International Journal of Natural and Social Sciences
IJNSS
Print: 2617-6637 < ISSN > Online: 2313-4461

Tannery industry impacts on hydrogeochemistry and heavy metal contents of two major rivers in Dhaka

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ARTICLE INFO

Article history

Received: 09 August 2022
Accepted: 05 September 2022

Keywords

Carbon and nitrogen, dissolve oxygen, heavy metals, hydrogeochemistry, oxidation reduction potential, tannery industry wastewater

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ABSTRACT

Dhaka city is highly vulnerable to environmental pollution as a result of overpopulation, rapid industrialization, and urbanization in recent decades. A survey was carried out during winter season of 2019 to investigate the effects of tannery industry effluents on hydrogeochemistry, chromium, nickel and lead concentrations in river water and sediments of Buriganga and Dhaleshwari rivers passing by the side of Dhaka City. Water and sediment samples were collected from the downstream of tannery industrial effluents discharge sites. The pH of the water samples collected from Buriganga river ranged between 7.04 and 7.60, whereas it was between 7.23 and 8.45 from Dhaleshwari river. The water samples of Dhaleshwari river had more organic carbon (258±102 mg C L^{-1}), NH_4^+-N (134±72.4 mg NL^{-1}) and NO_3^--N (24±24 mg NL^{-1}) compared to the water samples of Buriganga river (167±87 mg C L^{-1}, 114±26 mg NL^{-1}, and 11±6 mg NL^{-1}, respectively). The sediments from Buriganga river had very high chromium (Cr) (15.23±11.68 mg kg^{-1}), and lead (Pb) contents (36±23mg kg^{-1}) compared to the Cr (1085±2453 mg kg^{-1}), and Pb (17±9 mg kg^{-1}) contents in sediment samples from Dhaleshwari river. By contrast, the sediment samples from Dhaleshwari river had more nickel (Ni) content (232±143 mg kg^{-1}) than in sediments from Buriganga river (128±50mg kg^{-1}). The water samples from Buriganga river had Cr, Pb, and Ni contents below the detection limit, except ones ample for Pb (0.06 ppm) and Cr (0.01 ppm) and another for Ni (0.07 ppm). Only one water sample from Dhaleshwari river had detectable Pb (0.01 ppm) contents. Thirteen water samples from Dhaleshwari river had Cr ranged from0.01 to0.16 ppm while the remaining had Cr below the detection limit. The results indicated that occurrence of large quantity of heavy metals and organic pollutants in the sediments and river water can be a threat to the ecological status of two major rivers in Dhaka city and of the ecology of agricultural ecosystems near Dhaka city.

INTRODUCTION

The entry of heavy metals into the environment due to human and natural activities is one of the most important issues that the current world is facing. Production and use of a variety of chemicals and compounds due to rapid industrialization cause serious problems and risks for the environment (Shanbehzadeh et al., 2014). Environmental pollution through municipal, industrial, and agricultural wastes causes serious consequences to human health and to the ecology of the agricultural ecosystems. The ecology of the water bodies, particularly river water, in meeting the water demands of humans, animals and industries indicates the essential need to protect them against contamination. Water resources are contaminated by biological and chemical contaminants (such as heavy metals) day by day. Some heavy metals are essential as micronutrients, but their high concentration in the food chain can cause toxicity, endanger aquatic ecosystems and their users (Prabhu, 2009). Rivers are vital to human life as water resources, not only for providing drinking water but also for agriculture, leisure, and sporting activities including water sports and fishing.

How to cite this article: Mumu NJ, Jahangir MMR Mahjabin F, Asif MAA, Shahiduzzaman M and Islam MR (2022). Tannery industry impacts on hydrogeochemistry and heavy metal contents of two major rivers in Dhaka. International Journal of Natural and Social Sciences, 9(2): 01-12. DOI: 10.5281/zenodo.7088636

Tannery industry has long been important to Bangladesh's economy. Bangladeshi leather and leather goods exports $1.2 billion, accounting for 3.54% of the country's total merchandise exports in 2017 (Hossan, 2019). But these industries are one of the most polluting sectors, having a significant negative impact on the environment. Several chemicals are utilized during the leather production phases, including sodium sulphide, calcium oxide, sulphuric acid, formic acid, aldehyde, sulphur, acid color, neutralizing agents, formalin, heavy metals, and so on. These chemicals are then discharged into a river, pond, or open environment after being processed. As a result, excess Cr, Ni, Pb, and other heavy metals, as well as organic contaminants, are found in river water near this location. Organic contaminants generated by tanneries contaminate river sediment and water affecting the water quality in the surrounding area. The ammonia emitted by the tannery industrial estate causes eye ulcers, retinal degradation, and eventually blindness. Heavy metals accumulated in fish organs, disrupting their life cycle. They create genetic mutations, which lead to cancer in the long run. The chrome tanning technique is used in about 80 to 90% of leather processing. During the chrome tanning process, a large amount of Cr is disposed with the effluent. The tannery industries discharge about 15800 m^3/day of waste water with a high Cr concentration (BKH, 1995). According to the DoE, tanneries dump 22000 m^3 of untreated liquid toxic wastes into rivers every day, and Cr concentrations easily exceed the maximum allowable level set by the DoE and the WHO. The Ni concentrations in the Buriganga and Dhaleshwari rivers have been found to be high as a result of tannery effluent discharge. Higher Ni concentrations in plants have an impact on their growth. Pollution of river water, sediment, and soil occurs as a result of the released Pb from tanneries. Some phytoplankton's body functions can be disrupted when Pb interferes.

The western part of Dhaka city is surrounded by two major rivers which receive contaminants from leather industry effluents. Hazaribagh is situated at the south-west zone of Dhaka South City Corporation and known as the world's fifth most polluted zone, according to two major research organizations in Switzerland and the United States. Hazaribagh is home to nearly all of the tanneries in the country. These tanneries operate on 25 ha plots, processing 220 metric tons of leather every day and pouring 40 to 50 liters of liquid per kilo of leather into natural canals or directly onto the ground (UNIDO, 2000). Tanneries have been dumping solid and liquid wastes into low-lying areas, rivers, and canals without the treatment required by the Environment Conservation Act of 1995. The untreated discharge and dumping of trash near water sources gives it the appearance of a tannery waste lake (Zahid, 2017). In 2003, the government had chosen to relocate these industries out of the city to reduce pollution in the city and protect the Buriganga River, but their operations had already posed a threat to the ecosystem for decades (Zahid, 2017). The government also decided to construct the Bangladesh Small and Cottage Industry Corporation (BSCIC) Tannery Industrial Estate on 200 acres of land in Hemayetpur, Savar. However, tannery waste from the Savar Tannery Industrial Estate is currently polluting the Dhaleshwari river damaging the ecosystems and biodiversity of the river. According to the Société Générale de Surveillance (SGS), excess dangerous wastes are discharged into the river from the Hemayetpur Tannery Industrial area and polluting river water. There is very limited study on the hydrogeochemical properties and heavy metal concentration of Buriganga and Dhaleshwari river water and sediments which are hydrologically connected to the tannery industries. This monitoring type study was designed to (i) determine hydrogeochemical properties of surface water collected from rivers, along the waste water flow pathway of Buriganga and Dhaleshwari river; (ii) determine the levels of Cr, Pb and Ni in sediments and water along the waste water flow pathway.

MATERIALS AND METHODS

Sample collection and on-site hydrochemical analysis

The water and sediment samples were collected from the river waters and sediments of Buriganga and Dhaleshwari rivers in Hazaribagh Tannery Industrial Estate and Hemayetpur Tannery Industrial Estate, respectively. Samples were collected from thirty-four different locations of two industrial zones having different latitude, longitude and elevation. Eight samples (sediment and river water samples) were collected from Hazaribagh tannery site and the remaining from Hemayetpur tannery site (Figure 1). Samples were collected in about 500m interval along the water flow path. Sampling spots were geo-referenced using a Global Positioning System (GPS). While sampling, on site hydrochemical analysis for dissolved oxygen (DO), oxidation-reduction potential (ORP), pH and temperature were carried out with the help of Dissolved Oxygen Meter (Model: DO-5519), Oxidation-reduction Potential Meter edge® pH (HI2002) and Digital pH Electrode (HI11310).

Figure 1: Map of sampling points at Hazaribagh tannery site (left) and Hemayetpur tannery site (right).

Table 1: GPS location of the sampling points at Hazaribagh tannery site

Sampling points	X Coordinate	Y Coordinate
1	23° 44‘1“N	90° 21‘52“E
2	23° 44‘1“N	90° 21‘51“E
3	23° 44‘0“N	90° 21‘52“E
4	23° 45‘35“N	90°21‘14“E
5	23° 44‘35“N	90° 21‘6“E
6	23° 44‘28“N	90° 21‘7“E
7	23°44‘26“N	90° 21‘10“E
8	23° 44‘37“N	90° 21‘24“E

Table 2: GPS location of the sampling points at Hemayetpur tannery site

Sampling points	X Coordinate	Y Coordinate
1	23°46‘53“N	90◦ 14‘26“E
2	23◦ 46‘53“N	90◦ 14‘26“E
3	23◦ 46‘53“N	90◦ 14‘26“E
4	23◦ 46‘53“N	90◦ 14‘27“E
5	23◦ 47‘17“N	90◦ 14‘34“E
6	23◦ 47‘40“N	90◦ 14‘43“E
7	23◦ 47‘20“N	90◦ 14‘32“E
8	23◦ 47‘22“N	90◦14‘33“E
9	23◦ 47‘24“N	90◦ 14‘35“E
10	23◦ 47‘20“N	90◦ 14‘35“E
11	23◦ 47‘16“N	90◦ 14‘32“E
12	23◦ 47‘13“N	90◦ 14‘31“E
13	23◦ 46‘50“N	90◦ 14‘12“E
14	23◦ 47‘7“N	90◦ 14‘29“E
15	23◦ 47‘4 “N	90◦ 14‘28“E
16	23◦ 47‘1“N	90◦ 14‘27“E
17	23◦ 46‘46“N	90◦ 14‘10“E
18	23◦ 46‘50“N	90◦ 14‘28“E
19	23◦ 46‘48“N	90◦ 14‘26“E
20	23◦ 46‘45“N	90◦ 14‘26“E
21	23◦ 46‘42“N	90◦ 14‘25“E
22	23◦ 46‘39“N	90◦ 14‘23“E
23	23◦ 46‘36“N	90◦ 14‘22“E
24	23◦ 46‘34“N	90◦ 14‘21“E
25	23◦ 46‘33“N	90◦ 14‘21“E
26	23◦ 46‘33“N	90◦ 14‘21“E

Laboratory Analysis

The water samples were filtered using Whatman filter paper 41. Then the organic carbon content of the water samples was measured using the wet oxidation method outlined by Walkley and Black (1934). The water samples were not acidified after collection. The wet oxidization was performed with 5mL of water sample and 1N $K_2Cr_2O_7$ in the presence of concentrated H_2SO_4, concentrated

H_3PO_4 and an indicator. Then 1.05N $FeSO_4$ was used to titrate excess $K_2Cr_2O_7$. The following formula was used to calculate the organic carbon contents and the results were presented in mg kg^{-1}or mg L^{-1}.

To determine mineral N (NH_4^+-N and NO_3^-- N) content, the filtered sample solution was steam distilled with MgO and Devarda's alloy and titrated with 0.01N H_2SO_4 (Keeney and Nelson, 1982). For NH_4^+, a distillation tube was filled with 25 mL water and 0.7g MgO, and a conical flask was filled with 20 mL boric acid solution. The solution in the conical flask was titrated against 0.01N H_2SO_4 after 4 minutes of distillation to quantify the amount of ammonium. For NO_3^-, 0.7g Devarda's alloy and 0.3 g MgO were added in the same distillation tube and was trapped in another 20 mL boric acid solution. The solution in the conical flask was then titrated against a 0.01N H_2SO_4solution to measure the amount of nitrate in a 25 ml sample. The results were presented in mg kg^{-1}or mg L^{-1}.

The filtered water samples were prepared for digestion to determine the concentration of heavy metals in water samples. Digestion tubes were washed carefully and then soaked in acid bath containing HCl solution (46mL acid per liter distilled water) for 3 hrs. After drying of the tubes, 10mL water sample was taken in each tube. Then, 3 mL $HClO_4$, 7 mL HNO_3 were given to each tube containing samples. Then the tubes were set into the digestion chamber at 130℃ for 1hr. After digestion, the water samples were allowed to cool down and volume to 50mL solution. Then the solutions were filtered using Whatman filter paper 41.

Sediment samples were digested using Nitric acid-Perchloric acid method. Two-gram sediment sample was taken in 100 mL digestion tube. Then 5mL conc. HNO_3 was added to that and kept for overnight. After that, 2.5 mL perchloric acid was added and then the samples were digested at 1500℃ for 3 hours. Total concentration of heavy metals: chromium (Cr), lead (Pb) and nickel (Ni) in water and sediment samples was determined using an atomic absorption spectrophotometer (Hitachi ZA3000).

Statistical Analysis

Data on hydrogeochemical properties and heavy metal contents of sediments and surface water samples were processed in Microsoft Excel (2013). Normality of the data was checked by histogram. Descriptive statistics, co-efficient of variation and standard error of mean were calculated on Excel.

RESULTS

Hydrogeochemical properties and heavy metal contents in the Buriganga river water at Hazaribagh tannery site

River water temperature during sampling (March-April) ranged from 26.6° C to 28.9° C with a mean temperature of 27.3° C (Table 3). The river water pH was close to neutral with a mean value of 7.22. The pH value of the river water samples ranged from 7.04 to 7.60. The minimum and maximum ORP of the samples was found -30 mV and -5.3 mV, respectively and the average value was -11 mV. The highest DO measured during the sampling time was 3 mg L^{-1} with the mean value of 1.4 mg L^{-1} (Table 3). The coefficient of variation (CV) for ORP and DO were 72% and 68%, respectively which exhibited that the redox chemistry and DO of the water was highly spatially variable. The TOC content present in the river water samples of the Buriganga at Hazaribagh tannery site ranged from 20 to 271 mg C L^{-1} with a mean value of 167 mg C L^{-1} (Table 3). The wider range of TOC data between the sampling spots showed high spatial variability among the TOC distribution in the river water. Nitrogen concentration of the samples was measured in the form of ammonium and nitrate. There was no definite trend in ammonium concentration in water samples along the sampling sites. The lowest value of available ammonium and nitrate were 72 mg N L^{-1} and 4 mg N L^{-1}, respectively and the highest values of the same were 144 mg N L^{-1} and 24 mg N L^{-1} respectively (Table 3). Nitrate concentration in water decreases with the increase of distance from the waste water flow pathway.

Table 3: Hydrogeochemical properties of water samples at different sampling points of the Buriganga river receiving waste water from Hazaribagh tannery industries

Sampling points	Temp (°C)	pH	ORP (mV)	DO (mg L^{-1})	TOC (mg C L^{-1})	NH_4^+ (mg N L^{-1})	NO_3^- (mg N L^{-1})
1	26.8	7.18	-11	1.1	20	132	24
2	26.6	7.14	-9.9	3.0	188	112	16
3	26.7	7.60	-7.8	2.1	104	120	8
4	27.3	7.09	-5.3	1.2	188	144	8
5	28.9	7.16	-8.2	2.1	104	140	8
6	27.1	7.04	-10.4	0.6	271	72	8
7	27.6	7.51	-30	0.4	188	80	8
8	27.2	7.07	-5.7	0.5	271	108	4
min	26.6	7.04	-30	0.4	20	72	4
max	28.9	7.60	-5.3	3.0	271	144	24
mean	27.3	7.22	-11	1.4	167	114	11
CV (%)	3	3	-72	68	52	23	61

Average concentration of both Pb and Ni in the river water samples was 0.01 ppm (Table 4). Only one water sample was found having 0.01 ppm Cr. Concentration of Cr in most of the river water samples were below detection limit.

Table 4: Heavy Metals (Cr, Pb and Ni) concentration in water samples at different sampling points of the Buriganga river receiving waste water from Hazaribagh tannery industries

Sampling points	Cr (ppm)	Pb (ppm)	Ni (ppm)
1	0	0.00	0.07
2	0	0.00	0
3	0	0.00	0
4	0	0.00	0
5	0	0.00	0
6	0	0.00	0
7	0.01	0.06	0
8	0	0.00	0
min	0	0.00	0
max	0.01	0.06	0.07
mean	0	0.01	0.01
CV (%)	198	283	283

Concentration of heavy metals (Cr, Pb and Ni) in sediments of the Buriganga river at Hazaribagh tannery site

The concentration of Cr in the sediment samples of different sampling points at Hazaribagh varied widely with a range of 55 mg $kg^{-1}$to 35,050 mg kg^{-1} (Table 5). The lowest value of 55 mg $kg^{-1}$was found at sampling point 7 and the highest value was 35,050 mg kg^{-1}at the sampling point 2. The Pb content in river sediment of Buriganga river varied from 2 mg kg^{-1}at sampling point 7 to 64mg kg^{-1}at sampling point 2. The mean value of Pb in the samples was 36mg kg^{-1}(Table 5). The spatial variability of Pb and Ni in the sediment samples was highly remarkable. Average Ni concentration in the sediment samples was 128 mg kg^{-1}. The highest Ni content was found 199mg kg^{-1}at the sampling point 8 (Table 5). There were a number of discharge points along the course of the river. No definite trend of heavy metals was found along the river.

Hydrogeochemical Properties and Heavy Metal Contents in the Dhaleshwari River Water at Hemayetpur Tannery Site

The temperature of the river water samples along the twenty-six sampling points of the Dhaleshwari river ranged from 24.8℃ to 34.1℃ with an average value of 30.6℃ (Table 6). The pH of the river water samples was neutral to slightly alkaline and ranged from 7.23 to 8.45 with a mean value of 7.73. The water pH at sampling point 23 and 24 were more than pH 8. Maximum ORP value of the river water sample was found -24 mV, and minimum of the same was -78mV. The DO values of the water samples ranged from 1.1 mg L^{-1} to 7.6 mg L^{-1}, with an average value of 4.4 mg L^{-1}. The concentration of organic carbon in the river water samples varied widely. The maximum concentration of organic carbon found in the samples was 439 mg C L^{-1} while the minimum was 20 mg C L^{-1}. On an average, 258 mg C L^{-1} was present in the river water samples (Table 6). Available ammonium found in the water samples ranged from 44 mg N L^{-1} to 396 mg N L^{-1} with the mean value of 134 mg N L^{-1}. Nitrate was not found in six water samples, and the highest nitrate concentration of 80 mg N L^{-1} was reported in one sample. The CV (%) value of nitrate content showed a significant spatial variability among the sampling points.

Very low concentration of heavy metals was found the river water samples. Average Cr concentration was found 0.01 ppm in river water samples (Table 7). Maximum 0.16 ppm Cr was found in the Dhaleshwari river water samples. Ni contents were below detection limit in the river water samples (Table 7). Also, Pb contents were found below detection limit in the river water samples except one sample having 0.01 ppm Pb.

Table 5: Heavy Metals (Cr, Pb and Ni) concentration in sediment samples at different sampling points of the Buriganga river from Hazaribagh tannery industries

Sampling points	**Cr (mg kg^{-1})**	**Pb (mg kg^{-1})**	**Ni (mg kg^{-1})**
1	23273	54	141
2	35050	64	111
3	21105	39	87
4	7397	23	133
5	13762	41	196
6	18555	7	64
7	55	2	93
8	2645	56	199
min	55	2	64
max	35050	64	199
mean	15230	36	128
CV (%)	77	64	39

Table 6: Hydrogeochemical properties of water samples at different sampling points of the Dhaleshwari river receiving waste water from Hemayetpur tannery industries

Sampling points	Temp (℃)	pH	ORP (mV)	DO (mg L^{-1})	TOC (mg C L^{-1})	NH_4^+ (mg N L^{-1})	NO_3^- (mg N L^{-1})
1	25.1	7.70	-50.5	1.1	439	84	0
2	25.8	7.67	-43.6	6.6	271	248	8
3	25	7.49	-35.7	3.5	104	64	16
4	24.8	7.51	-31.6	3.3	20	76	8
5	30.5	7.66	-26	7.6	271	396	48
6	32	7.92	-38	7.1	355	168	36
7	30.6	7.40	-42	5.8	188	112	52
8	30.7	7.78	-28	6	271	44	76
9	30.9	7.82	-35	6.2	188	104	16
10	31.1	7.71	-36	7.3	188	88	32
11	31.9	7.78	-26	3.3	271	248	80
12	31.9	7.65	-25.5	4.5	355	176	64
13	34.1	7.78	-24.7	7.1	271	156	36
14	33.4	7.76	-24	3.9	355	156	28
15	32	7.82	-28	4	271	120	20
16	32.7	7.84	-56	3.4	104	116	12
17	32.7	7.66	-37	3.1	355	112	0

18	32.1	7.75	-50	3.4	271	100	12
19	31.2	7.74	-47.5	7.4	355	120	8
20	32.9	7.23	-26	3.8	355	84	0
21	31.7	7.47	-32	2.7	355	112	0
22	30.1	7.39	-27.6	2.2	355	84	0
23	31.1	8.45	-78	2.5	271	112	0
24	31.8	8.17	-71	1.6	188	120	8
25	30.1	7.88	-53.6	2.3	188	172	44
26	29.6	7.84	-53.1	5.6	104	120	12
min	24.8	7.23	-78	1.1	20	44	0
max	34.1	8.45	-24	7.6	439	396	80
mean	30.6	7.73	-39.5	4.4	258	134	24
CV (%)	8.4	3	-37	45	40	54	102

Table 7: Heavy Metals (Cr, Pb and Ni) concentration in water samples at different sampling points of the Dhaleshwari river receiving waste water from Hemayetpur tannery industries

Sampling points	Cr (ppm)	Pb (ppm)	Ni (ppm)
1	0	0	0
2	0	0	0
3	0	0	0
4	0	0	0
5	0.16	0	0
6	0.02	0	0
7	0	0	0
8	0	0	0
9	0	0	0
10	0	0	0
11	0.01	0	0
12	0	0	0
13	0.00	0	0
14	0.01	0	0
15	0	0	0
16	0	0	0
17	0.01	0	0
18	0.01	0	0
19	0	0	0
20	0.02	0.01	0
21	0.01	0	0
22	0.01	0	0
23	0.02	0	0
24	0.03	0	0
25	0.02	0	0
26	0.03	0	0
min	0	0	0
max	0.16	0.01	0
mean	0.01	0	0
CV (%)	221	510	0

Table 8: Heavy Metals (Cr, Pb and Ni) concentration in sediment samples at different sampling points of the Dhaleshwari river receiving waste water from Hemayetpur tannery industries

Sampling points	Cr (mg kg-1)	Pb (mg kg-1)	Ni (mg kg-1)
1	147	8	98
2	304	5	127
3	610	6	71
4	338	28	329
5	3177	22	59
6	1418	3	710
7	138	29	290
8	180	28	303
9	176	3	70
10	105	28	34
11	358	20	295
12	193	25	272
13	559	30	308
14	307	19	190
15	495	27	254
16	75	25	297
17	98	18	116
18	452	15	278
19	322	21	359
20	159	19	314
21	541	22	274
22	234	21	378
23	314	4	100
24	12353	10	169
25	3210	4	102
26	1946	13	245
min	75	3	34
max	12353	30	710
mean	1085	17	232
CV (%)	226	53	62

Concentration of heavy metals (Cr, Pb and Ni) in sediments of the Dhaleshwari river at Hemayetpur tannery site

High amount of Cr was present in the sediment samples of Dhaleshwari river at Hemayetpur tannery site. Average Cr concentration of 1,085mg $kg^{-1}$was found in the sediment samples (Table 8). The lowest total Cr content 75 mg $kg^{-1}$was observed at sampling point 16 and the highest of 12,353 mg kg^{-1} was found at the location of 24. The range of total Pb content in the sediment samples was 3 mg kg^{-1} to 30mg kg^{-1}. The average concentration of Pb in the sediment samples was found 17 mg kg^{-1}. There was wider variation in total Ni content in sediments of the Dhaleshwari river along the different sampling points. The highest concentration of Ni in the sediment samples was 710 mg kg^{-1} at sampling point 6 and the lowest content was 34 mg kg^{-1} at the sampling point 10. No definite trend of heavy metals was found in sediments along the sampling points.

DISCUSSION

Hydrogeochemical properties and heavy metal contents of Buriganga and Dhaleshwari river water

Temperature is a crucial indicator of water quality for aquatic creatures to survive. The most common physical test for water quality is temperature measurement. Warm water has a lower ability to hold DO than cold water. The problem of low DO levels is worsened by the fact that aquatic plants' metabolic rates increase when water temperature rises, increasing their biochemical oxygen need. Kumar et al. (2014) found average 12.7℃ temperature of the Ganga-river water affected by tannery effluents. The temperature range of the Buriganga river water ranged from 26.6℃ to 28.9℃. Average temperature of the Dhaleshwari river water samples near tannery industries was 30.6℃ during experiment.

Many species are sensitive to changes in the pH of water. The mean pH of the Buriganga river water samples was near to neutral (pH=7.22) that was lower (8.2) than the value found by Kumar et al. (2014). In the current study, average pH of the Dhaleshwari river water samples was 7.73, which was close to the standard value of pH 7.8 (Chowdhury et al., 2015). Rafid et al. (2019) found pH value 7.55 of the river water at Hemayetpur tannery area during pre-monsoon season. The pH fluctuations can stress the aquatic environment and harm some delicate aquatic flora and fauna species.

The ORP range from 650 mV to 750 mV is optimal for water sanitation giving a good understanding of the general water quality. This value is influenced by both natural and synthetic chemicals used to maintain water quality. Like surface water, ORP is frequently employed as a master variable in groundwater systems to characterize groundwater geochemistry. The ORP value can help to determine the ratio of oxidizing to reducing chemicals if the sample water has a dominant oxidation/reduction system. The ORP of a lake or river is a measure of its ability to cleanse itself or break down waste products such as impurities and dead plants and animals. When the ORP value is high, there is a lot of oxygen in the water. When the ORP is negative, the water is more anti-oxidizing. Average ORP of the Buriganga river water samples was -11 mV indicating reducing chemical agents were mostly present in the water samples. The ORP in river water samples ranged from -78 to -24 mV, showing that the Dhaleshwari river water was anti-oxidizing in nature.

The amount of DO in water is a key criterion for determining its quality. The amount of DO in water is an important factor controlling water quality for plant and animal viability. Measuring the amount of DO is crucial for understanding the water environment and its suitability for irrigation purpose and for biodiversity. Low DO levels debilitate aquatic animals, rendering them more susceptible to illness, parasites, and other pollutants. DO concentrations of 5–8 mg L^{-1} is appropriate for aquatic environments, and DO levels of less than 4 mg $L^{-1}$is considered crucial (Akan et al., 2007; Alam and Malik, 2008). According to Verma et al. (2008), the low DO levels (≤4 mg L^{-1}) in the waste water were the result of high organic pollution. The average DO value of the water samples in the current study of Dhaleshwari river was 4.4 mg L^{-1}indicating the river water samples were polluted and potentially highly dangerous for aquatic life. The DO at different sampling points of the Buriganga river ranged from 0.4 mg L^{-1} to 3 mg L^{-1} suggesting that the biological oxygen demand of the river water river water is high. Rahman and Hadiuzzaman (2005) also found lower levels of DO in industrially polluted water. Kumar et al. (2014) found the mean DO level 8.2mg $L^{-1}$and 1.9mg L^{-1}in river water and tannery effluents, respectively. The average value of DO in river water was 1.48 mg L^{-1} according to Rafid et al. (2019). Low DO is caused by high organic carbon levels.

To figure out the amount of carbon in any environmental samples, TOC is a quick and easy approach. While many countries do not regulate TOC levels directly, legislation generally regulates the quantities of particular volatile organic compounds, particularly TOC values of 0.05 mg C L^{-1}or less being recommended (DEFRA, 2019). According to International Standard method, water samples may contain organic carbon content ranging from 0.3 mg C $L^{-1}$to 1000 mg C L^{-1}. Carbon-containing compounds with varying levels of toxicity can be found in industrial waste effluents. These effluents are the sources of water carbon when mixed to river water through discharge channel. During the winter and summer seasons, organic carbon levels ranged from 0.18-3.3% and 0.59-1.8%, respectively (Islam et al., 2017).The average concentration of TOC present in the Buriganga river water samples during the current study was 167mg C L^{-1}. The concentration gave an idea about the abundance of organic carbon in river water of Hazaribagh site.High concentration of organic carbon (average 258 mg C L^{-1}) and nitrogen (average concentration of ammonium 134 mg N L^{-1}, nitrate 24 mg N L^{-1}) were present in the Dhaleshwari river water samples that exceed the standard limit fixed by WHO (1984).

In aquatic bodies, nitrogen concentrations over the standard value induce toxicity. The United States Public Health Service (USPHS) adopted drinking water standards in 1962, with a recommended nitrate-nitrogen level of 10 mgN L^{-1}. For regulated public water systems, the Environmental Protection Agency (EPA) has set a maximum contamination limit (MCL) of 10 mg N $L^{-1}$for nitrate-nitrogen and 1 mg N $L^{-1}$for nitrite-nitrogen. However, determining an exact amount at which nitrogen concentrations in water are safe or harmful is challenging. The concentrations of ammonia-N and total nitrogen along the tannery wastewater channel (drain) ranged from 520.44 to 401.23 mg N $L^{-1}$and 720.46 to 665.43 mg N L^{-1}respectively (Amainal, 2016). Average concentration of ammonium and nitrate in the river water samples of Buriganga were 114mg N L^{-1} and 11mg N L^{-1}respectively. Average nitrate concentration was close to standard value of nitrate. But in some samples the nitrate value exceeded standard level as the maximum was found 24 mg N L^{-1}.During the winter, total nitrogen content ranged from 0.09 to 0.24%, and 0.05 to 0.34% in the summer (Islam et al., 2017).

Heavy metal concentrations in river water have a major role in aquatic toxicity. Cr in excessively high quantities has negative impacts on aquatic living beings (Persoone et al.,1993). According to Chowdhury et al. (2015), the concentration of Cr in river water near the tannery was around 10,000 ppm. The standard concentration of Cr, Ni, and Pb for open water is 0.1 ppm (DoE, 2003). According to Das et al. (2011), Cr concentrations in nearby rivers ranged from 0.009 to 0.293 ppm. As said by Ahmed et al. (2010b), the Cr concentration in the Buriganga river was 0.587 ppm. In the dry season, Alam et al (2003) reported 0.001-0.008 ppm Cr. Tannery wastewater has been shown to have extremely high Cr concentrations, approaching 4000 ppm, resulting in considerable effluent Cr release to the environment (4.06 ppm) (Zahid, 2017).Chemical investigations of surface water conducted by UNIDO (2000) revealed that Cr (0.006-0.27 ppm) and Pb (0.25-0.47 ppm) concentrations were alarming. The Buriganga river water adjacent to the tannery area from the sluice gate discharge, midstream, and west end of the river was researched by UNIDO-GoB (2000) and Pb, Cr, and Ni concentrations were 3.26, 0.19-0.23, and 0.4-4.3 ppm, respectively, in river water near Hazaribagh. Sluice gate outlet accepting tannery wastewater with a high amount of Cr (16.41 ppm) is dissolving respective components and altering river water. The Cr concentration in river water from the middle and west end was found to be 0.018-0.024 ppm (UNIDO-GoB, 2000). The permissible limit of Cr in water is 0.05 ppm. Average Cr value in river water samples of Dhaleshwari was found 0.01 ppm that was low in comparison to other study and in Buriganga river the mean value was below detection limit. Ahmed et al. (2010a) reported that, Cr concentration in Dhaleshwari river was 0.441±0.042 ppm.The permissible limits of Pb and Ni fixed by WHO are 0.01ppm.In the current investigation, river water samples of the Buriganga were found having 0.01 ppm Ni, 0.01 ppm Pbon an average. Alam et al. (2003) revealed that in the Buriganga river Pb concentration varied between 0.005 to 0.014 ppm in dry season, which is close to the present study. Khan et al. (1998) found that the concentration of Pb in Buriganga river ranged from 0 to 0.0004 ppm which is lower than the current study but the maximum concentration of Pb found by Khan et. al (1998) was 0.008 ppm. Ahmed et al. (2010b) reported the lowest 0.007 ppm concentration of Ni present in Buriganga river during the dry season.The current study found Pb (except one sample) and Ni contents below the detection limit in river water samples of Dhaleshwari indicating the toxicity of Pb and Ni was very low in the river water samples. The average Cr and Pb, concentrations in Buriganga River were 297 and 731 ppm, respectively (Islam et al., 2017), whereas the concentrations in Ganga River, India, were 61.25–87.68, 10.71–14.26 ppm, respectively (Singh et al., 2017). According to a previous study, Cr, Pb concentrations in Dhaleshwari River water were 0.130, 0.201ppm respectively (Ahmed, 2012). Lipy et al. (2021) found 2.59 ppm Cr, 1.02 ppm Pb during monsoon and 3.35 ppm Cr, 1.32 ppm Pb during winter season in Dhaleshwari river water.

Heavy metal contents in sediments of Buriganga and Dhaleshwari river

Toxic heavy metals pose a severe hazard to the environment because of their non-biodegradable nature, extended biological half lifetimes, and ability to collect in many bodily organs. Heavy metals, like Cr, Pb and Ni were present in large amount in the sediment samples. The average concentration levels of the Cr, Pb and Ni in sediment samples were far above the standard permissible limits. The presence of excessively high concentration of Cr in the sediment might be due to the addition of significant amounts of Cr salts in the chrome tanning process. According to Das et al. (2011), Cr concentrations in tannery effluents ranged from 1.256 to 1.873 mg kg^{-1}andthe amount of Cr in effluent suspended sediments is even higher (~ 28,844 mg kg^{-1}). The Cr concentrations in canal water and canal water suspended solids were 0.443 and 20230 mg kg^{-1}, respectively (Zahid, 2017). Rafid et al. (2019) found, 49.3 mg kg^{-1}Cr in sediment during dry season and the minimum (below detection limit) was obtained in water.Average Cr value of sediment in Dhaleshwari river was found 1,085 mg kg^{-1}in the current study. The metal ions in the sediment of Buriganga river were present in the following order: Cr>Ni >Pb. In the current study, 15230 ppm Cr, 36 mg kg^{-1}Pb and 128 mg kg^{-1}Ni was found in the sediments of Buriganga river.

Das et al. (2011) reported that, Ni concentrations in tannery effluents at the Hazaribagh tannery site ranged from 0.004 to 0.009 mg kg^{-1} during the dry season. Cr and Pb concentrations declined considerably from the sediment depth of 3.0 m to the examined depth of 6.0 m, although Al, Fe, Mn, Zn, Ni, and Cu concentrations remained enriched (Zahid et al., 2006). Ahmed et al. (2010a) found 77.13 mg kg^{-1}Pb in sediments that is very high in comparison to the current study value of Dhaleshwari river. The average value of the Pb content in sediment samples was found 16.7 mg kg^{-1} (Mohiuddin et al., 2015a) that was close to the Dhaleshwari sediment sample value. Lipy et al., (2021) found average 96.02 mg kg^{-1}Cr and 23.69 mg kg^{-1}Pb in Dhaleshwari river water sediment samples. The average value of total Ni content in the sediment of Dhaleshwari river samples was very close to 147.06 mg kg^{-1} found by Ahmed et al. (2010a). Mohiuddin et al. (2011) found 160 mg kg^{-1}Ni content on an average in the sediments of river. Heavy metals concentration is higher in sediments than the river water due adsorption of metals. Metal concentrations in water and sediment were in the following order: Cr > Cd > Pb > Cu > As and Cr > Pb > Cu > As > Cd according to Lipy et al. (2021).

CONCLUSION

Environmental pollution is one of the world's significant issues, and it is worsening every day as a result of urbanization and industrialization. Tanning industries are absolutely necessary for the economy of our country, yet its effluent is released untreated into nearby water body. The heavy metal concentrations in the sediment samples analyzed in this study showed that almost all were above the provisional discharge limit set by the Environmental Protection Authority (EPA) and World Health Organization (WHO), demonstrating the tannery's poor treatment system. The explanation for the below detection limit or low concentration of heavy metals in most river water could be due to dilution by rain water and with the water moved from the uphill or precipitation of heavy metals. Furthermore, the levels of all accessible carbon and nitrogen in the river were high in the majority of the samples suggesting the risk of high organic pollution of river water. This water may pose a significant harm to the ecosystem and become carcinogenic to humans, even though other parameters don't really seem to be declining. Heavy metals abundance in the sediments will limit crop output in neighboring areas and have an impact on biodiversity. To reduce heavy metal contamination of water and sediment, tannery owners should strictly follow to tannery effluent minimization protocols. Heavy metal and other pollutant discharges into the environment must be carefully monitored and limited.

Acknowledgement

This research was done under the project “Resilient Rice Paddy Systems – Balancing Climate & Food Security” funded by GCRF (Global Challenge Research Fund, UK) (Project Ref.: EP/S515905/1).

Declaration

Conflict of interest: The authors report no declarations of interest.

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