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Risk assessment using ICP-MS of heavy metals in groundwater in Upper Egypt

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Abstract

It is of great importance to assess the pollution of groundwater as it makes up about twenty percent of the world's freshwater supply. Environmental laws in Egypt are correlated with protecting water resources from contamination and generally set the maximum limits for the concentration of different hazardous components in wastewater before it is discharged to sea water, rivers, groundwater and the public sewer system. Groundwater from Samalout, Al Minya governorate, Egypt, is studied by analysing its heavy metal content using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Furthermore, the obtained heavy metal concentrations are compared with permissible limits set by environmental organizations such as the World Health Organization (WHO) and the United States Environmental Protection Agency (US-EPA). Comparing the heavy metal concentrations with the groundwater in question clearly demonstrated that the water in this resource should not be directly used for drinking and requires some degree of treatment before usage. For example, concentrations of chromium and lead are far above the maximum permissible limit. The consequent health risks due to the usage of contaminated water are identified in this study as well.

Graphical Abstract

Egypt, 1995 (µg/l)	Average concentration found (µg/l)	Heavy Metals
-	8.91	V
< 50	1271.15	Cr
< 100	30.9	Mn
< 300	1061.4	Fe
-	2.15	Co
-	41.1	Ni
< 1000	209.94	Cu
< 5000	490.21	Zn
< 1	1.23	Hg
< 50	30.04	Pb
< 50	Nil	As
< 5	Nil	Cd

1. Background

Water is the source of life for all living organisms on the planet. Today, the world is facing challenges to cope with the increased need for freshwater. Preserving and maintaining water resources uncontaminated is essential for the well-being of every individual in society.

Water is generally obtained from two principal natural sources; surface water such as freshwater lakes, rivers, streams, etc. and groundwater such as borehole water and well water **[1]**. Both natural sources are at risk of contamination or pollution from various pollution sources.

Contamination of groundwater is considered to be one of the more serious environmental issues at the present time because groundwater makes up about 20 percent of the world's freshwater supply **[2]**. Contamination can occur naturally; mainly due to the friction between the soil and rocks, which usually contain high concentrations of heavy metals, and the water layers. This results in increased heavy metal concentration of the groundwater.

Some human activities have also been proven to cause pollution to groundwater. For example, the use of fertilizers and pesticides for agricultural purposes and, in some countries, the release of petroleum-based fuels from leaking underground storage tanks is considered to be an important contaminant. However, between the wide ranges of contaminants affecting water resources, heavy metals have been identified as the most dangerous risk. They cause particular concern due to the strong toxicity of heavy metals even at relatively low concentrations **[2]**.

Heavy metals are well-known for their ability to cause various negative effects on human health. Momodu and Anyakora report that the nature, symptoms and severity of the effects on human health on the whole depend on the type and the amount of ingested metal **[1]**. When heavy metals are digested by the human body, they form complexes with proteins already existing in the body. The formation of these complexes is very dangerous to human health because amine ($-NH_2$), thiol (–SH) and carboxylic acid (–COOH) groups are involved in the process. The bond created between the metals and these groups alters the natural structure of proteins. In addition, this bond destroys the molecules as they fail to perform their function correctly due to cell death. This in turn affects the catalytic characteristics of enzymes in general, which could lead to the formation of radicals that are very harmful due to their ability to oxidize the biological molecules present in the human body **[1]**.

Environmental laws in Egypt are correlated with protecting water resources from contamination and generally set the maximum limits for the concentration of different hazardous components in wastewater before it is discharged to seawater, rivers, groundwater and the public sewer system. For example, the Egyptian Environmental Law (48) from 1982 sets the legal limits for discharges in the Nile River and groundwater aquifers as listed in **Table 1** **[3]**, **[4]**.

Any establishment that does not comply with the aforementioned legal limits and standards shall be fined **[3]**, **[4]** and given a grace period to properly treat its wastewater discharge (usually a month). The license pertaining to the activity of said establishment shall be revoked if it fails to comply with the legal limits after the grace period **[3]**, **[4]**.

Legal limits are also set for potable and drinking water. No doubt that those limits are stricter than those for discharge because the water will be directly used for drinking while the discharged water, whether to the River Nile or seawater, undergoes a number of treatment processes before use. This study investigates the heavy metal content in groundwater found in one of the most populated areas in Upper Egypt, the El-Minia Governate.

2. Results and discussion

Inductively coupled plasma – mass spectrometry is a useful tool to determine trace elements in aqueous solutions **[5]**, **[6]**. **Table 2** shows the content found in groundwater using ICP-MS as well as the maximum allowable limits for the concentration of hazardous heavy metals in drinking water set by different national and international organizations.

As can be seen in **Table 2**, chromium, iron, nickel, mercury and lead have critical values according to the organizations listed. Assessing the risks on human health resulting from exposure is further discussed.

Chromium

High doses of chromium are associated with gastrointestinal disorders, hemorrhagic diathesis, and convulsions. Chromium represents a serious problem since, as can be seen in **Table 2**, the reported concentration is 1271.15 (µg/l) and the limits vary between 50 and 100 (µg/l). This chromium concentration is above all regulatory limits set by different countries and international organizations. Thus, the direct use of this source for drinking water should be prohibited. Calculations using equation 1, 2 and 3 reveal that, the total dose is 62.28 x 10^6 µg in 350 days. The potency factor for chromium is . The risk accompanying this intake is calculated to be 185%.

Iron

Iron has negligible health effects. The maximum permissible limits for iron are set mainly to maintain the water taste. The iron concentration (1061.4 µg/l) exceeds the limit set by the US EPA (300 µg/l), thus, the water taste is expected to be poor, as confirmed by the inhabitants using that water source.

Nickel

The nickel concentration (41.1 µg/l) exceeds the maximum permissible limits set by the EU (20 µg/l), the Iranian government (20 µg/l), the Australian government (20 µg/l), and the Indian government (20 µg/l) (**Table 2**). However, most of those limits were estimated in the 90s unlike the maximum permissible limits set by the US-EPA (100 µg/l) and WHO (70 µg/l) which were estimated in 2008. Moreover, the latter two organizations are considered to be more reliable for data accuracy. The nickel concentration is below the maximum permissible limits set by both organizations, accordingly, the nickel concentration is considered to be below the limits and it is not expected to cause any effect on human health, other than possible allergy due to accumulated Ni in the human body.

Mercury

Mercury poisoning results in a wide range of diseases including damage to lungs, kidney and autoimmunity and is also correlated with brain disorders and mental disturbances at extremely high doses **[13]**. The reported mercury concentration in the groundwater in question (1.23 µg/l) is less than the maximum permissible limit set by the US-EPA (2 µg/l) but it is above the maximum permissible limit set by the Egyptian government (1 µg/l), the EU (1 µg/l), and the Canadian government (1 µg/l). However, the limits set by the US-EPA are the most recent and accurate. Thus, the mercury concentration is not expected to cause any health risks from mercury poisoning by drinking water from this source.

Lead

The ingestion of lead is very dangerous to human health because it destroys the immune system, leaving the body vulnerable to all kinds of diseases. Recent studies indicate that exposure to lead is particularly harmful for children. Aside from the carcinogenic effects, continuous exposure is related to brain disorders and deterioration leading to learning disabilities. The lead concentration (30.4 µg/l) is lower than the maximum permissible limit set by the Egyptian government (50 µg/l), the Iranian government (50 µg/l), and the Indian government (100 µg/l). However, **Table 2** shows that it is almost double the limit set by the US-EPA (15 µg/l) and triple the limit set by the EU, WHO, the Australian government and the New Zealand government (10 µg/l). Therefore, it is expected to cause significant health problems. Using Equations 1, 2 and 3, the total dose in 350 days is found to be 1.47 x 10^6 µg. The potency factor for lead is $8.5 \times 10^{-3} \left(\frac{\mu g}{kg}.day\right)^{-1}$

The related risk is considered to be 7.31 x 10^{-3}.

The US-EPA has concluded that risk values between and or less are considered acceptable, while risk values of or more are regarded as serious and require attention **[14]**, **[15]**, **[16]**.

Table 1: Regulations from the Ministry of Water Resources and Irrigation Discharge in the Nile River & groundwater aquifers **[3]**, **[4]**.

Item	Maximum limits of Criteria and Specifications
Total solid material	< 500 mg/L
Temperature	< 3 ° over the prevailing rate
Dissolved Oxygen	> 5 mg/L
pH	6 to 9
Biochemical Oxygen Demand (BOD)	20 to 30 mg/L
Chemical Oxygen Demand (COD)	20 to 40 mg/L
Total Dissolved Solids (TDS)	800 to 1200 mg/L
Suspended Solids (SS)	< 30 mg/L
Hydrogen Sulfide	< 1 mg/L
Oil and Greases	< 5 mg/L
Phosphate	< 1 mg/L
Nitrates	< 30 mg/L
Phenols	0.01 to 0.002 mg/L
Fluorides	< 0.5 mg/L
Residual Chlorine	< 1 mg/L
Mercury	< 0.001 mg/L
Lead	< 0.001 mg/L
Cadmium	< 0.003 mg/L
Arsenic	< 0.01 mg/L
Chromium	< 0.02 mg/L
Copper	< 1 mg/L
Nickel	< 0.02 mg/L
Iron	< 1 mg/L
Manganese	< 0.5 mg/L
Zinc	< 1 mg/L
Silver	< 0.05 mg/L
Cyanide	< 0.005 mg/L
Selenium	< 0.001 mg/L
Boron	< 0.5 mg/L
Pesticides	All Types to be Nil
Sulfates	< 200 mg/L

Table 2: Average concentration of heavy metals found using ICP-MS and corresponding legal limits **[7]**, **[8]**, **[9]**, **[10]**, **[11]**, **[12]**.

Heavy Metals	Average concentration found (µg/l)	Egypt, 1995 (µg/l)	USEPA, 2008 (µg/l)	EU, 1998 (µg/l)	WHO, 2008 (µg/l)	Iran, 1997 (µg/l)	Australia, 1996 (µg/l)	India, 2005 (µg/l)	New Zealand, 2008 (µg/l)	Canada, 2006 (µg/l)
V	8.91	-	-	-	< 15	-	-	-	-	-
Cr	1271.15	< 50	< 100	< 50	< 50	< 50	< 50	< 50	< 50	< 50
Mn	30.9	< 100	< 50	< 50	< 400	< 500	< 500	< 100	< 400	< 50
Fe	1061.4	< 300	< 300	< 200	-	< 1000	< 300	< 300	< 200	< 300
Co	2.15	-	< 100	-	-	-	-	-	< 1000	-
Ni	41.1	-	< 100	< 20	< 70	-	< 20	< 20	< 80	-
Cu	209.94	< 1000	< 1300	< 2000	< 2000	< 1000	< 2000	< 1500	< 2000	< 1000
Zn	490.21	< 5000	< 5000	-	-	-	< 3000	< 5000	< 1500	< 5000
Hg	1.23	< 1	< 2	< 1	-	-	-	-	-	< 1
Pb	30.04	< 50	< 15	< 10	< 10	< 50	< 10	< 100	< 10	< 10
As	Nil	< 50	< 10	< 10	< 10	< 50	< 7	< 50	< 10	< 10
Cd	Nil	< 5	< 5	< 5	< 3	< 10	< 2	< 10	< 4	< 5

2.1 Experimental

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In this study, ICP-MS is used to determine the concentration of heavy metals in groundwater using a Perkin Elmer SCIEXDRC-e ICP-MS analyzer. Furthermore, the water quality is assessed and the associated risk based on the results obtained is then calculated. ICP-MS is considered to be the most efficient and fastest growing trace element analytical technique **[17]**, **[18]**, **[19]**, **[20]**. It has the ability to analyze all elements (from Li to U) present in a certain sample. The main advantage of ICP-MS is that it can be used to detect very low concentrations of heavy metals (as low as one part per trillion) in a specific sample.

Description of the study location

The samples were obtained from a groundwater extraction pump at a depth of 30 m located in Ahmed Orabi Street, Nazlet El-Amoudein, Samalot, the EL-Minia governorate, which is located in Upper Egypt. It is approximately 245 km south of Cairo. El-Minya is considered to be an important trading center on the west bank of the Nile. The principal industry in El-Minia is food processing; however, it is also well known for its carpet and cotton industry. The total area of El-Minia is approximately 32,279 km^2. The city has a population of around 4.2 million with a population density of 115 people / km^2. The source shown in **Figure 1** covers an area of approximately 30,000 m^2 and is used by 800 1000 inhabitants. The map in **Figure 2** shows the actual location of the groundwater under investigation.

Figure 1: Groundwater source

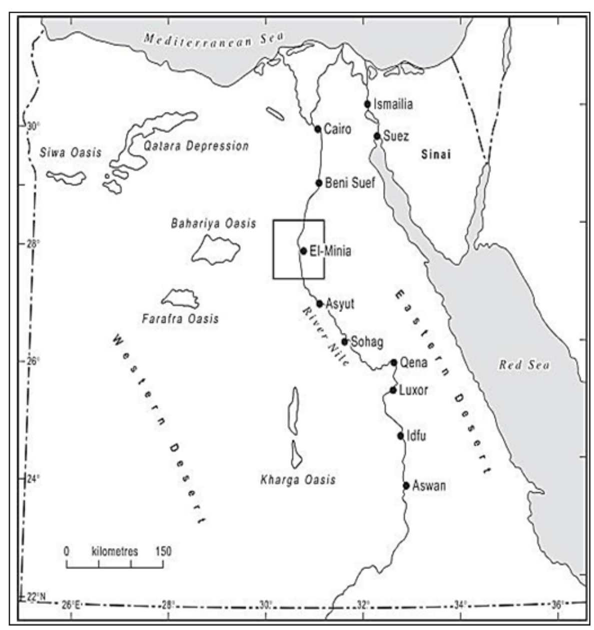

Figure 2: El-Minia on the Egyptian Map

Risk assessment

In order to calculate the risk associated with heavy metals contaminating the groundwater, the total dose is calculated first by multiplying the concentration found with the intake rate and the exposure duration according to Equation 1.

$$\text{Total dose } (\mu g) = \text{concentration of chemical } \left(\frac{\mu g}{l}\right) \times \text{ Intake rate } \left(\frac{l}{d}\right) \times \text{ exposure duration (d)}$$

Equation 1

The daily heavy metal intake is then calculated by the total dose per body weight multiplied by the average life time according to Equation 2.

$$\text{Daily heavy metal intake } \left(\frac{\mu g}{kg}.\text{day}\right) = \text{total dose } (\mu g) \ / \text{ body weight (kg) } \times \text{ Average life (day)}$$

Equation 2

The risk associated with heavy metal accumulation is calculated by multiplying the daily heavy metal intake with the potency factor specific to each heavy metal according to Equation 3.

$$\text{Risk } = \text{ daily heavy metal intake } \left(\frac{\mu g}{kg}.\text{day}\right) * \text{ heavy metal potency factor } (\mu g/kg.\text{day})^{-1}$$

Equation 3

3. Conclusions

Concentrations of chromium and lead are far above the maximum permissible limits set by different environmental organizations and countries and this will contribute to spreading a wide range of diseases such as brain disorders, nervous system breakdown, kidney and liver failure, gastrointestinal disorders, hemorrhagic diathesis, convulsions, and it will also increase the development of cancer and argyria amongst the population that drinks the water in question.

Concentrations of nickel and mercury do not exceed the limits set by the most reliable organizations (U.S. EPA and WHO) so they are considered safe and will not pose any health threats amongst the population.

The iron concentration does exceed the limits set by the U.S. EPA and WHO, however, it has negligible health effects. The maximum permissible limits for iron are set mainly to maintain the water's taste.

The best solution to avoid the aforementioned severe health effects is to find an alternative drinking source since the source used in this study is highly contaminated. Digging deeper might give cleaner water, since iron, manganese, copper, lead, zinc, chromium and cadmium have been found at a depth of 50 m present in ground water at a nearby source with values [mg/L] of 0.75, 0.11, <0.05, < 0.001, < 0.005, < 0.002 and < 0.0001, respectively.

However, if this is not feasible, the groundwater should be treated in order to adsorb excess heavy metals.

4. Conflicting interest

The authors declare that they have no conflicting interests.

5. Author's contribution

The idea of this research topic comes from Ghada Bassioni, as she is the main supervisor on this work. Samples were collected by Kirollos Ashraf. ICP-MS measurements were carried out by Amr Abd. All authors helped to draft the manuscript. All authors read and approved the final manuscript.

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