Water Quality Assessment and Heavy Metal Analysis of Ganga River System and Effluent Water of SIDCUL at Haridwar through Atomic Absorption Spectroscopy

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Abstract: Industrial effluent contains toxic heavy metals that can affect the water quality, human health, aquatic life, and the ecosystem. The contaminated water may able to spread various diseases and health risk for living organisms. This study throws light on the quality of Ganga river water and industrial effluent water of State Industrial Development Corporation of Uttarakhand Limited (SIDCUL) at Haridwar, Uttarakhand, India. Physico-chemical parameters (pH, dissolved oxygen (DO), and temperature) were studied to check the quality of water at study areas. Approximately all the research study areas were observed with the less amount or below the permissible limit of DO. The availability of total heavy metal ions concentration in effluent and river water was analysed by flame atomic absorption spectrometry (AAS). The total six toxic heavy metals (Fe, Mn, Cu, Cd, Zn, and Pb) were tested for their presence in effluent and water samples. The four heavy metals [Fe (0.3 mg/l), Pb (0.01 mg/l), Mn (0.4 mg/l), Cd (0.003 mg/l)] were found above their standard permissible limits in water and effluent as per the guidelines of 2019 of world health organisation (WHO). To balance water supply and demand in a healthy manner, water quality is an important factor.

Keywords: atomic absorption spectroscopy • ganga river • industrial effluent • heavy metals • pollution • water quality

Introduction

Humans and metals are associated with each other since the ancient period of civilization. Day by day humans are majorly dependent on technology and development, even in this modern era of industrialization, humans completely rely on a large number of metal ions for all aspects of their daily life. A large number of various types of metal ions are useful to run the industrial sector, but due to the lack of their balanced concentration many of these metal ions, become toxic to the health of living organisms. However, humans have consumed a large number of metal ions directly or indirectly in the form of micronutrients and macronutrients (Arya et al 2023). Heavy metals are essential trace elements for the body of living organisms. Some of the heavy metals such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and magnesium (Mg), are vital micronutrients and are required for the physiological functioning of organisms at a lower concentration. Essential heavy metals are important constituents of several key enzymes (Arya et al 2023). Apart from these benefits most of the metal elements can be toxic if, they may present above their permissible limit decided by world health organisation (WHO). If humans may be exposed to unbalanced concentrations of any heavy metal, it may cause severe health issues. Therefore, modernization and industrialization have played an important role in promoting metal pollution through dumping of the waste directly into natural water bodies. In India, the standard limit of heavy metals has been regulated by Central Pollution Control Board (CPCB).

Heavy metals are those metallic elements that have a relatively high density approximately ($>5g/cm^3$) (Arya et al 2023; Patil et al 2024)

with relatively high atomic weight (63.5-200.6 g mol^{-1}) (Tchounwou et al 2012). The effluent of industries becomes the major source to spread toxic heavy metal ions into the environment. Metal pollution may spread in the environment through two main important sources, the first is anthropogenic source and the second is natural sources (Arya et al 2023). The anthropogenic sources of heavy metals in water are metal finishing processes such as metal pickling, textile industries, fertilizers, pesticides, paints, plating and anodizing, pharmaceuticals and nuclear power plants, etc. The natural sources of heavy metal include wind-borne soil particles, sea-salt sprays, forest fires, rock weathering, and volcanic eruptions (Tchounwou et al 2012).

The waste effluent of industries mostly contains high concentrations of heavy metals. If this effluent directly come in contact with soil and natural water bodies it may affect the living organism and environment. Arsenic, cadmium, chromium, copper, lead, nickel, and zinc are some most commonly found heavy metals in waste water, that may create risks to human health and the environment (Lambert et al 2000). These metals get deposited in the bottom sediments and remain there for several years. Water effluent naturally contains a broad diversity of metals and each metal may be present at variable concentrations. When excess metals enter fresh water, it leads to a decline in pH due to which the metal solubility and metal ions mobility inside the water has increased. Therefore, metals are considered to be highly toxic in soft waters.

The presence of excess concentration of heavy metals (above their permissible limit) can form complex compounds within the cell, that become toxic to human- health and cause multiple numbers of diseases. Kaur and Kaur (2014) estimated that the number of deaths due to metal contamination in India was 580 people per day in 2014. But according to the "composite water management index" (CWMI) report, released in 2018 through NITI

Aayog this death toll reached up to about 2 lakh people every year (Pib.gov.in). The only reason for this increased number of deaths is the inadequate access to safe water, that may lead to several lethal diseases to human. As metals are non-biodegradable, they can cause environmental damage and leads to bioaccumulation in organisms. The ionic form of metal is generally considered more toxic because it can interact with other ions, form compounds, and have more bioavailability. According to Dash et al (2013) and Johnsen et al (2019), the toxicity of the metals depends on their concentration, chemical makeup, length of exposure, and source. It is easy for heavy metals to penetrate the food chain and build up in higher organisms. Generally, they cause weakness, headache, abdominal pain, dysfunction, vascular damage, damage to the central nervous system and body organs, gastrointestinal and kidney dysfunction, and sometimes cancer (Anjali Patil et al 2024).

If the effluent of these industries/waste water remains untreated in the atmosphere and directly drains into the freshwater bodies and soil, then the situation becomes vulnerable to humans, animals, aquatic and terrestrial life. Globally almost all the developed or developing countries are working on this serious health concern, as it can affect the growth, economy, annual planning, availability of food, and gross development of a nation (Dash et al 2013). Therefore, metal pollution creates an alarming situation for humans and becomes a major concern of present era (Vishwakarma et al 2020, Vishwakarma et al 2021, Vishwakarma et al 2023, and Patil et al 2024). The present study helps to analyse the presence of toxic heavy metal ions in the industrial effluent of SIDCUL and Ganga river water at Shri Parshuram Ghat, Haridwar, Uttarakhand (India) through atomic absorption spectrometry (AAS) and their impact on water quality.

Material And Methods

Study area: The study is focused on evaluating the quality of the water of the Ganga river at Shri Parshuram Ghat, and the Industrial effluent of SIDCUL, in Haridwar Uttarakhand. This study has covered polluted effluent water and clean Ganga water in Haridwar for analysis. Table 1 mentions the geographical coordinates (longitude and latitude) of every sampling point.

Table 1. Details of effluent and Ganga water sampling locations

Sampling sites	Sample Code	Type of sample	Latitude	Longitude	Activity/ Establishment
Site I	GW	Ganga stream water	29.93253006	78.14009652	Ganga ghat, Temple, solid waste dump sites, liquid waste exit, residential and commercial area, vehicle traffic, parking, market, recreational, vegetation
Site II	RW	Running sewer water containing industrial effluent	29.95875674	78.05718843	Solid waste dump sites, Industrial effluent dump site, vehicle traffic, commercial and residential area, market, industries, pharma factory, sewerage plant, seepage, garages, metal fabrication, cultivation
Site III	SW	Stationary pond containing industrial effluent	29.96105991	78.05762999	Solid waste dump sites, Industrial effluent dump site, commercial area, market, industries, pharma factory, sewerage plant, seepage, garages, metal fabrication, cultivation

Collection of samples

This study was carried out in March, 2021. The sampling procedure was performed with the collection of Ganga water and effluent water samples from various sites (Figure 1, 2 and 3). The samples of water were collected from 3 different sites of Haridwar district of state Uttarakhand, India. A composite sample was prepared by the collection of three grab samples from different places of each site (surface, depth of 15-25cm, and edge) named as stationary pond, running sewer, and Ganga water. The first sample was collected from the river stream of Ganga at Shri Parshuram Ghat, Haridwar (Site 1, GW) (Figure 1 and 2). Second sample was collected from the running sewage of industrial water effluent at SIDCUL, Roshnabaad (Site 3, RW) (Figure 3). Third sample was collected from the stationary water of a pond situated in SIDCUL, Roshnabaad (Site 3, SW) (Figure 3). The ecological significance and changes caused by humans at each site were taken into consideration while choosing the sampling locations. In order to prevent heavy metal precipitation in the samples, the collected unfiltered samples were kept in plastic sample bottles by adding concentrated HNO_3, and they were then promptly stored inside the cooling box. In order to check the concentration of various heavy metal ions, all the collected samples were sent to the laboratory for AAS.

Figure 1. Site 1, (A) Shri Parshuram Ghat, Haridwar; (B) Polluted site at ghat; (C) Polluted bottom of Ganga River

Figure 2. Pictures indicating polluted areas and waste water flow in Ganga approx. 500m away from site 1 (Shri Parshuram Ghat, Haridwar)

Figure 3. (A) Site 2, Running effluent water in SIDCUL; (B) Site 3, Stationary industrial effluent water in SIDCUL

Analysis of physico-chemical parameters

The quality of different types of raw water (surface, below the surface, and groundwater) is commonly affected by multiple pollution elements (Rana et al 2018). Therefore, regulation and maintenance of water quality are very important for environmental concerns. The physiological and biochemical properties of water are combined to form water quality. In India, Central Pollution Control Board (CPCB) has regulated these standards of the applications of water for large number of purposes based on water quality. Industries are one of the major factors that affect the quality of water. Industrial waste water is released into natural reservoirs either partially or incorrectly treated, or left untreated. Therefore, the analysis of physico-chemical parameters of the water samples such as temperature, pH, dissolved oxygen (DO), colour, odour, and taste were important to determine the quality of water in an industrial

area of SIDCUL and the nearby region of Ganga river. The assessment of these parameters was done according to the CPCB guidelines (www.cpcb.nic.in) and APHA methos (APHA, 2017) in triplicates. The colour of river water and effluent water was deeply observed. As the Ganga river has been connected with great religious beliefs in India therefore, the taste of GW was checked by drinking it. The taste prediction of the RW and SW was not possible as these were the highly toxic and polluted sites due to presence of effluent waste water. According to CPCB, the dissolved oxygen content of normal water should be at least 3.5 mg/l at all times of the year, and ideally, it should be at least 5.0 mg/l or 60% of the saturation value.

Analysis of heavy metals
An approach for figuring out how much of a specific metal element is present in a sample is called atomic absorption spectrometry, or AAS. The functional components of the AAS apparatus are the atomizer and monochromator instruments. AAS is a widely used and trustworthy method for determining the amounts of heavy metal ions. The identification was conducted using the Varian AA 240 atomic absorption spectrophotometer. The method was used to quantify the concentrations of lead (Pb), manganese (Mn), zinc (Zn), copper (Cu), iron (Fe), and cadmium (Cd). Every sample was processed in order using its standards.

Results And Discussion
Analysis of physico-chemical parameters

The results of average measurement of significant physicochemical parameters including temperature, pH, DO, colour, and odour are given below (Table 2).

Table 2: Physico-chemical properties result of collected samples

Name of sample	Temperature (^{0}C)	Odour of water	pH	Taste	Dissolved oxygen (mg.l^{-1})	Colour of water/effluent
GW	16.6	No odour	7.5	Similar to Mineral water	4.5	Transparent
RW	17.4	-	7.8	-	4.1	Light black, quite transparent
SW	19.8	-	8.0	-	3.9	Dark black with algal blooms

Temperature: The majority of waste water treatment procedures incorporate biological systems that are temperature-dependent, hence temperature evaluation is crucial. Waste water typically fluctuates in temperature with the time of year and region. The temperature can change from around 7 ^{0}C to 18 ^{0}C in colder regions and from 13 ^{0}C to 24 ^{0}C in warmer regions. As the samples were collected in summer therefore, the temperature of all the three samples falls between the range of 16 ^{0}C -20 ^{0}C.

pH (Hydrogen ion concentration): The negative logarithm of the concentration of H+ ions is known as pH. Thus, the power of hydrogen is the justification for the meaning of the term pH. In comparison to Ganga water the turbidity is less and water is transparent. Turbidity is found higher and water is not transparent in the samples collected from the running sewer and stationary water pond.

Alkalinity or acidity is a measurement of pH for any specific water sample. Although pH is the most basic and significant factor because most chemical processes in any aquatic ecosystem are controlled by variations in pH. Since these species are sensitive to variations in alkalinity, highly acidic or alkaline environments would be fatal to aquatic life (Shuter et al 1987). Therefore, controlling or regulating alkalinity should be the primary goal of any biological processing strategy. Furthermore, at a certain pH, the dangerous concentration of heavy metals rises significantly. Alkalinity is, therefore, a key factor to consider when assessing the condition of industrial wastewater. The standard allowable limit set by CPCB for the release of environmental contaminants from the pharmaceutical sector is a pH value of 6.0–8.5. The wastewater samples for the Haridwar district in the present investigation had pH values ranging from 7.5 to 8.0 at each of the three study sites. Table 2 shows that the SW wastewater sample from Site 3 had the highest recorded pH value, which is 8.0. The site 1, GW water sample had the lowest pH value, 7.5. All of the areas' average pH readings were found to be within the standard acceptable limit. Every site's average pH value was discovered to be within the standard permissible limit. From the pH analysis of water bodies located in Haridwar district, It is evident that drug manufacturers in this region are properly treating their waste effluent water before releasing it in order to maintain pH. However, the required pH of drinking water should be neutral but the estimated pH of site 1 (GW) is slightly basic that alarming all of us for its proper maintenance to avoid any major problems in the future. The pH of remaining sites 2 and site 3 is basic may be due to the presence of algae. Hill (2015), was suggested that the high value of pH in effluent water is mostly created due to presence of algae. Therefore, controlling the population of algae may prevent most causes of high pH in effluent.

Dissolved oxygen (DO): A broad range of aquatic organisms may use the atmospheric oxygen that dissolves in the river water and wastewater disposal region to breathe. The number of plants growing in the water, its temperature, the presence of rocks or other obstructions in the way, and the flow of water all affect the amount of oxygen present. Carbon dioxide is taken up by plants and released as oxygen; but, if there are too many plants, the oxygen will be completely consumed by bacteria during the decomposition process when the plants die. In comparison to very warm water, very cold water has a larger amount of oxygen. This may lead one to believe that wintertime water is high in oxygen, however this is false. Water bodies are practically sealed off during the winter when ice covers them, allowing very little oxygen from the environment to reach the water.

The oxygen level inside the water bodies changes with depth. For shallow areas such as pond, lake, and waste liquid effluent dumping sites in deep water, As, we descend more into water bodies, the amount of wind decreases and the oxygen content decreases. In all the deep-water systems, oxygen is generally very less in the bottom where water meets the sediment or mud (Kannel et al 2007). This is a result of the large number of living things and microorganisms that breathe and live in the sludge. Dead matter that sinks to the bottom and consumes oxygen is broken down by these bacteria and animals. Fish and other animals may suffocate and expire if the water's oxygen content is too low. Large-scale industrial expansion, extensive fertilizer usage, and human waste disposal can quickly contaminate water supplies and cause oxygen shortage. In general, dissolved oxygen concentrations in healthy water should be between 80 to 120

percent and greater than 6.5-8 mg/l (Wetzel 1983, Horne and Goldman 1994).

According to this data, the recorded DO values for all three sites are somewhere between 3.9 and 4.5 mg/l. The estimated DO of Site 1 (GW) was 4.5 mg/l. As the sample GW was collected from the Ganga river, therefore, the low DO values of this site have created a huge concern. Ganga is a holy river and the peoples have lots of religious beliefs for Ganga. The water of Ganga has been used for so many religious purposes and for medicinal aspects too. This degrading quality of Ganga water is not showing a good sign for the health of this river. This is the largest river in India that crosses so many states across the country and provides water to about 40% of the Indian population across 11 states. At Haridwar this river enters the plain region of Uttarakhand state, in the beginning of its long journey the degrading quality of its water is not a good sign for our health and religious beliefs. That may lead to a devastating condition in the future. The biggest reason for pollution in this river is Industrial contaminants, human waste, and various religious activities. Therefore, today Ganga is considered to be the fifth most polluted river in the world (Flynn 2016). This pathetic situation of Ganga may poses significant threats to human health and environment. The estimated DO of Site 2 was 4.1 mg/l which shows that the DO of this site is below the standard limit and not providing favourable conditions for the survival of aquatic life. Site 3 has been recorded with the lowest DO i.e., 3.9 mg/l, it is indicated that this water body has a very low level of oxygen, and survival of any aquatic organism is difficult at this place. The low level of DO shows that this site has a high bacterial load and microbial activities. As the high number of algal blooms have been noticed on the surface of the water, therefore, it could be the important reason behind the less DO at site 3. As the algae die and decompose, this process consumes dissolved oxygen (Butler and Burrows 2007). This can result in insufficient amounts of dissolved oxygen available for fish and other aquatic life. Industries in this area have suggested that they should work on the proper discharge of their waste water concerning DO and other important physico-chemical factors. The dumping sites of effluent in this area needs a huge attention and improvement for their treatment and cleaning strategy to maintain the hygiene and water quality.

Colour: Color is a qualitative indicator used to assess the pollution level in industrial effluents and water. The shade of dove grey indicates that the wastewater has accumulated over time or has undergone some degree of degradation (Gupta et al 2018). Extreme bacterial breakdown occurring in anaerobic circumstances is reflected in the dark gray or black color of wastewater. According to Gupta et al (2018), waste water's black color indicates the production of several sulfides. Therefore, the visible transparent colour of GW water was considered as less contaminated or polluted on the basis of its appearance. The black colour of RW and SW reflected the extreme bacterial decomposition under the anaerobic condition with the formation of various sulfides.

Analysis of heavy metal ions: The metal values in waste water samples of the study areasi.e., Shri Parshuram Ghat and SIDCUL, Haridwar were determined through AAS. The obtained results of the metal analysis were compared with the standard limits of metals for water as per the guidelines. The details of obtained results are given in Table 3. According to guidelines of WHO, the standard permissible limit of metals for water are Fe (0.3 mg/l), Zn (5.0 mg/l), Cu (2.0 mg/l), Pb (0.01 mg/l), Mn (0.4 mg/l), and Cd (0.003 mg/l). The mentioned results have been showing that 4 metal ions viz., Fe, Cd, Pb, and Mn are found above their permissible limits

approximately at all the three sites. That is an alarming situation and may harm the environment and human health too.

According to Meszaroba et al (2019), iron (Fe) and manganese (Mn) are two of the most common and vital trace elements that are needed for cellular homeostasis, development, and numerous physiological activities as well as appropriate body growth. The proteins that include heme are the other type of Fe, which is found in Fe-sulfur cluster-containing proteins as a cofactor.

Table 3. AAS Results of collected water samples

Heavy metal	Standard permissible limit of WHO in 2019 (mg/l)	Name of the Samples	Detected metal concentration (mg/l)
Iron (Fe)	0.3	GW	1.949
		RW	0.776
		SW	5.285
Zinc (Zn)	5.0	GW	0.0219
		RW	0.2780
		SW	0.2629
Copper (Cu)	2.0	GW	0.041
		RW	0.120
		SW	0.117
Lead (Pb)	0.01	GW	0.18
		RW	0.32
		SW	0.27
Manganese (Mn)	0.4	GW	0.203
		RW	7.954
		SW	0.425
Cadmium (Cd)	0.003	GW	0.025
		RW	0.126
		SW	0.039

Heme-Fe-containing proteins include cytochromes, hemoglobin, peroxidase, and catalase. Fe, primarily supports cellular respiration, electron transport, and oxygen transport (Mezzaroba et al 2019). The daily requirement of Mn is provided by dietary sources, which also supply the complete quantity required to regulate many critical physiological functions, including blood sugar management, bone formation, reproduction, immunological response, and the metabolism of lipids, proteins, and carbohydrates. The primary roles of Mn include as a cofactor in a variety of cellular and metabolic processes, neurotransmitter synthesis and metabolism, and neuronal and glial function (Mezzaroba et al 2019). However, a toxic Fe overload can result in internal haemorrhage, vomiting, nausea, upset stomach, and in extreme instances, even a coma (Daram et al 2005). Similarly, an excess of Mn leads to oxidative stress, inflammation, and problems with cognition and reproduction. It may cause "manganism," a disorder that resembles Parkinson's disease (Mezzaroba et al 2019).

Cadmium (Cd) is another extremely dangerous element whose effects are more acute on the liver and kidneys. This may be because these tissues are able to manufacture Cd-inducible proteins called metallothioneins, which form strong connections with cells to protect them from the damaging effects of cadmium ions (Genchi et al 2020). Many malignancies, including those of the breast, prostate, nasopharynx, lung, pancreas, and kidney, may be linked to environmental exposure to Cd. According to the findings of some recent research, Cd can alter mammalian cells in ways that carry significant pathogenic hazards, such as the growth of several kinds of cancer. The risk of osteoporosis may also be increased by Cd (Genchi et al 2020). Lead

(Pb) is an additional very hazardous metal that has been connected to issues with bone development and health. Lead poisoning at high concentrations can cause stunted growth in kids. Osteoporosis develops as a result of lead exposure (Wang et al 2009). Pb is also thought to be naturally carcinogenic to humans. Increased blood lead concentrations have an impact on newborns' and kids' postnatal development, behaviour, puberty delays, and hearing. Pb damages the kidneys, heart, reproductive system, and central nervous system (CNS) in adults. It might prevent the fetus from growing normally throughout pregnancy (Kumar et al 2020). Narin et al (2000) were also done analysis of water sample to check metal concentration through flame AAS. This method was used to determine presence of Cu, Cd, Pb, Ni, Mn, Co, and Cr in samples of water. In a previous study large number of heavy metals such Cr, Mn, Fe, Co, Au (III), Cd (II), Ni, Cu, Zn, Cd and Pb were detected in water samples (Mahmoud et al 2010). Cu (II), Fe (III), Mn (II), Ni (II), Pb (II), Pd (II), Co (II), Cr (III), and Zn (II) are some metals that were identified from aqueous solution through AAS (Kenawy et al 2000). Padilha et al (1999) revealed that heavy metals such as Cd (II), Co (II), Cu (II), Fe (III), Ni (II), Pb (II) and Zn (II) are present in natural water and determined via AAS. The study of Islam et al (2016) was investigate the contamination level of waste water in the Kushtia industrial region of Bangladesh. This study results the presence of some toxic metals like Pb, Cu, Mn, Cd, Cr, in effluent water.

Conclusion

The water quality of the effluent water and Ganga river is based on the location and seasons of the sampling sites. This data was collected just after the lockdown and first wave of the pandemic COVID-19. During that period various manufacturing activities, social interaction and religious activities was limited or restricted by the government as per the instructions of WHO. Still, the detection of toxic metal pollutants in restricted period of the lockdown is a huge concern. That may indicate that the situation could be worst in normal situation. According to the result data analysis of selected physico-chemical parameters, the condition of water resources is not found healthy and satisfactory in district Haridwar, Uttarakhand. The analysis of these factors has majorly contributed to the study of the water quality at contaminated sites. Eventually, the analysis indicated that the river water quality is slightly polluted and metal-contaminated. The availability of industrial areas near the river system may majorly contribute to affecting the quality of river water. This polluted water affects both environment and the health of living organisms. Therefore, proper treatment of industrial effluent and polluted water resources is necessary to avoid water pollution. The regulation of industrial discharge and industrial activities by the government and locals may also suggested to maintain the water quality.

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