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Analysis of Heavy Metal Concentration in Groundwater and Surface Water in Unnao Tehsil, Uttar Pradesh, India

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Abstract

Water pollution and its consequences are among the most significant topics for research and debate. The anthropogenic contamination of water is not just restricted to surface water bodies but has now percolated to the groundwater too. Industrial sewage and runoff are some of the major causes of such contamination. Industries like tanneries that are heavily dependent upon water and chemicals pose an additional hazard to water quality. Heavy metal compounds used in the industry, containing nickel, cadmium and chromium, have contaminated the water sources and thus have become part of our food chain. The present study examines the pollution implications of industrial sewage and contamination by the leather industry of Unnao Tehsil, Unnao District of Uttar Pradesh. The study is primarily based on 12 water samples collected from different sources and their analysis based on 14 water analysis parameters, of which 8 are heavy metals. The study has found a high concentration of cadmium, nickel and chromium in the groundwater, with very high Total Dissolved Solids (TDS) in some samples. The seepage of the tannery sewage and sludge is considered the major reason. The groundwater samples near the tanning region have shown overall higher contamination. The water samples from Common Effluent Treatment Plants (CEPT) are satisfactory, though their TDS is quite high. Changes observed between the pre-monsoon and post-monsoon differ in intensity and distribution for most metals. These variations are due to increased seepage during the post-monsoon period in some cases and dilution in the pre-monsoon period in others. The study highlights the anthropogenic factors causing contamination of heavy metals in water, as significant correlations exist among the metals. The river Ganga is found to be most contaminated with high levels of chromium (7.18 – 5.01 mg/l) across the seasons, with higher quantities downstream, indicating influx of the metal from the study area. The contamination and pollution of the ground and surface water sources need special attention and planning for mitigation and clean-up.

Keywords: Water Pollution; Leather Industry; Industrial Sewage; Water Analysis; Heavy Metals; Unnao; Uttar Pradesh; India

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Introduction

Water is an invaluable resource for life and all other activities on the earth since it exists in all three physical forms—solid, liquid, and gas. The five elements of life, as described by Ayurveda, are *Prithvi* (Earth)*, Agni* (Fire)*, Jal* (Water)*, Vayu* (Air) and *Akash* (Space). 70 per cent of the human body consists of water. Some animals, like jellyfish, are 99 per cent water. Water is the most significant component of the biosphere since it is necessary for the survival of all living forms and aids in the movement, circulation, and cycling of nutrients throughout the biosphere. With the increase in population and industrialisation, there has been a significant decline in water quality. Although water, like other natural substances, can purify itself during the recycling process, this ability deteriorates when humans add too many unfamiliar, unwanted compounds to the water (Mengistie et al., 2016). With the onset of industrialisation and the scientific revolution, new synthetic materials and heavy metal compounds have been introduced to the drinking water sources through seepage and discharges, contaminating the water and rendering it unusable for life forms.

According to Shireen et al. (2018), water pollutants are considered hazards if they have the potential to harm human health. Some of these heavy metals may be unsafe and have negative physiological, physical, and mental impacts. These outcomes differ depending on the metal, its dosage, how it is administered, and the individual involved (Jaishankar et al., 2014). Some people exhibit morbidities early, some later, and some may not exhibit them at all. These metals have an impact on people in such a way that their build-up in the body causes a decline in both their physical and mental health (Gaur et al., 2012). A total of 12 poisonous heavy metals, including lead, copper, aluminium, arsenic, cadmium, nickel, and mercury, interfere malevolently with the body's enzyme systems and metabolism, while the body requires about 70 friendly trace elements, also known as heavy metals (Schafer et al., 1985). They are well-known environmental pollutants owing to their toxicity, longevity in the atmosphere, and ability to accumulate in the human body via bioaccumulation (Mitra et al., 2022). Mercury, nickel, lead, arsenic, cadmium, aluminium, platinum, and copper are a few of them. Heavy metals can become strongly toxic by mixing with different environmental elements, such as water, soil, and air, and humans and other living organisms can be exposed to them through the food chain (Mitra et al., 2022). These heavy metals can be extremely hazardous and have no physiological use in the body (Gaur et al., 2012). If heavy metals enter and collect in body tissue more quickly than the body's detoxification mechanisms can eliminate them, a progressive build-up of these toxins will occur. The body tissues can become toxic without high-concentration exposure, and with time, the concentration can rise to toxic levels (Gaur et al., 2012). Blood and cardiovascular, endocrine (hormonal), energy production pathways, enzymatic, gastrointestinal, immune, nervous (central and peripheral), reproductive, and urinary systems are among those in which toxic metal elements can cause impairment and dysfunction (Gaur et al., 2012).

Chromium (Cr) is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. The excessive concentrations of this metal ultimately destroy crops and impart serious health hazards in human beings by entering through the food chain if such polluted effluents are employed for irrigation without proper wastewater treatment (Vernay et al., 2007). Low-level exposure can irritate the skin and cause ulceration. It is a carcinogen and causes respiratory problems if inhaled (Mitra et al., 2022). Long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. It often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Gaur et al., 2012). It can damage DNA in several ways, including DNA double-strand breaks (DSBs), which generate chromosomal aberrations,

micronucleus formation, sister chromatid exchange, formation of DNA adducts and alterations in DNA replication and transcription (Matsumoto et al., 2006). Cadmium (Cd) in humans, with long-term exposure, is highly toxic; it causes 'itai-itai' disease, a painful rheumatic condition; it causes hypertension and adversely affects the cardiovascular and gastrointestinal systems. High exposure can lead to obstructive lung disease and has been linked to lung cancer and damage to humans' respiratory systems (Gaur et al., 2012; Mitra et al., 2022). During acute exposure, it accumulates in the liver and is linked to a variety of hepatic dysfunctions and causes liver failure and therefore can increase the risk of cancer (Mitra et al., 2022). Nickel (Ni) has many adverse effects on humans, causes allergies, nasal and lung cancer and kidney and cardiovascular diseases owing to the inhalation of contaminated air (Genchi et al., 2020). Small amounts of copper (Cu) and zinc (Zn) pose no hazards and are, in fact, essential for human health as well as the growth of plants and animals (WHO, 1996; APHA, 2005). While copper is vital for human survival, excessive intake can lead to adverse effects on the liver, kidneys, and stomach, and may result in anaemia (Gaur et al., 2012). Additionally, excessive copper concentrations in drinking water can negatively impact its taste (Omer, 2019).

Since the tanning industry depends so heavily on water for its operation, this risk has long been related to the sector. The tanning industry is one of India's most polluting sectors. According to the Central Pollution Control Board (CPCB), 12 of India's 88 industrial zones, or "critically contaminated industrial clusters/areas," are tanneries. Pollution is created during several of the sub-processes of the tanning process since 175 different chemicals, both organic and inorganic, are used (Schjolden, 2000). Some of the most common chemicals used in the tanning industry are sodium chloride (NaCl for hide salting), calcium hydroxide ($Ca(OH)_2$ for liming), sodium sulphide (Na_2S for hair removal), ammonium salts, acids (most commonly used is sulphuric acid (H_2SO_4)), magnesium oxide (MgO), sodium bicarbonate ($NaHCO_3$) and chromium (III) oxide (Cr_2O_3 for tanning). Other chemicals include biocides, surfactants, enzyme preparations — trypsin, amylase, pepsin, lipase, bactericides, soda ash, preservatives, lime, caustic soda, acids, acid salts, ammonium chloride, ammonium sulphate, oropon, formic acid, oils, grease, dyes, phenolics, melamine, acrylics, polymers, naphthalene, etc. Some of these chemicals, such as chromate and dichromate salts, ethanol, benzene, toluene, aniline, butyl acetate, sulphuric acid and ammonium hydrogen sulphide, are considered carcinogenic (IARC, 1987; Budhwar et al., 2005; Subramani et al., 2010). The pollution load from the tanning procedure is 50% greater than the weight of the finished hides. Numerous academics have reported that tanneries are responsible for the soil and water contamination in Unnao and other tanning regions in India and abroad (Arif et al., 2020; Gupta et al., 2018; Mengistie et al., 2016; Hansen et al., 2020; Hutton & Shafahi, 2019; Patel et al., 2021; Reda, 2016; Parveen et al., 2017; Tadesse & Guya, 2017; Saxena et al., 2020). Therefore, the problem of pollution in the tanning area is not new; it has existed for a very long period. The most urgent issue about tanneries has been the rise in chromium content in soils and groundwater. However, additional factors such as altered soil and water pH, high TDS, high calcium content, high levels of heavy metals, and others are also connected to it.

The present study deals with groundwater and surface water contamination in Unnao Tehsil, which houses a tanning industry. The objective of the present study is to find the extent of water pollution in groundwater and major surface samples. The study further aims to analyse the seasonal variation of the parameters in the samples. The samples were analysed for both pre- and post- monsoon. Water samples were collected in both the pre-monsoon and post-monsoon seasons to measure seasonal variations in physico-chemical characteristics and pollutant concentrations. This enables the evaluation of the impact of monsoonal rainfall, groundwater recharge, pollutant seepage with water and surface runoff on water quality in the study area. In this study, the pre-monsoon

samples are collected in April (before the onset of rains and the effect of the previous monsoon has diminished) and post-monsoon in December (after the monsoon has ended and recharge effects are visible).

Study Area

Unnao District is located on the left bank of the River Ganga, in the Lucknow Administrative Zone of Uttar Pradesh. The district, with Kanpur Nagar, houses one of the largest tanning industrial areas of the country. The present study deals with Unnao tehsil of the district, which has all three tanning-dominated industrial areas of the district. The Unnao tehsil consists of three blocks: Sikandarpur Karan, Sikandarpur Sarosi, and Bichhiya. There are three industrial areas in Unnao Tehsil. The oldest is the Uttar Pradesh State Industrial Development Corporation (UPSIDC) Eastern Unnao Industrial Area, which has the most diverse industries and is home to most allied businesses as well as leather factories. The other two are the Banthar Leather Technology Park (BLTP), which is solely dedicated to the production of leather and the Akrampur-Chakrampur Industrial Area (ACIR), which is a private area with other businesses like steel and chemicals as well as leather factories. While the UPSIDC and BLTP each have a functional Common Effluent Treatment Plant (CETP) – CETP Unnao and CETP Banthar, the factories in the ACIR oversee cleaning the industrial sewage through Effluent Treatment Plants (ETPs) located within the industries, before disposal.

Methodology

The methodology of the study aimed at the assessment of the contamination in the various types of water bodies of the tehsil with consideration towards their association and proximity to the tanning areas. To understand the impact and spread of the contamination, the samples were distributed throughout the tehsil. Twelve samples in total were taken twice, from the same sampling stations, once in the post-monsoon and then again in the pre-monsoon. There are six surface water samples and six groundwater samples. Two samples from the River Ganga, two industrial sewage samples and two CETP outlet water samples were among the six surface water samples. Upstream samples of the River Ganga were collected from village Katri Rautapur, and downstream samples were collected from village Katri Bediya Khera. The two sewage samples were taken from the industrial drain of ACIR in Galgalaha village and the Loni Drain at Bypass Bridge near CETP Unnao (Table 1). From CETP Unnao and CETP Banthar, the CETP outlet samples were collected. The six groundwater samples were gathered from the villages of Chandpur, Hadha, Algangarh, Bhavdevna, Maswasi, and Satan. Maswasi, Chandpur, and Algangarh are close to the industrial areas, whilst the other villages are farther away. All the water sampling stations are shown in Figure 1 and Table 1. Protocols related to the collection, preservation and testing of the samples using reagents were followed for all the samples.

The 14 parameters tested include colour, odour, potential of hydrogen (pH), total dissolved solids (TDS), dissolved oxygen (DO), 5-day biological oxygen demand (BOD_5), total chromium (Cr), cadmium (Cd), iron (Fe), copper (Cu), nickel (Ni), manganese (Mn), zinc (Zn), and calcium (Ca) (heavy metals). Various other scholars and researches have worked on similar parameters while working on the tanning industry (Chandra et al., 2009; Dwivedi & Vankar, 2014; Dowlath et al., 2021; EcoFriends, 2002; Grosser & Celery, 2019; Jothilingam et al., 2020; Maurya et al., 2019; Sahu et al., 2007; Sinha et al., 2016; Swaroop et al., 2018; Thanikaivelan et al., 2005). Biochemical parameters of DO and BOD_5 are not tested for groundwater samples. pH is affected when there are any additions in the samples; many impurities impart colour and odour to the water and are the first things that can be noted about the water quality. Water bodies laden with industrial impurities have high TDS, and their DO and BOD are also affected. Chromium is associated with tanneries, as its salts are used as tannage, and other heavy metals are present as impurities in the tannage salts and are used in the finishing processes.

Table 1: Water Sample Description			
Sample Station No.	**Source**	**Sample Location**	**Source Type**
1	**Groundwater**	**Village Hadha**	**IM-II 130'**
2		**Village Alangarh**	**IM-II 110'**
3		**Village Bhavdevna**	**IM-II 60'**
4		**Village Maswasi**	**IM-II 120'**
7		**Village Satan**	**IM-II 60'**
8		**Village Chandpur**	**IM-II 180'**
9	**Surface water**	**River Ganga Downstream**	**River Water**
10		**River Ganga Upstream**	**River Water**
11	**Industrial drain**	**Loni**	**Industrial Drain**
12		**ACIR-Drain**	**Industrial Drain**
5	**Treated water**	**UPSIDC CETP Outlet**	**CETP Outlet**
6		**BLTP CETP Outlet**	**CETP Outlet**
Source: Field Survey April 2022, Computation by Researcher			

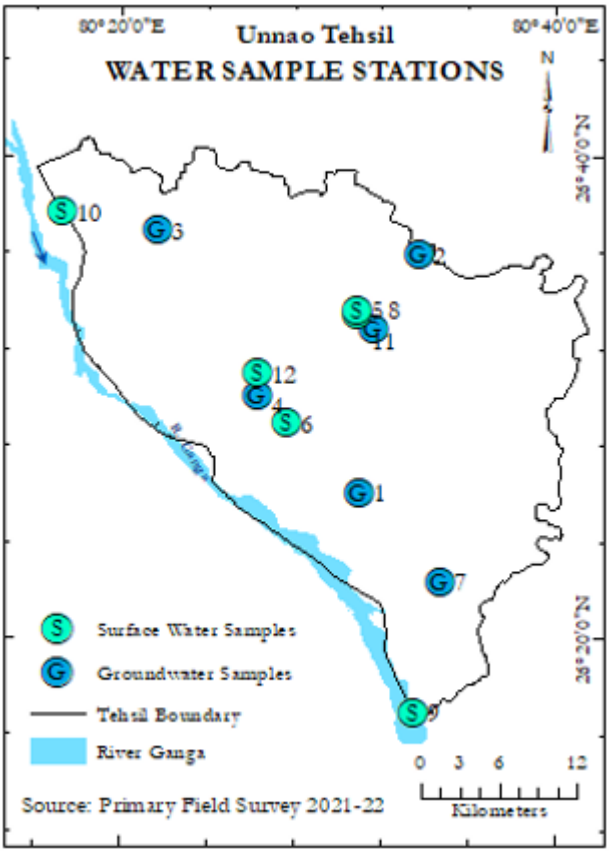


Figure 1: Location of Sample Stations in the Study Area
Source: Authors

On-site measurements were done for colour, smell, TDS and pH. Colour and smell were observation-based. For TDS and pH, Lab Junction Pocket TDS meter and Lab Junction Pocket pH meter were used. Samples for biochemical parameters that include dissolved oxygen (DO) and biochemical oxygen demand (BOD_5) were collected in 300 mL BOD bottles with tight stoppers. BOD_5 samples were incubated at 20°C for 5 days, while DO was tested within 8 hours of sample collection. The Rideal-Stewart Modified Winkler's Method, also known as the permanganate method of titration, was employed to measure DO and BOD_5 (Rideal & Stewart, 1901). For the sample preparation of heavy metals, a 10 mL sample was digested with

5 mL of concentrated nitric acid (HNO_3). The residual solution for the atomic absorption spectrometry (AAS) method was diluted with Millipore water to 10 mL. Heavy metal presence in the produced samples was examined using a Perkin Elmer AAnalyst 800 Atomic Absorption Spectrometer. Standardisation for each element was conducted using pre-prepared standard solutions. Data analysis was carried out using SPSS and Microsoft Excel, and mapping was done in ArcGIS.

Results and Discussion

The physical parameters of colour, odour, TDS, pH, and biochemical parameters show minimal variation across seasons. All the samples, irrespective of origin, have a distinct colour ranging from light yellow to black. Thus, all the groundwater samples do not meet the desirable Bureau of Indian Standards (2012) standards for drinking water (Table 4), though there are no set limits for effluent water. Except for Maswasi (Sample 4), located near industrial areas, all groundwater samples are odourless. The red colour in water is generally attributed to the high iron content, but the sample has not been reported for iron content at all in both seasons, which shows that some other chemicals may have been responsible for this distinct colour. The industrial drains (S. 11, 12) have a strong and unpleasant odour like domestic sewers. The TDS levels in most samples exceed the recommended values (S. 2, 4, 5, 6, 7, 8, 11, 12), with Maswasi (S. 4) displaying the highest TDS concentration among groundwater samples, comparable to that of industrial drains (S. 5, 6) (Tables 2 & 3, Figure 2). The industrial drains (S. 11, 12) and CETP Outlets (S. 5, 6) have shown TDS far exceeding the limits. CPCB (2013) have also recorded high TDS from CETP Outlets.

Table 2: Water Analysis of Samples for Pre-Monsoon

Sample Station No.	Physical				Biochemical		Heavy Metals							
	Colour	Odour	pH	TDS	DO mg/l	BOD mg/l	Cr mg/l	Cd mg/l	Fe mg/l	Cu mg/l	Ni mg/l	Mn mg/l	Zn mg/l	Ca mg/l
1	Light Yellow	Odourless	8	355	-	-	**0.020**	**0.018**	0.120	0.023	**0.319**	0.045	0.062	58.800
2	Light Yellow	Odourless	7.2	**845**	-	-	**0.008**	**0.025**	0.062	0.026	**0.430**	**0.450**	0.051	**92.600**
3	Colourless	Odourless	7	281	-	-	0.000	**0.021**	0.000	**0.079**	**0.334**	0.099	0.003	30.400
4	Reddish Yellow	Disagreeable Odour	7.3	**1700**	-	-	0.000	**0.030**	0.000	**0.052**	**0.621**	**0.398**	0.430	**133.400**
5	Colourless and Transparent	Odourless	7.6	**3000**	7.500	3.100	0.008	0.039	0.000	0.110	0.967	0.003	0.013	370.000
6	Yellow and Transparent	Odourless	9.55	**4010**	6.000	6.850	0.023	0.047	0.000	0.036	1.030	0.056	0.011	272.000
7	Light Yellow	Odourless	7.13	**995**	-	-	0.000	**0.021**	**0.787**	0.010	**0.543**	**0.712**	0.012	42.800
8	Light Yellow	Odourless	7.5	**585**	-	-	0.000	**0.023**	0.000	0.011	**0.584**	0.096	0.005	39.200
9	Mud Colour	Muddy Odour	7.45	150	4.130	2.530	**7.180**	0.033	**3.270**	0.089	0.832	1.830	0.302	112.400
10	Mud Colour	Muddy Odour	7.45	185	4.330	3.470	**6.230**	0.024	**11.600**	0.493	2.000	0.557	0.024	68.000
11	Black	Foul	7.2	**2200**	0.000	0.000	0.000	0.019	0.000	0.008	0.582	0.027	0.000	27.200
12	Black	Foul	7.49	**1850**	0.000	0.000	0.000	0.020	0.000	0.007	0.615	0.017	0.002	21.000
Minimum			7	150	0	0	0	0.018	0	0.007	0.319	0.003	0	21
Maximum			9.55	4010	7.500	6.850	7.18	0.047	11.6	0.493	2.000	1.83	0.43	370
Mean			7.572	1346.334	3.660	2.658	1.222	0.027	1.320	0.079	0.738	0.3575	0.076	105.65
Standard Deviation			0.646	1182.836	2.819	2.330	2.504	0.008	3.227	0.129	0.437	0502	0.133	103.883

Red Bold numbers signify that the values exceed the acceptable limits according to Indian Standards in their respective categories.

Source: Field Survey April 2022, Computation by the Researchers

Table 3: Water Analysis of Samples for Post-Monsoon

Sample Station No.	Physical				Biochemical		Heavy Metals (mg/l)							
	Colour	Odour	pH	TDS	DO mg/l	BOD mg/l	Cr mg/l	Cd mg/l	Fe mg/l	Cu mg/l	Ni mg/l	Mn mg/l	Zn mg/l	Ca mg/l
1	Light Yellow	Odourless	8.06	350	-	-	**5.290**	**0.007**	0.000	0.005	**0.226**	**0.108**	0.055	55.600
2	Light Yellow	Odourless	7.29	**820**	-	-	0.046	**0.006**	**2.310**	0.012	**0.197**	**0.109**	0.000	**90.500**
3	Colourless	Odourless	7.85	260	-	-	0.048	**0.004**	0.000	**0.070**	**0.125**	**0.254**	0.008	29.300
4	Reddish Yellow	Disagreeable Odour	7.2	**1690**	-	-	0.023	**0.022**	0.000	0.100	**0.079**	**0.395**	1.280	**120.800**
5	Colourless and Transparent	Odourless	7.55	**2550**	7.670	3.300	0.000	0.010	0.000	0.025	0.297	0.186	0.002	385.000
6	Yellow and Transparent	Odourless	**9.45**	**3910**	5.900	7.030	0.043	0.006	0.000	0.039	0.253	0.214	0.000	257.000
7	Light Yellow	Odourless	7.23	**940**	-	-	**0.070**	**0.016**	0.000	0.017	**0.127**	**0.169**	0.031	34.000
8	Light Yellow	Odourless	7.6	**570**	-	-	**0.064**	**0.021**	0.000	0.002	**0.026**	**0.156**	0.000	35.600
9	Mud Colour	Muddy Odour	7.55	140	7.500	2.570	**6.260**	0.009	**3.250**	0.018	0.516	0.112	0.000	95.200
10	Mud Colour	Muddy Odour	7.52	170	7.470	2.500	**5.010**	0.015	**10.500**	0.021	1.350	0.141	0.000	40.800
11	Black	Foul	7.27	**2140**	0.000	0.000	0.243	0.026	0.000	0.005	0.331	0.006	0.000	25.100
12	Black	Foul	7.46	**1760**	0.000	0.000	0.607	0.010	0.000	0.026	0.303	0.108	0.000	20.000
Minimum			7.2	140	0	0	0	0.004	0	0.002	0.026	0.006	0	20
Maximum			9.45	3910	7.670	7.030	6.26	0.026	10.5	0.1	1.35	0.395	1.28	385
Mean			7.669	1275	4.757	2.567	1.475	0.013	1.338	0.028	0.319	0.13	0.114	99.075
Standard Deviation			0.590	1115.643	3.414	2.368	2.356	0.007	2.953	0.028	0.335	0.092	0.352	107.004

Red Bold numbers signify that the values exceed the acceptable limits according to Indian Standards in their respective categories.

Source: Field Survey December 2021, Computation by the Researchers

The industrial drains (S.11, 12) exhibit hypoxic (low oxygen) to anoxic (no oxygen) conditions, indicating poor water quality and limited organic matter. Organic waste, including sewage from households and animals, industrial waste from paper and leather manufacturing, slaughterhouse sewage, and agricultural effluent, significantly reduces dissolved oxygen (DO) levels (Haddad et al., 2021). It is important to note that the Loni drain receives water from the CETP Unnao Outlet and the industrial drain. Thus, the samples contained both the CETP outlet water and industrial drain water. The very low DO level in the Loni Drain (S.11) indicates high contamination from industrial effluent. In the pre-monsoon period, the upstream section of the river Ganga (S.10) had a higher BOD_5 level compared to the downstream (S.9). Conversely, during the post-monsoon period, lower BOD_5 levels in the river Ganga water suggest a noticeably improved water quality. The absence of BOD_5 in the industrial drain waters indicates poor water quality, as it signifies the absence of organic matter and potentially no biological forms. (Tables 2 & 3, Figure 3).

Table 4: Quality Standards by WHO and BIS for Drinking Water and Effluents				
Parameters		**WHO Standards for Drinking Water**	**BIS Standards for Drinking Water**	**Indian Standards for Effluents**
Physical Parameters	Colour		Colourless	
	Odour		Odourless	
	pH	6.5 - 8.5	6.5 - 8.5	5.5 - 9.0
	TDS	600-1000 mg/l	500 Permissible up to 2000 mg/l	100 – 600 mg/l
Biochemical Parameters	Biological Oxygen Demand			30-350 mg/l
Heavy Metals (mg/l)	Chromium	0.05 mg/l	0.05 mg/l	2.0 mg/l
	Cadmium	0.003 mg/l	0.003 mg/l	2.0 mg/l to 1.0 mg/l
	Iron	0.3 mg/l	0.3 mg/l	3.0 mg/l
	Copper	2.0 mg/l	0.05 mg/l permissible up to 1.5 mg/l	3.0 mg/l
	Nickel	0.07 mg/l	0.02 mg/l	3.0 mg/l
	Manganese	0.08 mg/l	0.1 mg/l permissible up to 0.3 mg/l	2.0 mg/l
	Zinc	Surface - 0.01 mg/l Groundwater - 0.05 mg/l	5 mg/l permissible up to 15 mg/l	5 mg/l permissible up to 15 mg/l
	Calcium		75 mg/l permissible up to 200 mg/l	
Sources: BIS, 2012; WHO, 2022				

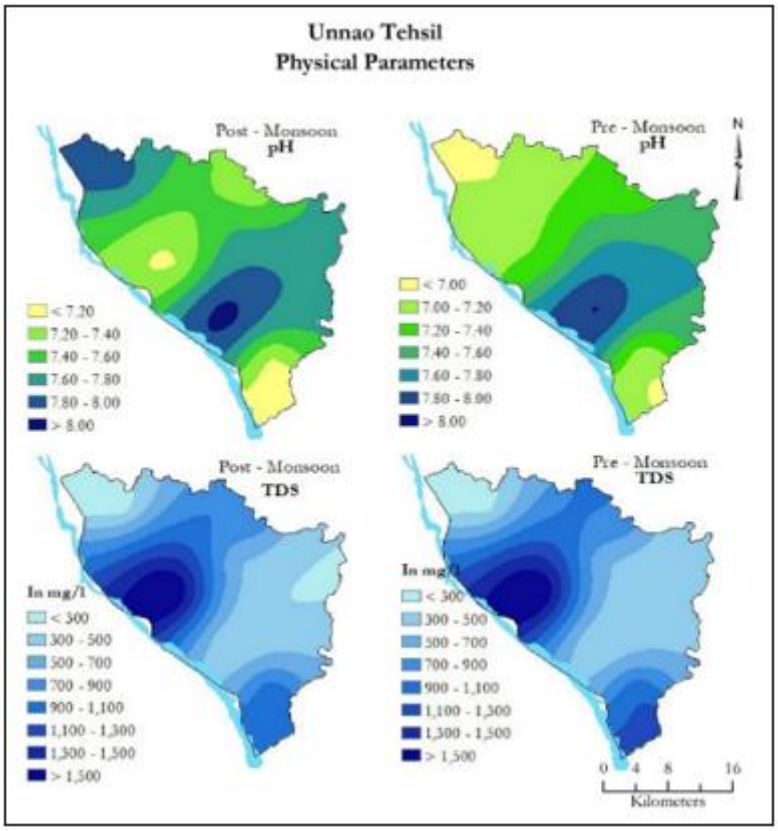


Figure 2: pH and TDS Level in the Groundwater during Pre- and Post-Monsoon season in Unnao Tehsil
Source: Authors

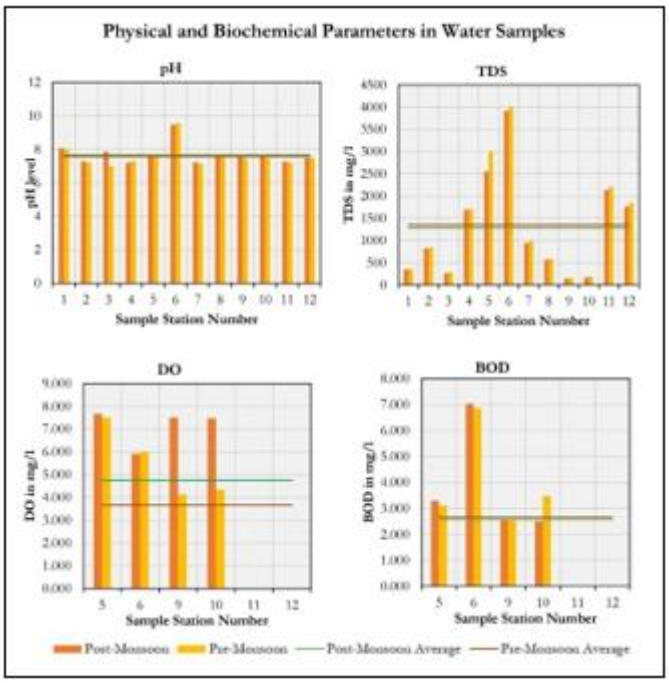


Figure 3: Pre- and Post-Monsoon Variability in pH, TDS, DO and BOD Levels at Selected Sample Stations
Source: Authors

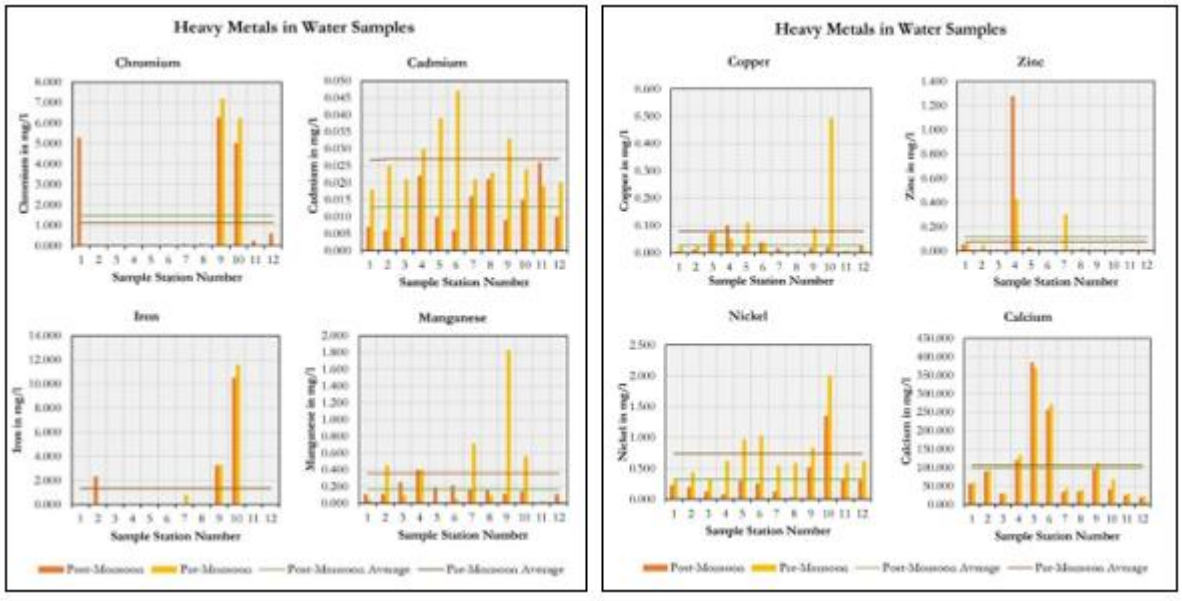


Figure 4: Pre- and Post-Monsoon Variability in Heavy Metals at Selected Sample Stations
Source: Authors

Only Maswasi (S.4) reported low chromium levels during post-Monsoon among all groundwater samples; Algangarh (S.2), Bhavdevna (S.3), Satan (S.7), and Chandpur (S.8) were above the recommended levels. Hadha (5.290 mg/l) (S.1) had recorded levels that were more than 100 times the limits (Table 4), indicating that the water quality had deteriorated in post-monsoon. Higher concentrations of chromium in the post-monsoon period indicate surface runoff and increased percolation of the metal in the groundwater. In the pre-monsoon period, only Hadha (S.1) and Algangarh (S.2) showed low

levels of chromium, significantly lower than the post-monsoon period. Similarly, high chromium content in groundwater samples was found in Kasur, Pakistan, a region with a thriving leather industry, by Afzal et al. (2013), and Tripathi & Chaurasia (2020) attributed it to leaching of solid waste containing chromium. Due to the significantly higher levels of chromium in the water than recommended, treatment is necessary before use. The amount of chromium in Ganga waters is notably higher in the downstream sample (S.9) indicating anthropogenic contribution. Due to the religious and cultural significance of the river, care should be taken to preserve the sanctity of its sacred waters. Chromium content in industrial drains (S.11, 12) and CETP Outlet (S.5, 6) lies within the effluent range, though Sahu et al. (2007) have found higher chromium levels in Loni drain, which shows that, over the years, chromium is more successfully recovered both in CETPs and ETPs. (Tables 2 & 3, Figure 4).

All the groundwater samples (S.1, 2, 3, 4, 7, 8) had cadmium levels that were higher than acceptable in both seasons, with higher values in pre-monsoon (Tables 2, 3, and 4). The surface water samples (S.5, 6, 9, 10, 11, 12) have shown similar values, though they fall within the standard limits. Contrary to the findings of EcoFriends (2002), where high levels of cadmium and nickel in CETP waters were reported, their content in the present samples (S.5, 6), though exceeding the drinking water standards, is within the BIS effluent standards. Figure 5 shows that the concentrations are higher around the industrial areas. This shows that cadmium may no longer be used in tanning or other industrial operations, but the previous accumulation in the groundwater is still present. According to Maurya et al. (2019), heavy metal concentrations in fish living in the River Ganga were significantly higher than the safe limits set by the WHO and FAO. Additionally, they discovered that fish from the River Ganga rapidly bioaccumulate lead, cadmium, and chromium, and these heavy metals have high BAFs (Bioaccumulation Factors). Consequently, these findings suggest that waterborne heavy metals pose a potential health risk to the population. (Table 2, 3 and Figure 4).

The Ganga waters exhibit significantly high iron concentrations, with upstream (S.10) concentrations higher than downstream (S.9). It is worth noting that industrial drain water (S.10, 11) and treated water samples (S. 5, 6) do not contain any iron. Although iron is not toxic, bacterial activity and oxidation can result in changes in taste, an oily coating, and a reddish deposit in the water. Consequently, the water becomes unappealing and unsuitable for drinking. In the pre-monsoon period, only three villages (S. 1, 2, 7) had groundwater with elevated iron content, and only Satan (S. 7) had an unacceptable level. The industrial areas and nearby villages (S.2, 4, 7) have shown elevated levels of manganese. However, the levels of manganese in all surface water samples were within acceptable limits. (Tables 2, 3, 4 & Figure 5).

Figure 6 illustrates a higher concentration of copper in the western and northwestern regions during the post-monsoon period, with a larger area falling into the highest category. In contrast, during the pre-monsoon period, the metal was more concentrated in the north and northwestern regions, with a greater area falling into the lowest category. Surface water samples consistently show copper concentrations within acceptable limits. Zinc concentrations are generally low in post-monsoon samples, while copper concentrations are higher compared to pre-monsoon. (Tables 2, 3, and 4; Figure 6). All the water samples were within the Indian acceptable standards for Zinc.

Nickel levels in all groundwater samples (S.1, 2, 3, 4, 7, 8) collected during both seasons exceeded the permissible limits. Figure 6 highlights two areas with notably high nickel concentrations, one in Hadha (S.1) and the other in the east at Algangarh (S.2). Conversely, surface water (S. 5, 6, 9, 10 ,11, 12) samples consistently demonstrated nickel levels within acceptable ranges. The industrial drains are sources of arsenic, cadmium, mercury, and nickel (EcoFriends, 2002). Similar outcomes were also across the remaining samples, with

minor variations. Additionally, it is noticeable that the levels of nickel in pre-monsoon samples are higher compared to post-monsoon samples (Tables 2, 3 & 4, Figures 4 & 6).

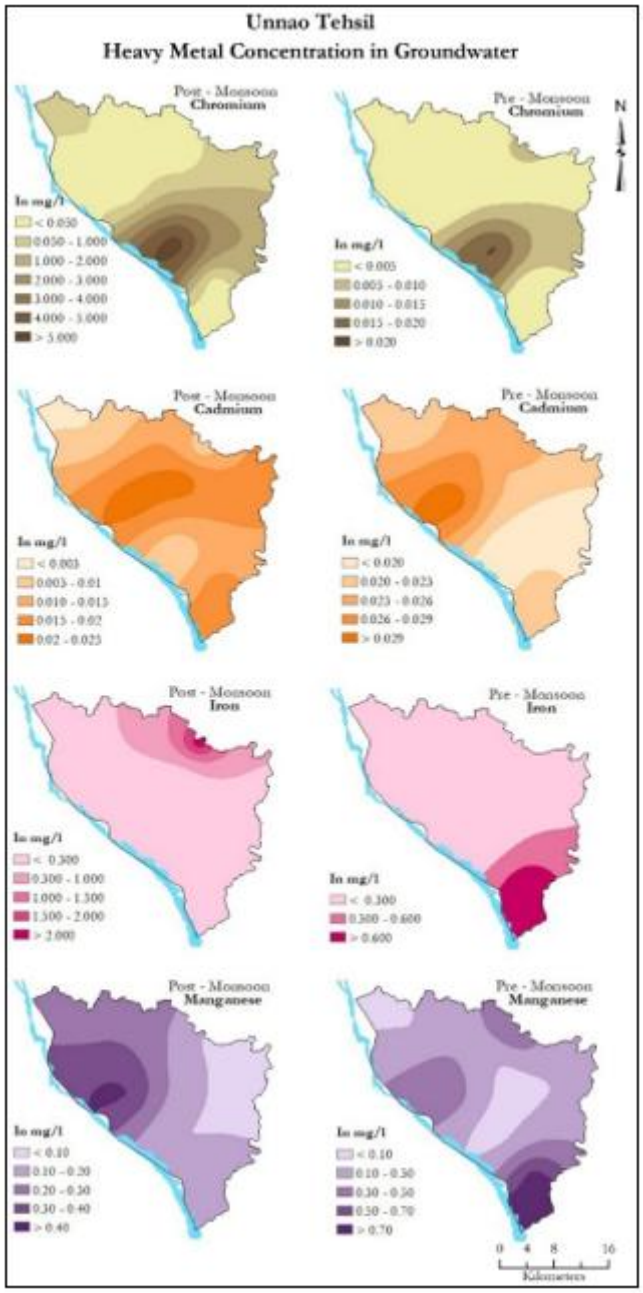


Figure 5: Concentration of Chromium, Cadmium, Iron, Manganese in Groundwater in Unnao Tehsil during Pre- and Post-monsoon Seasons
Source: Authors

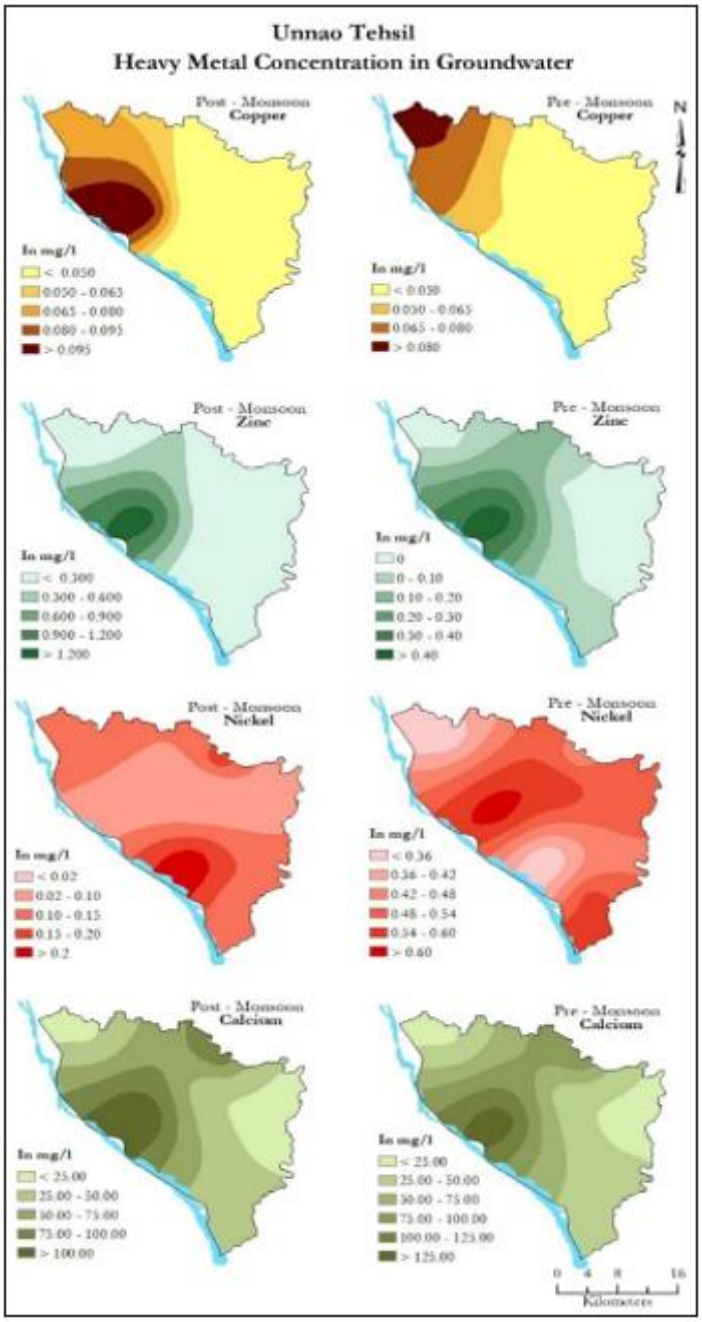


Figure 6: Concentration of Copper, Zinc, Nickel and Calcium in Groundwater in Unnao Tehsil during Pre- and Post-Monsoon Seasons
Source: Authors

Maswasi (S.4) and Algangarh (S.2) had the highest incidence of calcium during both seasons, which supported their high TDS values. All the groundwater samples fall within the acceptable range according to Indian Standards except Maswasi and Algangarh. Figure 6 depicts the same conclusions as those mentioned earlier. The amount of calcium in effluent water is not subject to any standards. Despite having low calcium levels, Loni Drain (S.11) and ACIR-Drain (S. 12) exhibit high TDS values, which may indicate excessive magnesium levels or other factors. The pre-monsoon values have a narrow range but a greater mean than the post-monsoon values (Tables 2, 3 & 4; Figures 6 & 7).

doi:10.20896/cczd7a81



Figure 7: ACIR Drain (left) and Loni Drain (right)
Source: Authors

Correlation

During the pre-monsoon season, several pairs of metal concentrations exhibited positive correlations at the 1% significance level: iron and chromium (0.804), copper and iron (0.954), nickel and iron (0.871), nickel and copper (0.893), manganese and chromium (0.783), and calcium and cadmium (0.888). This shows that iron, chromium, copper, nickel and manganese may have a similar source while calcium and cadmium may have another source. All correlation values exceeded 0.75, indicating a high positive correlation between the occurrences of these metals. Copper and chromium (0.683), nickel and chromium (0.650), pH and cadmium (0.685), TDS and cadmium (0.670), TDS and calcium (0.693), and TDS and pH (0.625) also demonstrated positive correlations at the 5% significance level, with all values surpassing 0.55, indicating a moderate positive correlation. This shows that copper, chromium, and nickel have a similar source and pH, while cadmium, TDS, and calcium may have a different source (Table 5).

During the post-monsoon period, pairs of metal concentrations exhibited positive correlations at the 1% significance level: nickel and iron (0.941), manganese and copper (0.896), zinc and copper (0.768), and zinc and manganese (0.757). This shows that manganese, copper and zinc have a similar source and nickel and iron have a different one. All correlation values exceeded 0.75, indicating a strong positive correlation between the occurrences of these metals. Additionally, at the 5% significance level, positive correlations were observed for iron and chromium (0.591), nickel and chromium (0.616), and TDS and calcium (0.655). This shows that iron, chromium and nickel have similar sources, while TDS and calcium have different sources. All these values surpassed 0.55, indicating a moderate positive correlation (Table 6).

Notably, the positive correlations among nickel, iron & chromium and TDS & calcium observed in the post-monsoon season (Table 6), are repeated in the pre-monsoon season. This consistent positive correlation among metal concentrations in the samples strongly suggests their shared origins. The findings underscore the interrelated nature of these metal occurrences during both pre-monsoon and post-monsoon periods.

Table 5: Correlation between Parameters for Pre-Monsoon Season									
Parameter	**Cr mg/l**	**Cd mg/l**	**Fe mg/l**	**Cu mg/l**	**Ni mg/l**	**Mn mg/l**	**Zn mg/l**	**Ca mg/l**	**pH**
Cd mg/l	**0.113**								
Fe mg/l	**.804****	**-0.048**							
Cu mg/l	**.683***	**0.046**	**.954****						
Ni mg/l	**.650***	**0.350**	**.871****	**.893****					
Mn mg/l	**.783****	**0.120**	**0.380**	**0.195**	**0.186**				
Zn mg/l	**0.322**	**0.213**	**0.015**	**-0.029**	**-0.045**	**0.555**			
Ca mg/l	**-0.058**	**.888****	**-0.117**	**0.053**	**0.291**	**-0.092**	**0.080**		
pH	**-0.082**	**.685***	**-0.086**	**-0.065**	**0.231**	**-0.213**	**-0.130**	**0.533**	
TDS	**-0.444**	**.670***	**-0.389**	**-0.275**	**0.085**	**-0.451**	**-0.150**	**.693***	**.625***
****. Correlation is significant at the 0.01 level (2-tailed).**									
***. Correlation is significant at the 0.05 level (2-tailed).**									
Source: Computation by the Researchers									

Table 6: Correlation between Parameters for Post-Monsoon Season									
Parameter	**Cr mg/l**	**Cd mg/l**	**Fe mg/l**	**Cu mg/l**	**Ni mg/l**	**Mn mg/l**	**Zn mg/l**	**Ca mg/l**	**pH**
Cd mg/l	**-0.203**								
Fe mg/l	**.591***	**-0.011**							
Cu mg/l	**-0.293**	**-0.024**	**-0.150**						
Ni mg/l	**.616***	**0.003**	**.941****	**-0.193**					
Mn mg/l	**-0.301**	**-0.026**	**-0.160**	**.896****	**-0.265**				
Zn mg/l	**-0.172**	**0.399**	**-0.148**	**.768****	**-0.226**	**.757****			
Ca mg/l	**-0.204**	**-0.264**	**-0.170**	**0.149**	**-0.076**	**0.284**	**0.052**		
pH	**0.022**	**-0.488**	**-0.135**	**0.047**	**-0.043**	**0.117**	**-0.238**	**0.395**	
TDS	**-0.540**	**0.052**	**-0.413**	**0.164**	**-0.235**	**0.134**	**0.099**	**.655***	**0.510**
***. Correlation is significant at the 0.05 level (2-tailed).**									
****. Correlation is significant at the 0.01 level (2-tailed).**									
Source: Computation by the Researchers									

Conclusion

The water contamination in the study area has reached a level where it is not only impacting surface water but also groundwater. Chromium is commonly associated with the tanning industry. In contrast to the general association of elevated chromium levels with the tanning industry, in the present study only a few samples have shown elevated levels of chromium, including the alarming levels in the River Ganga, while consistently elevated levels of cadmium and nickel contamination are found, indicating an omnipresence of potential carcinogenic metals in drinking water. Changes observed between the pre-monsoon and post-monsoon differ in intensity and distribution for most metals. These variations are due to increased seepage during the post-monsoon period in some cases and dilution in the pre-monsoon period in others. The study highlights the anthropogenic factors causing contamination in metals, as significant correlations exist within the metals. However, the study has limitations in understanding the pollution from industrial sewage, which may be more severe than assessed. The red colour of the Maswasi water needs to be investigated since the general understanding of high iron values is ruled out. Other sources of water pollution, such as agriculture, domestic sewage and industries other than leather, could be investigated for a further and wider understanding of the water pollution in the study area. Villages near the industrial region, particularly Maswasi, Algangarh, Chandpur, and Hadha, exhibited poor water quality results, with southward villages more polluted than their northern counterparts. Immediate implementation of groundwater clean-up technologies is recommended to mitigate contamination to some extent. Further investigation into other chemicals, especially the organic compounds and contents of high TDS, can help to better understand the problem and measures in preventing further damage.

Ganga water is the recipient of sewage and runoff. BIS has no heavy metal or related restrictions associated with the bathing waters, that is, rivers, lakes and reservoirs. The river water is profusely used for irrigation, recreation, and religious practices and thus can affect human health through food and dermal absorption. Hence, special attention, treatment, and planning are urgently needed for the Ganga River. Additionally, stricter monitoring and examination of tanneries and other industries are essential to control further spread and increase of contamination.

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Ethical Approval

Not applicable. The study is based on the water sample collection and testing of physical, biochemical, and chemical parameters. It does not involve any human participants or collection of any personal data.

Conflict of Interest

The authors have no conflict of interest regarding the material, research, methodology and results of the paper

AI Use Statement

Artificial intelligence-assisted tools have solely been used for limited linguistic and editorial refinement of the manuscript. Research design, methodology, analysis, interpretation and conclusions have been written by the authors, who thereby take complete responsibility of the content.

Declaration Regarding the Authenticity of References

All the articles, publications and other sources cited in the present study and included in the reference list are authentic, have not been fabricated, falsified or misrepresented. Every reference has been included in good faith and to the best of my knowledge represents a genuine scholarly or documentary source used to support the research.

Author Contribution Statement

Anushka Gupta: Conceptualisation, methodology, software contribution, validation, formal analysis, investigation, resources, data curation, writing – original draft, visualisation of data, funding acquisition
Srabani Sanyal: Review & editing, guidance and supervision, project administration

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Data Availability Statement

All data and materials used in this research are available upon request to ensure the transparency and reproducibility of the findings presented.

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