Analysis of heavy metal concentration from sugar mill and its impact on groundwater "a case study of shaheed benazirabad (SBA) Sindh Pakistan"

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Abstract. Shaheed Benazirabad, Sindh, Pakistan, faces significant water issues that endanger human health in its residents. Mismanagement, insufficient facilities, and inefficient management systems exacerbate water scarcity. Consequently, the region experiences water disruptions, waterborne infections, and substantial water wastage. To analyze the heavy metals (HM) concentrations, maximum 35 water samples were gathered from industrial area of Habib Sugar Mill. These samples included spent wash in ponds (n = 3), wastewater in Simnala (n = 4), and (n = 28) groundwater from the industrial area through operational community tube wells, dug wells and open wells were collected by using plastic bottles. The concentration of Cd, Cr, Cu, Fe, Mn, Ni, Zn, As, and Pb were analyzed by flame atomic absorption spectrophotometer (AAS) with a standard burner head under the terms recommended via manufacturer. After analyzing the collected samples of wastewater, Pb, Cd, As, and Ni concentrations were found in excess than the recommended limits set by the PAKEPA. Additionally, the concentrations of Cd, Mn, Ni, Pb, Fe, Cr, and As of groundwater samples were exceeded the guidelines of WHO for drinking water quality, which make it unsafe for consumption. In contrast, the levels of Cu and Zn were within acceptable limits.

1 Introduction

The growing desire for a superior standard of life has triggered a significant growth in household and factory-based techniques, thus a substantial quantity of unpurified waste innate in industrial wastewater directly or indirectly contaminant water bodies [1]. Industrial effluent from various industries such as pharmaceutical companies, oil, gas, petroleum, sugar mills, textiles factories, leathers, steel, polymers, and agrochemicals farming and multiple industries from all over the country generate wastewater which comprises impurities enormously, including toxic and non-toxic material, organic and inorganic chemicals, aromatic compounds, and many other decomposable hazardous material dives into the

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environment. Through the study it is proved that each year 3.4 million people are dying because of the waterborne disease in the result of industrial effluents [2].

Consequently, the industrial discharge from these manufacturing factories exhibits a peculiar quantity of waste such as Dyeing waste, toxic odorous as well as it emits the poisonous mist resulting it is a perceptible health risk for human [3].

The sugar industry is recognized significantly for commercial use worldwide, containing with considerable number of organic contaminants in wastewater. To maintain the volume like quality and quantity both of water various techniques are used which have a crucial contribution in safe water from industrial discharge the implication of potable water employment during the manufacturing procedure generates an equal quantity of wastewater, corresponding to the concentration and formation varied in impurities, demonstrate the relevance competent of stewardship approaches [4].

1.1 Heavy Metals

Heavy metals (HMs) constitute a class of waterborne contaminants celebrated for their profound and enduring hazardous properties [5]. Universally recognized as some of the most menacing and persistent pollutants within aquatic ecosystems, HMs warrant special consideration [6]. Amid the realm of deleterious and resilient waterborne pollutants, heavy metals hold a pivotal status due to their intrinsic peril to human existence, stemming from their toxicity, capacity for bioaccumulation, and sustained presence in the environment [7]. Notably, regions worldwide, particularly in less developed nations, grapple with the critical issue of heavy metal contamination in aquatic environments. This predicament arises from the continuous discharge of inadequately treated wastewater, primarily originating from agricultural and industrial operations, into surface water reservoirs [8] In remote, pristine aquatic settings, the extent of heavy metal contamination inherently remains low, significantly influenced by geological processes such as bedrock and soil weathering, serving as the primary natural source of heavy metals [9]. Heavy metals are neither necessary nor capable of breaking down naturally., and highly toxic substances characterized by a density exceeding 5 g/cm^3, which is fivefold greater than that of water. Heavy metals, even at minimal concentrations manifest substantial toxicity and pose significant human health risk [10]. HV concentrations amplified in drinking water surpassing the standards set by the USEPA, align a major threat to human, environment, aquatic life as well as aquacultural with worldwide consequences [11].

The contaminants commonly identified in research encompass Cr, Fe, Pb, As, Ni, Cd, Co, Zn, Ni, and Mn [12]. "Heavy metals fall into two groups: those that are biologically essential and those that are not. Metals like Al, Cd, Hg, Sn, and Pb, which are nonessential, have no defined biological functions and become increasingly toxic at higher concentrations. Conversely, essential HV such as, Zn, , Cu, Co, Cr, and Ni have important biological roles. "and Fe play critical roles in biologaical processes. Their toxicity arises from imbalances, either excess or deficiency [13]. These metals are major environmental pollutants with significant impacts on human health [14]. The consequences of heavy metal contamination on human well-being are profound, leading to issues like skin damage, respiratory ailments, and cardiovascular problems [15].

2 Research Methodology

This research aimed to evaluate the impact of distillery waste evaporation ponds on groundwater near Habib Sugar Mill in Nawabshah, Sindh, Pakistan. 35 samples of water were gathered. (3 spent wash in ponds, 4 waste water in simnala, and 28 underground samples

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from hand pumps, dig wells, tube wells, shallow, and deep aquifers) were collected at a distance of 2 to 3 kilometers from the main source to determine the heavy metals concentration (Mn, Ni, Pb, Zn, Co, Cr, Cd, Cu, and As) by Utilizing atomic absorption (AAS), after analyses the findings were matched the permissible levels for potable or drinking water as well Industrial effluent set by World Health Organization [WHO] and Pakistan Environmental Protection Agency [PAK-EPA].

2.1 Study Area

The research has been conducted at Habib Sugar Mill, situated in Nawabshah City district Shaheed Benazirabad, Sindh. Pakistan, the population of Nawabshah is about 1195950 (Census 2022). In Shaheed Benazirabad, Rohri canal is the major source of water for irrigation and ground water is the primary source for human consumption. while in cities, both groundwater and surface water are utilized through a water scheme and supply system.

As the city's population rapidly grows, the demand for necessities, including potable water, also increases. Industries like Habib Sugar Mills and the city's sewage system discharge effluents into the canal (Gujar Wah or Simnala) running alongside the city, significantly affecting the quality of both surface and groundwater.

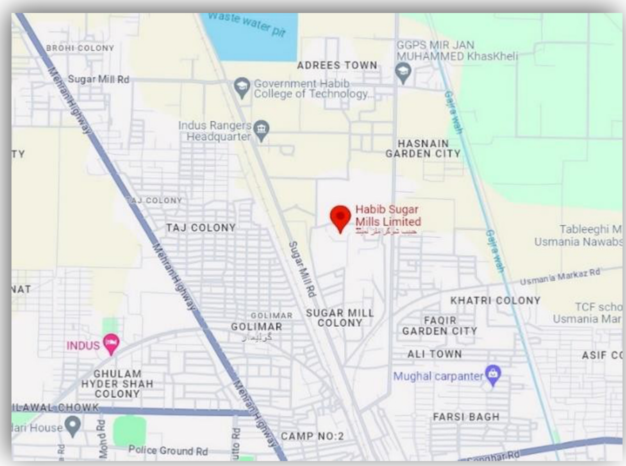

Fig. 1. Google Map for Study Area (Shaheed BenazirabadD, Sindh, Pakistan).

The methodology involved collecting water samples from various sources, diluting them with double- distilled water, and analyzing them using AAS. Samples of water were gathered using pre-washed 1.5-liter plastic bottles. Sampling was carried out three times between January to March, and an average (n = 3) was calculated.

Heavy metals (Cd, Mn, Ni, Zn, Zn Pb, Co, Cr, Cu, Fe, Mn, Ni, and As), were determined by using standard analytical methods. For metal analysis, the samples of spent wash were watered down with (1: 100) double distilled water. Groundwater samples (250 ml) were treated with 1.25 ml of HNO3, and then they were heated in an apparatus named water bath until it is being reduced about 15 ml, and filtered, after that, with distilled water it was diluted to 25ml.

2.2 Chemical Analysis

The chemicals which were utilized were of analytical grade. For preparing 1000nppm stock salts 100 ml of metal salt were dispersed as an appropriate quantity and if needed for further dilution deionized water will be used. By using an air-acetylene flame of atomic absorption spectrophotometer (AAS) with a standard burner head the concentrations of, Pb, Cd, Co, Ni, Cu, Fe, Zn, Mn, and Cr were analyzed specifically the Perkin Elmer A Analyst 800 following by the manufacturer's recommended conditions, by using Win Lab Software via computer, the spectrometer was operated. Sampling analyses were conducted in quadruplicate (n = 4), with an accurate and integration time of 4 seconds and time for delay is also 4 seconds. Arsenic concentration was measured by using the MERCK field test kit for and its concentrations was ranging between 0.05 to 0.300 mg/L. and also it was analyzed in the lab through hydride generation, moreover 10% arsenic samples were determined in the laboratory using hydride generation with the Perkin Elmer Analyst 800 connected to the Perkin Elmer FIAS 100 Flow Injection Systems.

2.3 Interviews and surveys

Assessing the data collected from interviews survey, and water quality testing for heavy metals concentration to write the conclusions regarding the effects of contamination of heavy metals in drinking water affected by sugar industrial effluent. The Question paper was designed to conduct the structured interviews with individuals of the surrounding in the sugar mill to collect the information on the impacts of groundwater contamination on public health. Include questions about human consumption of drinking water, waterborne diseases, agricultural usage, impact on aquatic life as well as aquaculture. Maximum 100 participates participated for interview survey, through this survey the major factors of effects were evaluated for long term and short-term impact. Here is the questionnaires paper.

2.4 Relationship Between Laboratory Report & Survey Report

The research is supported through community survey and interviews, along with laboratory reports, both revealed the substantial influence on groundwater contamination on the residents in the vicinity of sugar mill industry, and suggested for further betterment of the wellbeing.

3 Results and Discussion

The research wrapped up in this thesis was carried out to analyze the effect of sugar mill wastewater and its impact on groundwater. A total of 35 water samples (3 spent wash in ponds, 4 wastewaters samples in simnala, and 28 underground samples from hand pumps, dig wells, tube wells, shallow, and deep aquifers) Samples were gathered at distances of 1.5 to 3 kilometers from the primary source to ascertain the concentration of heavy metals like Cd, Co, Cr, Ni, Pb, Cu, Mn, Zn, and As through atomic absorption spectroscopy (AAS).

The acquired results for groundwater samples and spent wash and wastewater from Simnala were then matched with the acceptable levels established by the World Health Organization (WHO) and Pakistan Environmental Protection Agency (PEPA) for drinking water and industrial effluents.

The average concentrations of copper (Cu) in spent wash were measured 0.2 mg/L, in wastewater, 0.12 mg/L, and in groundwater samples were measured 0.5 mg/L. Cu 0.184

mg/L in spent wash samples surpasses the PAK EPA threshold of 0.5 mg/L for industrial effluents. Likewise, the average Cu 0.124 mg/L in wastewater slightly surpasses the PAK EPA limit. However, the Cu 0.46 mg/L in groundwater samples from the vicinity of the sugar mill is below the World Health Organization (WHO) guideline value of 2.0 mg/L, deeming it safe for drinking, environmental sustainability, and aquatic life.

The average concentrations of cadmium (Cd) in spent wash were measured 0.17 mg/L, in wastewater it was measured 0.1 mg/L, and groundwater water samples were 2.0015 mg/L, respectively. Since the average value of Cd is 0.117 mg/L in spent wash samples, it is higher than the limit set by PAK EPA (Pakistan Environmental Protection Agency) (0.1 mg/L) for industrial effluents. Cd in wastewater is 0.113 mg/L, which meets the PAK EPA's (0.1 mg/L) limit, and the Cd 0.015 mg/L in groundwater samples from the vicinity of the sugar mill is greater than the recommended guideline of WHO value of 0.003 mg/L, which can be considered unsafe for human consumption and poses human health risks like kidney damage and disease, bone fractures and osteoporosis, cancer, neurological damage, reproductive issues, respiratory problems, and cardiovascular disease. Safe for Environmental Aquatic Life and Aquaculture.

The average concentrations of chromium (Cr) in spent wash are 0.95 mg/L, in wastewater, 0.7 mg/L and groundwater samples were measured 0.28 mg/L. Since Cr 0.95 mg/L in spent wash samples is higher than the limit set by the PAK EPA (0.5 mg/L) for industrial effluents, the average value of Cr 0.7 mg/L in wastewater is higher than the PAK EPA (0.5 mg/L). Cr 0.28 mg/L in groundwater samples from the vicinity of the sugar mill, which is higher than the guideline value of WHO of 0.05 mg/L, can be considered unsafe for human consumption and poses human health risks like cancer, respiratory problems, skin irritation and allergic contact dermatitis, kidney and liver damage, neurological damage, reproductive issues, gastrointestinal problems, and environmental risks like soil contamination and reduced fertility. Water pollution (groundwater and surface water), air pollution, accumulation in food chains, and disruption of ecosystem balance. Aquatic life risks include toxicity to fish and other aquatic organisms, bioaccumulation in aquatic food chains, alterations in aquatic ecosystem balance, reduced biodiversity, and impacts on commercial fisheries and aquaculture.

The average concentrations of manganese (Mn) in spent wash were observed 50.54 mg/L, in wastewater, 34.9 mg/L and in groundwater samples it was determined 15.85 mg/L. Mn 50.54 mg/L in spent wash samples exceeds the PAK EPA limit of 2.0 mg/L for industrial effluents. Similarly, the average Mn concentration of 34.9 mg/L in wastewater is above the PAK EPA limit of 2.0 mg/L. Furthermore, Mn 15.85 mg/L in groundwater samples from the vicinity of the sugar mill significantly surpasses the guideline value of WHO 0.4 mg/L. This elevated concentration is considered unsafe for drinking purposes and may lead to health issues such as neurological effects, cardiovascular disease, and bone disease. Additionally, it poses environmental risks including soil contamination, reduced fertility, and water pollution (both groundwater and surface water). air pollution, Accumulation in food chains, Disruption of ecosystem balance. Aquatic life risks, like toxicity to fish and other aquatic organisms, Bioaccumulation in aquatic food chains, alterations in aquatic ecosystem balance, Reduced biodiversity, Impacts on commercial fisheries and aquaculture.

The average concentrations of nickel (Ni) in spent wash were observed 0.12 mg/L, wastewater, 0.16 mg/L and groundwater water samples were 1.6 mg/L. Since Ni 0.16 mg/L in spent wash samples is measured as a belove than the limit of the PAK EPA (0.5 mg/L) set for industrial effluents, the average value of Ni 0.16 mg/L in wastewater is lower than the PAK EPA (0.5 mg/L). Ni 1.6 mg/L in groundwater samples from the vicinity of the sugar mill, which is above than the WHO guideline value of 0.07 mg/L, considered unsafe for human consumption and human health. Human health risks like cancer, respiratory problems, skin irritation and allergic contact dermatitis, kidney and liver damage, neurological damage, reproductive issues, and gastrointestinal problems are safe for environmental, aquatic, and aquaculture life.

The average concentrations of zinc (Zn) in spent wash, wastewater, and groundwater samples were 0.15 mg/L, 0.03 mg/L, and 0.3 mg/L. The average concentration of Zn is 0.15 mg/L in spent wash samples is below the Pakistan Environmental Protection Agency (PAK EPA) limit of 2.0 mg/L for industrial effluents. Similarly, the average Zn concentration of 0.03 mg/L in wastewater is significantly lower than the PAK EPA limit of 2.0 mg/L. Furthermore, the average Zn concentration of 0.3 mg/L in groundwater samples from the vicinity of the sugar mill is below the World Health Organization (WHO) guideline value of 3.0 mg/L, indicating it is safe for human consumption and poses no specific human health risk, the environment, aquatic life as well as aquaculture.

The average concentrations of iron (Fe) in spent wash, wastewater, and groundwater samples were 1.72 mg/L, 1.23 mg/L, and 0.74 mg/L, respectively. The average concentration of Fe is 1.72 mg/L in spent wash samples is below the Pakistan Environmental Protection Agency (PAK EPA) limit of 3.0 mg/L for industrial effluents. Similarly, the average Fe concentration of 1.23 mg/L in wastewater is also below the PAK EPA limit of 3.0 mg/L. However, the average Fe concentration of 0.74 mg/L in groundwater from the vicinity of the sugar mill exceeds the guideline value of World Health Organization (WHO) of 0.3 mg/L, rendering it unsafe for human consumption due to its unpleasant taste and odor. This elevated concentration poses health risks such as liver damage, cirrhosis, heart problems, diabetes, metabolic disorders, neurological damage, and gastrointestinal issues. Nevertheless, it is considered safe for environmental, aquaculture, and aquatic life.

The average concentrations of lead (Pb) in spent wash were observed 1.22 mg/L, wastewater, 0.9 mg/L, and groundwater samples were measured 1.4 mg/L. Pb is 1.22 mg/L in spent wash samples exceeds the PAK EPA set of 0.1 mg/L for industrial effluents. Similarly, the average concentration of Pb 0.9 mg/L in wastewater also surpasses the PAK EPA limit. in wastewater is higher than the PAK EPA (0.1 mg/L). Pb 1.4 mg/L in groundwater samples from the vicinity of the sugar mill is above than the guideline value of WHO of 0.01 mg/L, which can be considered unsafe for human consumption and cause health issues like neurological damage, kidney damage and disease, cardiovascular disease, reproductive issues, gastrointestinal problems, anemia and blood disorders, and cancer, particularly for pregnant women, children, and infants. Environmental risks like soil contamination and reduced fertility Water pollution, air pollution, accumulation in food chains, Disruption of ecosystem balance, Aquatic life risks like toxicity to fish and other aquatic organisms, bioaccumulation in aquatic food chains, alterations in aquatic ecosystem balance, Reduced biodiversity, Impacts on commercial fisheries and aquaculture.

The average value of As 2.5 mg/L in wastewater is higher than the PAK EPA (0.2 mg/L), As is 9.5 mg/L in groundwater samples from the villages of surrounding area of the sugar mill is significantly higher than the guideline value of WHO 0.01 mg/L, which can be considered unsafe for human consumption and cause potential health issues including cancer, skin lesions, and other health issues. Human health risks like cancer (skin, bladder, lung, kidney, and liver), neurological damage, cardiovascular disease, Reproductive issues, Gastrointestinal problems, kidney damage and disease, increased risk of diabetes, and metabolic disorders. Environmental risks like soil contamination and reduced fertility, water pollution (groundwater and surface water), air pollution, accumulation in food chains, and disruption of ecosystem balance. Aquatic life risks like toxicity to fish and other aquatic organisms, bioaccumulation in aquatic food chains, alterations in aquatic ecosystem balance, reduced biodiversity, and impacts on commercial fisheries and aquaculture.

Table 1. Concentration of Heavy Metals in the Spent Wash Samples.

S. No	Parameters	P1	P2	P3	MIN.	Max.	Average
1	Cu mg/L	0.21	0.18	0.16	0.16	0.21	0.184
2	Cd mg/L	0.18	0.17	0.16	0.16	0.18	0.17
3	Cr mg/L	1.01	0.94	0.9	0.9	1.01	0.952
4	Mn mg/L	51.35	50.8	49.6	49.6	51.35	50.54
5	Ni mg/L	0.15	0.12	0.1	0.1	0.15	0.124
6	Pb mg/L	1.31	1.19	1.14	1.14	1.31	1.218
7	Zn mg/L	0.08	0.06	0.05	0.05	0.08	0.064
8	Fe mg/L	1.8	1.72	1.64	1.64	1.8	1.72
9	As mg/L	10	10	10	10	10	10

Table 2. Concentration of Heavy Metals in the Wastewater Samples.

No.	Parameters	W1	W2	W3	W4	Min.	Max.	Average
1	Cu mg/L	0.14	0.12	0.11	0.1 0	0.11	0.14	0.12
2	Cd mg/L	0.14	0.12	0.1	0.09	0.09	0.14	0.11
3	Cr mg/L	0.85	0.76	0.71	0.63	0.63	0.85	0.74
4	Mn mg/L	41.3	38.15	32.25	28.4	28.4	41.3	3.5
5	Ni mg/L	0.09	0.08	0.07	0.05	0.05	0.09	0.16
6	Pb mg/L	1.07	0.97	0.86	0.71	0.71	1.07	0.98
7	Zn mg/L	0.04	0.03	0.02	0.01	0.01	0.04	0.03
8	Fe mg/L	1.52	1.36	1.27	0.86	0.86	1.52	1.23
9	As mg/L	25	25	25	25	25	25	25

Table 3. Concentration of Heavy Metals in the Village Water Samples.

No.	Parameters	Minimum		Maximum		Average
		Villages	Conc. mg/L	Villages	Conc. mg/L	Conc. mg/L
1	Cu	V8	0.13	V23	1.43	0.4
2	Cd	V2	1.29	V8	2.81	1.9
3	Cr	10	0.17	v18	0.41	0.3
4	Mn	V16	9.61	V13	19.85	15.9
5	Ni	V1	0.02	V13	18.42	0.9
6	Pb	V13	0.78	V4	1.71	1.4
7	Zn	V8	0.04	V13	1.93	0.24
8	Fe	V5	0.07	V13	1.13	0.7
9	As					9.5

In water samples from villages 1 and 2, arsenic was found in the highest concentrations. Conversely, in samples from villages 8, 9, 10, 12, 14,16, 17, 19, 22, 23, and 25, arsenic was detected at the lowest levels. The mean concentrations of arsenic (As) in spent wash, wastewater, and groundwater samples were 1.0 mg/L, 2.5 mg/L, and 9.5 mg/L, respectively. The average As concentration of 10 mg/L in spent wash samples exceeds the guidelines which is set by the PAK EPA of 0.2 mg/L for industrial effluents.

4 Conclusion

In the culmination of the above results and discussion, this research highlighted that, the current state of industrial wastewater and its impact on groundwater is rapidly increasing and has significant concern. Industrial wastewater always contains chemically hazardous waste, specifically HM (Pb, As, Cr, Cd, As, Zn, Mn, etc.) 70 % of HM exceed the safe limits set by PAK-EPA and WHO in spent wash, wastewater, and groundwater samples. Copper and zinc levels were within safe level only. and Iron (Fe) level observed above than WHO guideline value in some of the groundwater samples, which is caused for an unpleasant taste and odor. Arsenic (As) concentration was significantly observed above the WHO guideline value in groundwater samples, and with posing a significant health risk for human as well as aquatic lives. Contamination of heavy metals like into the groundwater has substantial health risk to living organisms. Heavy metals like Pb, Ni, As, Cr, Cd, etc. accumulate in the body through consumption and can cause various diseases such as cancer, neurological damage, kidney damage, reproductive problems, developmental delays, cardiovascular disease, respiratory problems, gastrointestinal problems, and many other health risk.

The research concludes that sugar mill wastewater has contaminated the groundwater in the surrounding area with heavy metal concentrations, posing significant health and environmental risks. Urgent action is needed to treat the wastewater and monitor the groundwater quality to prevent further contamination.

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