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Assessing The Selective Heavy Metal Quantity in Three River Water Samples in Khulna by Using ICP-MS

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ABSTRACT

Water contamination due to heavy metals is becoming a major concern for humans and other living organisms. Heavy metals can be spread into water by many natural and anthropogenic sources. Rapid industrialization and urbanization have led to a wide distribution of heavy metals, such as Pb, Cr, Ni, Cd, Fe, Hg, As, Zn, etc. Heavy metals within the permissible limit are essential to all living organisms, but concentrations above the permissible limit, when compared to many national and international organizations such as WHO (2021), WARPO, and BWWA, may cause many physiological disorders. The objective of this study was to investigate the elemental concentrations and health effects of heavy metals in 20 water samples from Khulna, Bangladesh, using the ICP-MS method. The previous works were performed only on Rupsha River and ICP-MS method was never used to determine the amount of the heavy metals in the sample of this specific area. Previously explored methods include Atomic Absorption Spectrophotometer (AAS), Instrumental Neutron Activation Analysis (INAA), High Resolution Germanium detector (HPGe) etc. The experiment was conducted in 3 rivers (Bhairov, Rupsha, and Moyur) of Khulna. The maximum and minimum concentrations of Fe and Ni in samples were determined in the range of (12.40-91.20) and (2.08-53.50) ppb, respectively. The average concentration of heavy metals detected in sample for iron was 43.36 ppb, while for nickel it was 7.98 ppb, both far below the permitted limits established by the WHO, specifically 14.45% for iron and 7.98% for nickel. All the waters analyzed met the WHO's suggested guidelines. This investigation gives details about water pollution due to heavy metals and their sources, along with their health effects.

Keywords: Heavy metal, Water, Impact, Contamination

1. Introduction

Water contamination due to heavy metals is hazardous to all sorts of ecosystems, human health, and living species. Since these elements do not dissolve in the environment and can accumulate in living tissue, interrupting the food chain. There are two types of heavy metals: non-essential (Cd, Ni, As, Hg, Pb, Cr) and essential (Mo, Mn Cu, Ni, Fe, Zn, Co). When essential metals are present in large excess in the environment, they lead to toxicity. Excess heavy metals in water come from both natural and manmade causes [3]. Natural sources include mineral-rich rock weathering and air salt precipitation caused by volcanic eruptions and forest fires. The primary anthropogenic source is the discharge of wastewater and sludge from industrial activity. Heavy metal ions such as As(III)/As(V), Pb(II), Cd(II), Ni(I), Cr(III)/Cr(VI), Zn(II), Cu(II), Hg(I)/Hg(II), and Co(II) are increasingly being discharged into streams, lakes, rivers, and oceans due to rapid urbanization and industrialization [1-3]. Industries like sugar mills, thermal power plants, distilleries, fertilizer and cement industries, oil refineries, paper and pulp industries, tanneries, insecticides, pharmaceuticals, and textiles use dyes and dye intermediates are the main source of heavy metal emissions [2,7]. Heavy metals can cause serious damage to human bodies. Such as Lead poisoning is especially dangerous for children since it can cause behavioral issues, learning challenges and developmental delays. Nickel allergy occurs frequently, resulting in skin eruptions and rashes. Long-term exposure to high nickel concentrations may raise the risk of lung and nose cancer [8]. Large amounts of iron supplements may upset your stomach and prevent you from absorbing other important minerals, which might result in deficiencies. Acute iron poisoning caused by extremely high supplement dosages can, in extreme circumstances, cause organ failure and even death [9,10]. Heavy metal detection is necessary for monitoring different parameters such as water quality monitoring, human health, ecological impact, source identification, pollution control and sustainable development. Many studies have investigated the occurrence and effect of heavy metals in groundwater and drinking water. Priti Saha and Biswajit Paul investigated the impact of heavy metals in water in India [2]. Bhargava, Gupta, Vats and Goel also worked on the heavy metals and their impact on health [4]. Leila Mehdizadehtapeh, Ismail Hakki Tekiner, and Haydar Ozpinar investigated heavy metal levels in drinking and well-water samples using the ICP-MS method [6]. Many studies have also been conducted in the different rivers of Bangladesh [5, 22-24]. Our research was conducted in three rivers of Khulna (Bhairov, Rupsha, and Moyur). The objective of this experiment was to check the concentration of heavy metals in river water, identify sources and probable effects on humans. In this experiment, the maximum and minimum concentrations of Fe and Ni in samples were

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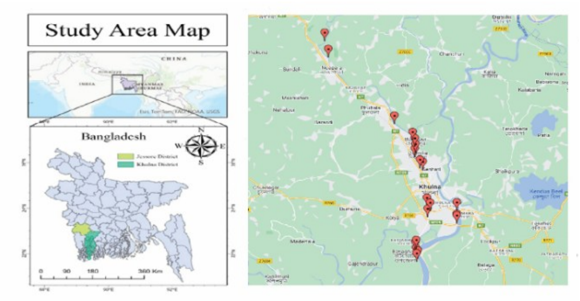
determined in the range of (12.40-91.20) and (2.08-53.50) ppb respectively. The investigation also illustrated that the concentration of all heavy metals was below the permissible limit.

2. Methodology

2.1 Sample Collection

During the period of January 2024 to June 2024, twenty water samples were randomly collected on test tubes from different points of Khulna and Jessore district's river (Bhairov, Rupsha & Moyur). From all the samples, two (Sample 5 &18) were taken from the Jessore district while the other eighteen were from the Khulna district. Surface level water was collected as samples.



. Fig. 1: Map of the study area of Bhairov, Rupsha & Moyur River, Bangladesh

Every location was chosen to be close to an industrial region. A lot of industries directly release their industrial waste into river water such as cement industries (Seven Rings Cement, Premier Cement Mills), battery industries (Hamko Battery, Abdullah Battery),ship building and dockywards (Khulna Shipyard Limited),fish and seafood industry (Fresh food limited, Bionick Seafood Exports, Moyuri Fisheries and Hatchery),jute mills (Star Jute Mills),tannery and leather processing industries (Khulna Leather Complex) and numerous small and medium sized brick kilns operate along these riverbanks. There is a significant risk of heavy metal contamination of the water in certain areas if industrial waste is dumped directly into the river.

2.2 Sample Analysis

For the analysis and quantify of the heavy metals of the collecting samples, we were used ICP-MS (Inductively Coupled Plasma Mass Spectrometry) machine because it is a rapid analysis method with a short preparation time with a good accuracy (detect trace elements up to ppt level). The equipment was from SHIMADZU and the model was ICPMS-2030LF which has a specific standard deviation of less than 2%. The ICP-MS machine can able to detect multiple trace elements in a single run. Most important reason for using the method is its high accuracy due to its stable plasma source and sensitive detection method [11][12].

All the samples were transferred to the Laboratory for ICP-MS analysis. Digestion was conducted to the water samples with 3ml of 2M Nitric Acid (HNO_3) for dissolving the undissolved metals in water. The digestate was allowed to cool at room temperature. It was filtered using 0.45µm filter paper after cooling. The filtration was necessary to remove the solid particles that was present in the water samples [13]. Before analyzing the collected water samples, a known concentration solution was run to generate a calibration curve for determining the concentration of the obtained water samples using intensity [14].

3. Results & Discussion

The analysis of heavy metals in river water offers important information on environmental contamination and its possible effects on aquatic ecosystems and humans. The concentration of heavy metals in river water samples was evaluated using ICP-MS, a popular analytical method recognized for its precision and sensitivity in identifying trace elements [20]. Three samples (Sample 18,19,20) were used for qualitative analysis in order to provide a general overview of the concentration of all the metals. Because of the ICP-MS method run took a lengthy time, so not all of the samples were chosen for the qualitative analysis. For analyzing the qualitive and quantitative analysis, calibration curve is needed to calculate the concentrations of the heavy metal of the collecting water samples. The calibration curve was generated by running six known solutions.

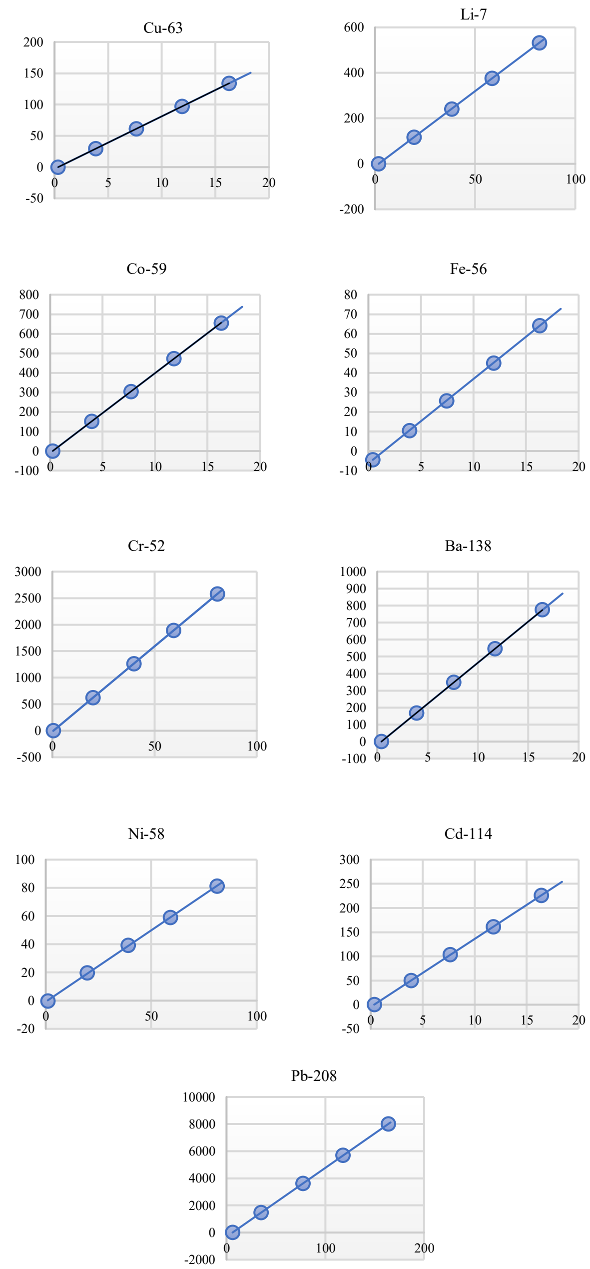


Fig. 2: Calibration curve of various metal for known solution. Each graph has concentration (in microgram per liter) in its x-axis and intensity in y-axis.

According to the qualitative analysis, most of the component's concentrations varied very little among studies.

Table 1: Qualitative analysis of Rupsha, Bhairov & Muyur river for only three samples (sample 18, 19 & 20) in ppb

Sample No.	Al	As	Ca	Cd	Co	Cr
18	33	0.34	230	0.085	0.052	0.21
19	36	0.34	230	0.085	0.052	0.21
20	18	0.34	230	0.085	0.052	0.21

Sample No.	Cs	Cu	Dy	Er	Fe	Hg
18	0.025	0.24	0.036	0.031	0.27	0.06
19	0.025	0.24	0.036	0.031	0.27	0.06
20	0.025	0.24	0.036	0.031	0.27	0.06

Sample No.	K	Mg	Ni	Pb	Sr	Zn
18	29	16000	0.056	0.015	0.17	0.14
19	29	12000	0.056	0.015	0.45	0.14
20	29	18000	0.056	0.015	0.20	0.14

From the data Table 1, a few metals, including Al, B and Mg were on the large range. However, as they are not heavy metals, further research was not conducted on them. Two metals that are chosen for further analysis are the most prevalent heavy metals: Fe and Ni. Due to lack of enough reagents for experimentation and the need of excessive amount of time for qualitative analysis of different heavy metals, the idea for data collection was scrapped for other metals. Thus, only Ni and Fe were selected for additional analysis due to their potentially hazardous effects on the ecosystem as a whole.

Qualitative analysis has been conducted for many metals. Therefore, quantitative analysis was performed only for the specific heavy metals, iron and nickel. Initially, several samples were analyzed to determine the average concentration, and then the average concentration value was compared to the permissible limit established by WHO.

The Concentrations of the heavy metals of the river water (Rupsha, Bhairov & Muyur river) are shown in Table 2. The concentrations of the heavy metals of the river water were studied in order to determine the potential source of the harmful impacts on the ecosystem.

The concentrations of Fe in river water samples ranged from 12.40 to 91.20 ppb. All samples were below the acceptable limit (<300 ppb). Nonetheless, three samples (samples no. 5, 14, and 20) have a significant amount of cadmium. Mining, metal refining, manufacturing, iron pipes, storage tanks, and metal corrosion are the primary sources of iron emissions [16]. Sample 5 was collected very close to the electronics factory. Samples 14 and 20 were collected near the Akij cigarette warehouse and a number of hotels, which may have dumped their rubbish into the river. Thus, there is a high possibility of iron contamination in water. Although iron is a vital mineral, having too little or too much of it in our bodies can have severe health consequences, including an increased risk of infection. Overconsumption of iron can cause excessive iron storage, which can lead to cirrhosis, coronary artery disease, congestive heart failure, bleeding, and gastric ulcers.

Table 2: Concentrations of Heavy Metals (including Fe & Ni) in microgram per liter of 20 samples (ICP MS method)

Sample No.	Concentrations of Heavy Metals in microgram per liter (ppb)	
	Fe	Ni
1	34.60	2.71
2	31.30	2.68
3	53.80	2.08
4	48.20	4.27
5	91.20	5.48
6	48.60	3.13
7	53.80	2.17
8	72.00	3.38
9	35.30	2.49
10	29.00	4.98
11	51.10	53.50
12	37.70	4.34
13	12.40	2.55
14	81.80	4.13
15	41.60	3.41
16	15.90	2.47
17	12.60	2.25
18	16.30	6.38
19	13.70	2.82
20	86.20	44.40

Table 3: Permissible limit of heavy metal ions in water [15]

Heavy Metals	WHO's permissible limit (ppm)	WHO's permissible limit (ppb)
Fe	0.30	300
Ni	0.10	100
Cd	0.005	5
Cu	0.05	50
Cr	0.05	50
Pb	0.05	50
Co	0.1	100
Zn	5	5000
Hg	0.01	10

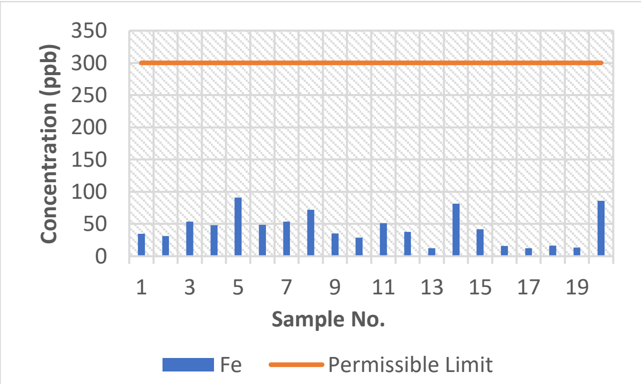


Fig. 3: Comparison of the Fe concentration of all samples with permissible limit

Iron excess can also be poisonous and harmful to organs. Excessive iron levels may also raise the risk of bacterial skin diseases such as cellulitis and abscess [16-17]. Instead of the old chemical technique, biological iron removal plants are now used.

This method utilizes specific bacteria to oxidize the iron content of raw water. The naturally occurring microorganisms oxidized. The microorganism's qualities are required to complete the method here [18].

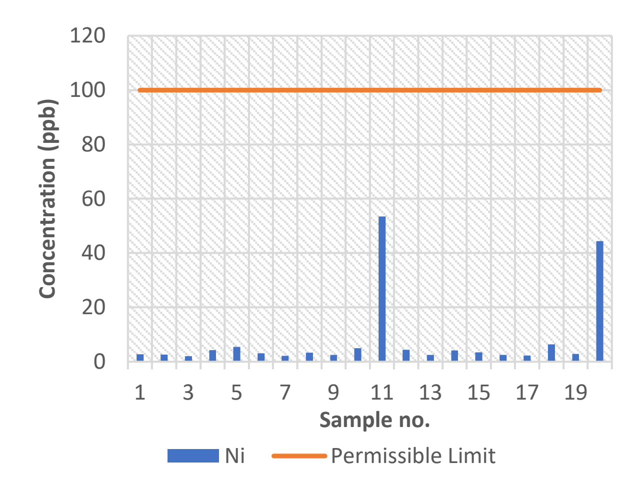


Fig. 4: Comparison of the Ni concentration of all samples with permissible limit

Ni concentrations range from 2.08 to 53.50 parts per billion. All samples had values less than the permitted limit (<100 ppb). However, a significant amount of nickel is found in a few tests (samples 11 and 20). The primary sources of nickel emissions include metal smelting, electroplating, the combustion of fossil fuels (especially coal), and the improper disposal of nickel-containing objects (such as batteries, electronics, and metal goods) [19]. Nickel has gained popularity due to its widespread use as a corrosion-resistant coating [20]. Sample 20 was gathered near the Akij cigarette warehouse and several hotels, which may have discharged rubbish into the river. Sample 5 was collected in close proximity to the agricultural farm and feed mill. Argo-farms discharge garbage directly into the water and use a number of strong medications to boost productivity. Nickel contact can harm human health in a variety of ways, including allergies, cardiovascular and renal disease, lung fibrosis, and lung and nose cancer [21]. Traditional techniques of dewatering sludge include precipitation and the use of polymers in a lamella clarifier, followed by filtering. However, the very complex alkaline zinc/nickel does not like to precipitate; therefore, the bonded metals remain in solution [20].
According to other papers using different equipment such as AAS, the ppm values for nickel and iron were found to be quite high compared to the permissible limit of WHO, whereas the value attained from ICP-MS was significantly lower. ICP-MS delivers more accurate data compared to AAS because of its better photosensitivity, lower detection limits, interference reduction, and better dynamic range [25].

The concentration of heavy metal samples at point sources, such as Seven Rings Cement, Khulna Shipyard Limited, Moyuri Fisheries and Hatchery and Star Jute Mills, was higher compared to that of non-point sources. The reason behind it might be because as the water starts flowing, it spreads over a larger area, leading to greater diffusion and dilution of metals. This results in a lower concentration of heavy metals in nonpoint sources.

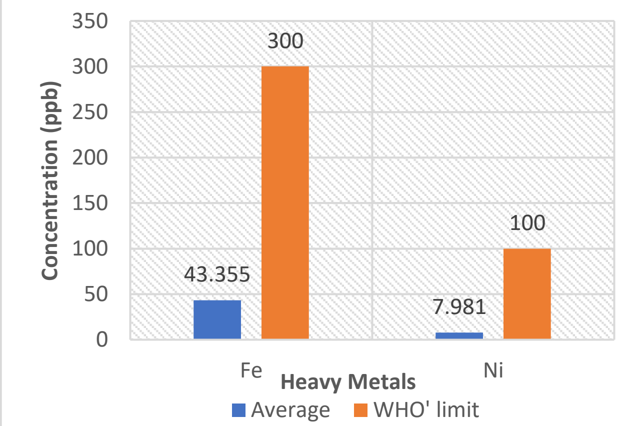


Fig. 5: Bar chart between average concentration of heavy metal over permissible limit

Table 4: Comparison between average concentration of heavy metal over permissible limit

Heavy Metals	Concentrations (ppb)		
	Obtained Data	WHO's permissible limit	Remarks
Fe	43.36	300	Low (around 14.45% of permissible limit) Fe content is present
Ni	7.98	100	Extremely low (around 7.98% of permissible limit) Ni content is present

4. Conclusion

This study indicated that there was low heavy metal contamination in all the water samples of the river's of Khulna. The major source of heavy metals in Khulna is anthropogenic, which includes the discharge of wastewater and sludge from industrial activities. Agronomic and household activities also elevate the level of heavy metals in the adjoining water system. Heavy metals are mostly harmful and pollute the environment. Heavy metals are non-biodegradable and water-soluble, making them easily absorbed by plants and humans. Heavy metal pollution disrupts not only ecosystems but also reduces biodiversity by causing species susceptible to metal toxicity to migrate or die, resulting in a less balanced environment. Excessive heavy metal concentrations in water can lead to acute and chronic ailments, as determined by national and international standards. Iron at high levels may damage organs and cause issues such as gastrointestinal disorders, liver damage, hemochromatosis, and neurological effects, while nickel is associated with allergic reactions and can lead to chronic respiratory issues, kidney damage, and cancer over prolonged exposure. Effective rules and strategies are important to control heavy metal contamination. Identifying regions with elevated amounts of heavy metals is crucial for reducing contamination. As it can be seen, the permissible limit for Fe and Ni assessed in this study was significantly lower compared to the limit imposed by WHO. The concentrations of nickel and iron are within acceptable limits for maintaining a healthy ecosystem. If the concentration of heavy metal exceeded allowable limit remediation procedures such as phytoremediation and chemical treatments should be employed. Existing industries should be encouraged to use safer alternatives to reduce metal use through recycling and conservation, while sustainable irrigation practices should be implemented to nullify the contamination of agricultural lands. Therefore, water quality monitoring is crucial for protecting both human health and the environment.

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Nomenclature

WHO	: World Health Organization
ICP-MS	: Inductively Coupled Plasma Mass Spectrometry
PPM	: Parts Per Million
PPB	: Parts Per Billion