, S-4, S-8, & S-9).

Chromium

The research area's highest and least chromium values are 0.002 mg/L & 0.005 mg/L, respectively. According to the World Health Organization, the maximal permissible value for chromium is 0.05 mg/L. The chromium concentrations found in the research region are within WHO standards' acceptable limits.

Copper

Copper concentrations were observed to be less than detectable limits in 70% of groundwater tests. Copper has a maximum acceptable level of 2mg/L, according to the World Health Organization. Copper concentrations in the research region were found to be below WHO standards' acceptable range.

Iron

The concentration of iron within groundwater samples ranged between 0.001 mg/L - 1.201 mg/L. The highest and lowest amounts of iron content were found in samples 2 and 7, respectively. According to IS: 10500, the maximal allowable amount for iron is 0.3 mg/L. The iron concentrations found within the study region are well below acceptable limits.

Mercury

The quantity of mercury in groundwater samples was determined to be below the detectable level. In pursuant to WHO recommendations, the maximal allowed level of mercury in potable water is 0.006 mg/L. The mercury contamination levels in the research region were reported to be below the WHO's allowed limit.

Manganese

Manganese concentrations in groundwater samples ranged between 0.001 mg/L - 0.993 mg/L. The highest and lowest manganese concentrations were found in samples 7 and 1, respectively. Manganese was detected in all of the samples in the study region.

Molybdenum

The concentration of molybdenum in the groundwater of the study area ranged from 0.002mg/L to 0.014mg/L. The highest and lowest molybdenum concentrations were detected in samples six and four, correspondingly. Molybdenum was discovered in 7 samples from the research region.

Nickel

Nickel values ranged from 0.001 mg/L - 0.006 mg/L, with the highest and lowest amounts found in samples six and one, accordingly. As per the World Health Organization, the maximum permitted level for nickel is 0.07 mg/L. Nickel concentrations in the research region were found to be below WHO standards' acceptable range.

Lead

The concentration of lead within groundwater samples fluctuated between 0.002mg/L and 0.007mg/L. According to the World Health Organization, the maximal permitted limit for lead is 0.01 mg/L. The measured lead contamination levels in the research region are within WHO standards' acceptable range.

Selenium

The amount of selenium in the groundwater samples ranged from 0.015mg/L to 0.048mg/L. The highest and lowest selenium concentrations were detected in samples five and one, respectively. According to the World Health Organization, the maximum acceptable level for selenium is 0.04 mg/L. The selenium concentrations found in the study region are within WHO standards' acceptable range.

Zinc

Zinc concentrations in every sample over the investigation region spanned around 0.006 mg/L through 1.336 mg/L. The maximal & minimal concentration of zinc levels is observed in samples number two and one respectively. Zinc concentrations in the research region were reported to be within acceptable limits.

10 heavy metals had been found in 1 or even more samples, as per the findings. $Mn > Fe > Zn > Se > Cu > Mo > Pb > Cd > Ni > Cr > As > Hg$ was the average concentration amount of heavy metals within research region. In all samples, the hazardous elements arsenic & mercury were determined to be around the detection level. Another hazardous metal lead (S-2, S-3, and S-9) was identified in 30% of samples (S-2, S-3, and S-9) as well as its concentration has been below WHO limits. Cd, Cr, Fe, Mn, Ni, Se, and Zn were detected in 100% of the samples, with concentrations spanning from 0.003-0.004, 0.002-0.005, 0.001-1.201, 0.001-0.993, 0.001-0.006, 0.015-0.048, & 0.006-1.336 mg/L, correspondingly. Apart from cadmium, the concentrations of all other six heavy metals were revealed to be less than WHO standards. Copper was revealed in 30% of samples at concentrations ranging from 0.001-0.015 mg/L, which was considered to be less than WHO acceptable limits. In 70% of the samples, the molybdenum content was found to be under WHO acceptable standards inside this concentration range of 0.002-0.014 mg/L.

In 40% of samples, the cadmium content above the Who is allowed level (S-3, S-4, S-8 & S-9). Cadmium is a very hazardous environmental & industrial contaminant that has been designated as a human carcinogen [Group 1 by the International Agency for Research on Cancer; Group 2a by the Environmental Protection Agency (EPA); and 1B by the European Chemical Agency]. Cadmium is widely utilized in a variety of industrial processes. Cadmium is used in the manufacturing of alloys, pigments, & batteries, among other things. Cadmium can be seen as hydrated ions or perhaps in ionic compounds with some other inorganic materials. Insoluble forms are stationary and will deposit & absorb to sediments, whereas soluble forms move in the water. Drinking water holding high amounts of cadmium irritates the stomach, causing vomiting, diarrhea, as well as mortality in certain cases. Kidneys will be harmed, and bones will get brittle and readily shatter. It is the cause of the well-known illness "itaiitai."

Rainwater washing off soil contaminants and polluting aquifers is the most likely source of cadmium contamination. The level of cadmium was detected to be over the WHO allowed level in Tirupati, varying from

0.012 to 0.051 mg/L, but under the WHO legal limit in SPSR Nellore^{20, 21}. Cadmium levels of 0.002 mg/L were found in certain samples from Coimbatore, Tamil Nadu²². In north Rajasthan, cadmium pollution in underground water was detected at 0.006 mg/L, above the WHO¹⁶ acceptable level. Pesticide usage has resulted in high levels of cadmium in several Gujarat locations²³. Due to pollution of dyes, paints, and pigments manufacturing sectors, higher cadmium concentrations in water samples of the Cuddalore industrial region were found in the range of 0.05-0.56mg/L²⁴.

The probable cause of cadmium pollution in the four sample locations of the study area may be due to leaching of cadmium from dying industries into the groundwater. Another toxic metal, lead was also found in three locations which may be due to leaching from acid battery industries. So, periodical monitoring and elaborate study on heavy metal pollution in groundwater is suggested.

Conclusion:

A total of 10 groundwater specimens were taken and tested for heavy metals in this current investigation. Except for cadmium, the findings indicated that 11 heavy metals were discovered within WHO standards' acceptable range. Cadmium concentrations were found to be over the WHO permitted limit in 40% of the research area's samples. As a result, it is recommended that the polluted sources of concern undergo further treatment to minimize the concentration of this detected trace metal, which might pose a health risk. Trace metal levels should be checked on regular basis using proactive techniques.

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Conflict of interest statement

The authors declare no conflict of interest.

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