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Spatial Distribution and Source Identification of Water Quality Parameters of an Industrial Seaport Riverbank Area in Bangladesh

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Citation: Islam, M.S.; Nakagawa, K.; Abdullah-Al-Mamun, M.; Khan, A.S.; Goni, M.A.; Berndtsson, R. Spatial Distribution and Source Identification of Water Quality Parameters of an Industrial Seaport Riverbank Area in Bangladesh. *Water* **2022**, *14*, 1356. https://doi.org/10.3390/w14091356

Academic Editor: Dimitrios E. Alexakis

Received: 2 April 2022
Accepted: 19 April 2022
Published: 21 April 2022

Abstract: The Pasur River is a vital reservoir of surface water in the Sundarbon area in Bangladesh. Mongla seaport is located on the bank of this river. Many industries and other commercial sectors situated in this port area are discharging waste into the river without proper treatment. For this reason, geospatial analysis and mapping of water pollutant distribution were performed to assess the physicochemical and toxicological situation in the study area. We used different water quality indices such as Metal Index (*MI*), Comprehensive Pollution Index (*CPI*), and Weighted Arithmetic Water Quality Index Method (*WQI*) to improve the understanding of pollution distribution and processes determining the quality of river water. Multivariate statistical methods were used to evaluate loads and sources of pollutants in the Pasur River system. The results indicate that the sources of contaminants are both geogenic and anthropogenic, including untreated or poorly treated wastewater from industries and urban domestic waste discharge. The concentration range of total suspended solid (TSS), chloride, iron (Fe), and manganese (Mn) were from 363.2 to 1482.7, 108.2 to 708.93, 1.13 to 2.75, and 0.19 to 1.41 mg/L, respectively, significantly exceeding the health-based guideline of WHO and Bangladeshi standards. The high Fe and Mn contents are contributions from geogenic and anthropogenic sources such as industrial waste and construction activities. The average pH value was 8.73, higher than the WHO and Bangladeshi standard limit. *WQI* (ranging from 391 to 1336), *CPI* (6.71 to 23.1), and *MI* (7.23 to 23.3) were very high and greatly exceeded standard limits indicating that the Pasur River water is highly polluted. The results of this study can be used as a first reference work for developing a surface water quality monitoring system and guide decisionmakers for priorities regarding wastewater treatment.

Keywords: industrial riverbank; surface water; pollution status; Pasur River; Bangladesh

1. Introduction

According to the United Nations, about one-third of the world's population drinks contaminated water [1]. Clean water is essential for human health, aquatic and terrestrial ecosystems, and life-supporting activities. However, industrial, urban, and agricultural activities release untreated effluents into surface water, creating an alarming water pollution situation in Bangladesh [2]. Pathogenic bacteria (total coliform and fecal coliform) gradually degrade water quality. In the oil refinery industry, conventional oil, gas, and coal bed methane are often accompanied by large volumes of contaminated water [3]. These industries give a high load of organic pollutants such as phenols, which are potentially dangerous for the environment and human health. Industrial wastewater also contains nitrogen, phosphorus, and heavy metals such as Fe, Cr, Ni, Cd, Zn, and Mn [4]. Geogenic sources may also contribute to the pollution load in river water systems. These sources include rock–water weathering, biological activity, sediment erosion, benthic distress, and riverine system flow regime changes [5,6]. Iron and manganese exist naturally in rivers; they may also be released to water from natural geologic deposits. The Earth's crust is a major source of Mn to the atmosphere, soil, and water.

Exposure to heavy metal pollution is a significant threat to the environment and public health worldwide [7] and especially in the developing world. Heavy metals enter the food chain through biomagnification and eventually affect human health [8]. The discharge of heavy metal waste into receiving waters may result in many physical, chemical, and biological disorders such as damaged DNA and gene expression changes [9]. Heavy metals in effluents are moderately soluble in water depending on pH and may affect the total and effective exposure to humans and accumulation in soils and plants [10]. Fly ash from thermal power plants and the cement industry is either discarded of as dry disposal in landfills or discharged into natural drainage systems such as rivers. These disposal methods result in metal contamination of surface and groundwater resources that eventually will turn up in the food chain [11]. Polluted water is the main reason that several diseases such as cancer; congenital disabilities; and skin, lung, brain, kidney, and liver conditions are several times more prevalent in the investigated area than elsewhere in the country. Waterborne diseases, such as hepatitis (A, B, and C), cholera, typhoid, dysentery, and diarrhea, are also caused by polluted water [12]. To control geogenic and anthropogenic sources of pollution and prevent them from growing to levels detrimental to human beings, programs to monitor pollutants in the river water and sediments are necessary [13].

The Pasur River is one of the most important waterways for economic growth in Bangladesh. It passes through the Mongla Seaport and the Mongla shantytown of the Bagerhat district in Bangladesh. Mongla is the second largest seaport in Bangladesh. It consists of the Pasur channel beside the Sundarban mangrove forest [14]. The Sundarban mangrove forest is the largest remaining tract of mangrove in the world. Beside the river lies the coal-based Rampal power plant station.

This study was carried out on the Pasur River in the Mongla port area. A significant site of oil refinery (petroleum and vegetable oil), cement, dye and paint, leather, and shipbreaking industries is established near the Pasur River. The industry directly discharges poorly or untreated toxic effluent into the Pasur River that becomes increasingly polluted [15]. The river water is used for different functions such as industrial purposes, household activities, bathing, irrigation of fields, and cooking foods by the adjacent rural populations. In some cases, in the dry season, when the drinking water is at crisis level, local rural people use the river water for drinking purposes after boiling. The river was once an important freshwater source for drinking and domestic uses, fisheries, and agricultural irrigation. The river is still used for fishing, and fishermen use smaller or larger boats for fishing. Polluted fish is another crucial reason to assess and monitor the surface water of this river.

Given the above, this study focused on assessing the Pasur River water quality by using water quality evaluation indices such as Water Quality Index (*WQI*) [16,17], Comprehensive Pollution Index (*CPI*) [18,19], and the Metal Index (*MI*) [20,21]. Though some research has been conducted for this river [22], there are still no systematic studies focusing on both physicochemical parameters and toxic metal pollution and pollution source determination in the concerned area. Assessment of pollution status is, thus, insufficient in this area. It is also essential to identify the pollution sources. For this purpose, we used multivariate analysis to indicate sources of water pollutants, including metals [23,24]. Therefore, the objectives of this study were (i) to determine the water quality parameters of the Pasur River by using physicochemical and toxicological parameters, (ii) to use water quality indices such as *WQI*, *CPI*, and *MI* for assessing the physicochemical and toxicological properties with spatial distribution for the Pasur River, and (iii) to identify the source of pollutants including metal contamination in water by using multivariate analysis methods.

2. Materials and Methods

2.1. Study Area

The Pasur is the largest river in the Sundarban (Mangrove Forest) region, located at 89°30′0″ E and 21°45′0″ N. This river is known as Rupsha in Khulna. To the north of Khulna in the Jashore region, the river is known as Bhairab River, and to the south of Khulna, from the Chalna area, it is named Pasur River, and this location is known as Mongla Upazila. Mongla Port Municipality is the second largest seaport of the country, export processing zone, and fishing industry area on the shore of the Pasur River. The study was conducted in the Pasur River at Mongla Port Municipality area in Mongla Upazila of Bagherhat District in Khulna, Bangladesh. It is located about 55 km south of Khulna City and 131 km north of the Bay of Bengal. Land use is concentrated to manufacturing industries, forest, upland fields, and urban areas. The geology is mainly constituted by tidal deltaic deposits but the northern and western area by marsh clay and peat deposits. The southern region also contains mangrove swamp deposits and north-eastern area deltaic silt deposits. The western and central parts of the eastern region of the study area are constituted by agricultural areas and the eastern and northern area is constituted by industry mixed with urban areas (Figure 1).

Mongla Port was established in 1954 on the Pasur and Mongla River junction bank, where 1280 cargo ships were handled in the fiscal year 2019–2020. According to Bangladesh 2011 census, the municipality area is 19.4 km^2 with a population of about 40,000 [25].

The location of the present study was 22°47′ N and 22°60′ N and 89°60′ E and 89°52′ E. The river passes through the right side of the Trikona and Dubla islands and discharges into the Bay of Bengal. The river is deep, so big ships can enter the Mongla Port year-round. The river width varies. It is about 460 m wide at Rupsha, 790 m at Bajuyan, and 2.44 km at Pasur-Shibsha. The river is about 142 km long. The Pasur River and all its tributaries are tidal channels. The river is now also an effluent channel as it receives more than 80% of the wastewater generated from urban areas and industrial sites.

More than 49 small and large manufacturing and processing industries are located in the study area that discharge waste and wastewater into the river without proper treatment. Jute processing, cement manufacturing, fertilizer manufacturing, oil refinery industry, construction materials, and automobile oil storage activities are included in this area [22]. The sampling points were selected based on assumed representative connections between the river and pollution sources. The study area location and samplings points are shown in Figure 1.

2.2. Methods

The surface water quality varies with rainfall. During the rainy season, due to increased rain, the concentration of pollutants in surface water can either be decreased by dilution or increase due to surface runoff due to first flush [27]. The present research collected water samples during the rainy season at 20 sampling points. Sampling sites were selected based on functional area, including industry, urban, and agricultural areas, as shown in Figure 1.

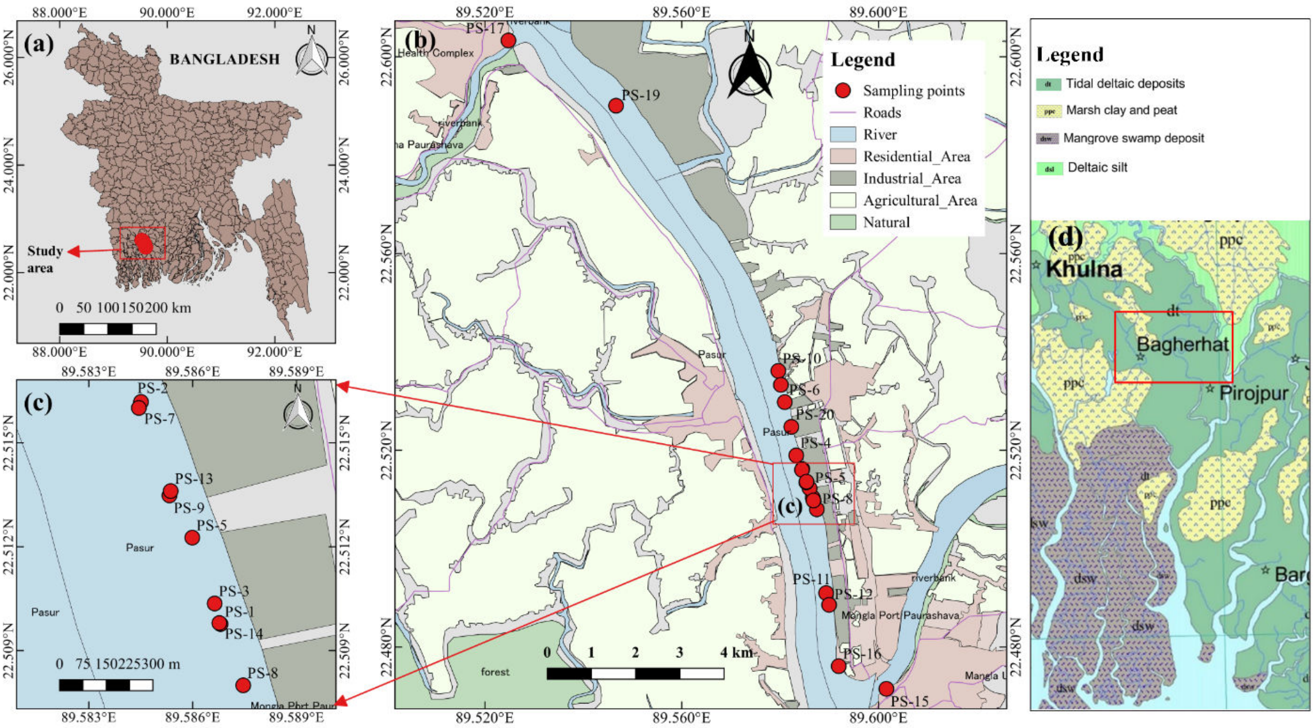

Figure 1. Location of (**a**) study area; (**b**,**c**) sampling points; (**d**) geological map of the study area [26].

Collection, storage, and transportation of water samples were performed according to standard guidelines [28]. Three water samples were randomly collected from each sampling site and then thoroughly mixed into a 1.0–1.5 L sample and transferred to clean 500 and 100 mL polyethylene bottles, respectively. This was undertaken to guarantee representative samples from each sampling point. At the same time, survey work was conducted at every sampling station to collect background information of the sampling area. The 500 mL samples were preserved with 5 mL of 55% HNO_3 per liter of water and maintained at 4 °C in the refrigerator for physical and chemical parameter analysis. The 100 mL samples were preserved with 2 mL of 6 N nitric acid for metal analysis. Before sample collection, all bottles were washed with 10% nitric acid and de-ionized water. The 100 mL samples were put in a beaker, and 5 mL concentrated HNO_3 was added and boiled at 130 °C on a hot plate until the volume was reduced to about 25 to 30 mL. HNO_3 addition was continued and repeated until the solution became clear. Then, the solution was cooled and filtered with deionized water passing through a Whatman no. 41 filter [29,30]. Ultra-pure HNO_3 was used for sample digestion. Temperature, pH, and total dissolved solids (TDS) were measured on site by a calibrated apparatus. The pH was determined by a portable calibrated pH Meter (HI 2211, HANNA Romania, Romania) and TDS was determined by calibrated multimeter (CT-676, BOECO Germany, Hamburg, Germany). Chloride, total alkalinity, total suspended solids (TSS), total hardness, iron, and manganese were measured by Mohr's titration, acid-base titration, filtration, EDTA complexometric titration, and flame-AAS method, respectively. Before analysis, all laboratory equipment was immersed in 10% nitric acid for 48 h, rinsed with distilled water, and dried in an oven. All chemicals and reagents used were of analytical grade. Deionized water with electrical conductivity less than 0.5 μS cm^{-1} and resistivity ~18 MΩ cm at 25 °C was used for the preparation of all solutions. A blank sample was prepared and analyzed for water samples to ensure that the chemicals used in the preparation did not contaminate the samples. By employing approved standard solutions (HACK, Love Land, Colorado, USA), calibration curves (linearity $\geq$ 0.995) were created to check the quality of measurements. To prepare spiked calibration standards, 2, 5, 10, and 15 mg/L of mixed standard and known concentration solution was added. The spiked calibration standard was added after every ten samples. Recovery rates of metals spiked in water fluctuated from 93 to 100%. The detection limits were 0.006 and 0.004 mg/L for Fe and Mn, respectively. Replicate analysis (RSD less than 5%) of the traceable Certified Reference Materials (CRM) and randomly selected samples were measured to check the analyses' precision and accuracy. All samples were measured in triplicate (RSD less than 5%), and the mean was used. Maps of the study area, spatial distribution of water quality indices, and cluster groups were produced using GIS software (QGIS, version 2.18.2).

2.3. Water Quality Index (WQI)

The Water Quality Index (*WQI*) is used for the assessment of both groundwater and surface water pollution levels [31,32]. The *WQI* is calculated using the weighted arithmetic method, initially proposed by Horton [33] and developed by Brown et al. [34,35]:

$$WQI = \frac{\sum Q_n W_n}{\sum W_n}, \tag{1}$$

where Q_n = quality rating of n-th water quality parameter; W = unit weight of n-th water quality parameter. Q_n is calculated by:

$$Q_n = \left[\frac{V_n}{V_s}\right] \times 100, \tag{2}$$

For the pH, this becomes:

$$Q_{pH} = \left[\frac{V_n - V_i}{V_s - V_i}\right] \times 100, \tag{3}$$

where V_n = actual amount of n-th parameter present; V_i = ideal value of the parameter (V_i = 0, except for pH (V_i = 7)); V_s = standard permissible value for the n-th water quality parameter.

The unit weight (W_n) of the various water quality parameters is inversely proportional to the recommended standards for the corresponding parameters.

$$W_n = \frac{k}{V_s}, \tag{4}$$

where k = constant of proportionality calculated by:

$$k = \frac{1}{\sum V_s}, \tag{5}$$

The *WQI* value falls into five categories such as *WQI*: < 50 → Excellent, grade 1; 51–100 → Good, grade 2; 101–200 → Poor, grade 3; 201–300 → Very poor, grade 4; and > 300 → Likely not suitable for drinking, grade 5 [36].

2.4. Comprehensive Pollution Index (CPI)

The Comprehensive Pollution Index (*CPI*) assesses the overall water quality status [37,38]:

$$PI = \frac{C_i}{S_i}, \tag{6}$$

$$CPI = \frac{1}{n}\sum_{i=1}^{n} PI, \tag{7}$$

where PI is the pollution index of the i-th parameter; C_i is the measured concentration of the i-th parameter; S_i is the standard permissible concentration of the i-th parameter in the water, and n is the total number of parameters. We used health-based guidelines from the WHO and the Department of Environment (DoE), Bangladesh, standard for maximum permissible concentrations. According to Mekuria et al. [39], the *PI* is a Single Factor Evaluation Index (*SFEI*) for each water quality parameter. When the value of $PI < 1$, the water quality meets surface water quality standards. *PI* > 1, indicates that the water quality exceeds the standards, hence, the water is polluted.

The water quality can be classified into five categories based on the calculated value of *CPI* such as *CPI*: 0–0.20, Category 1, Clean; 0.21–0.40, Category 2, Sub clean; 0.41–1.00, Category 3, Slightly polluted; 1.01–2.00, Category 4, Medium polluted, and ≥2.01, Category 5, Heavily polluted [40].

2.5. Metal Index (MI)

The *MI* assesses the overall quality of surface and drinking water by [41,42]:

$$MI = \sum \frac{C_i}{(MAC)_i}, \tag{8}$$

where C_i is the mean concentration of *i*-th metal and *MAC* is the maximum allowable concentration of each metal. The maximum limit of *MI* is 1, and *MI* > 1 is a threshold of warning. The classification of water quality based on *MI* is < 0.3, class-I very pure; 0.3–1.0, class-II pure; 1.0–2.0, class-III, slightly affected; 2.0–4.0, class-IV, moderately affected; 4.0–6.0, class-V, strongly affected; and >6.0, class-VI, seriously affected [43].

2.6. Statistical Analysis

Pearson correlation, principal component analysis (PCA), and hierarchical cluster analysis (HCA) were performed to identify relationships among the examined water quality parameters in the studied area to infer sources (geogenic or anthropogenic). Pearson correlation analysis represents the strength of the relationship between different parameters. PCA and HCA are the most common multivariate statistical methods for classifying and interpreting large datasets from environmental monitoring programs that reduce the dimensionality of the data. Data were processed using SPSS 17.0 for Windows; IBM, USA, and JMP Pro 15.

3. Results and Discussion

3.1. Water Quality Guidelines

A summary of the analyses results is shown in Table 1. Concentrations were compared to standard health-based guidelines by the WHO [44,45] and the Department of Environment (DoE), Bangladesh [46]. Temperature is an essential physical water quality parameter. The photosynthesis activity of green plants, physicochemical processes, and microbial biodegradation rate are greatly influenced by temperature. According to DoE guidelines for water in Bangladesh, the temperature should be maintained between 20–30 °C. The average and median temperature in the river water of the study area were 28.7 and 29.2 °C, respectively. The maximum and minimum temperature were 31.2 and 18.3 °C at the sampling location PS-16 and PS-9, respectively. The minimum temperature is caused by tidal flows of the river, excessive rainfall (128.7–321.9 mm), or sometimes discharging cooling water from industrial sites. Samples at PS-12, PS-13, PS-14, PS-15, PS-16, PS-17, PS-18, PS-19, and PS-20 occasionally exceeded the standard limit (Table 1). In previous studies, the temperature range of the Buriganga River in Bangladesh varied from 22.8 to 31.4 °C [47].

pH is a physical water quality parameter that is crucial for aquatic life. The toxicity of metals to aquatic life, different chemical and biochemical reactions, and the suitability of water for different uses are associated with water pH [39]. The recommended pH by WHO and DoE health-based guidelines varies from 6.50 to 8.50. In the study area, the median pH was 8.72 (Figure 2a), slightly higher than the recommendations. Maximum and minimum pH was 8.97 and 8.43 at PS-11, PS-13, and PS-18, respectively (Table 1). All sampling sites showed pH higher than the WHO and Bangladesh standards except PS-18 and PS-19. The low pH value at sampling locations PS-18 and PS-19 is attributed to relatively low anthropogenic influence. The higher pH may have been influenced by dissolving alkaline waste materials from Mongla municipal domestic area and poor or untreated industrial effluents from industry near the study area.

Table 1. Comparative study of physicochemical parameters of Pasur River water with WHO and DoE Standards.

Sample ID	Temperature (°C)	pH	TH (mg/L)	TDS (mg/L)	TSS (mg/L)	Chloride (mg/L)	Alkalinity (mg/L)	Fe (mg/L)	Mn (mg/L)
PS-1	27.00	8.57	75.23	144.44	643.96	215.07	100.61	1.48	0.40
PS-2	27.33	8.57	153.80	278.12	791.58	213.13	92.85	2.25	0.68
PS-3	27.33	8.60	71.91	136.68	1482.71	250.94	88.33	1.84	0.51
PS-4	27.67	8.67	64.72	127.74	426.64	224.59	91.67	1.13	0.46
PS-5	28.00	8.80	72.97	147.77	728.27	206.48	94.67	2.10	0.70
PS-6	27.00	8.53	85.12	142.28	567.09	221.13	92.67	1.41	0.38
PS-7	27.57	8.53	78.97	146.52	988.60	241.09	94.00	2.06	0.79
PS-8	28.67	8.73	163.67	354.58	852.60	108.15	106.00	1.97	0.71
PS-9	18.33	8.93	34.80	135.18	582.34	148.61	91.00	1.15	0.34
PS-10	28.33	8.70	56.70	134.78	1004.90	170.47	91.33	2.23	0.19
PS-11	29.67	8.97	173.47	326.18	926.84	708.93	67.67	2.75	1.41
PS-12	30.57	8.87	67.28	163.81	657.54	271.51	92.00	2.32	0.86
PS-13	30.33	8.97	207.51	455.24	763.97	212.30	93.33	2.49	1.01
PS-14	31.00	8.87	79.74	153.15	363.21	233.06	87.33	1.14	0.44
PS-15	30.50	8.93	276.55	524.60	666.32	214.06	98.67	1.86	0.68
PS-16	31.17	8.93	57.69	151.67	807.87	261.32	88.67	2.32	0.97
PS-17	30.33	8.70	77.52	142.53	582.32	205.03	98.00	2.19	0.79
PS-18	31.00	8.43	76.89	144.64	674.90	191.70	93.00	2.22	0.78
PS-19	30.33	8.47	65.16	133.58	572.16	211.11	97.67	1.62	0.55
PS-20	31.00	8.80	472.64	893.27	652.45	368.87	165.33	1.72	0.61
Maximum	31.17	8.97	472.64	893.27	1482.71	708.93	165.33	2.75	1.41
Minimum	18.33	8.43	34.80	127.74	363.21	108.15	67.67	1.13	0.19
Average	28.66	8.73	120.62	241.84	736.81	243.88	96.24	1.91	0.66
STD. Dev.	±2.88	±0.18	±102.89	±193.09	±242.82	±120.8	±17.85	±0.47	±0.28
WHO STD. [a,b]		6.5–8.5	500	1000	-	250	-	0.3	0.1
DoE STD.[c]	20–30	6.5–8.5	200–500	1000	10	150–600	-	0.3–1.0	0.1

[a, b] World Health Organization (WHO) [44,45]. [c] Department of Environment (DoE), Bangladesh [46].

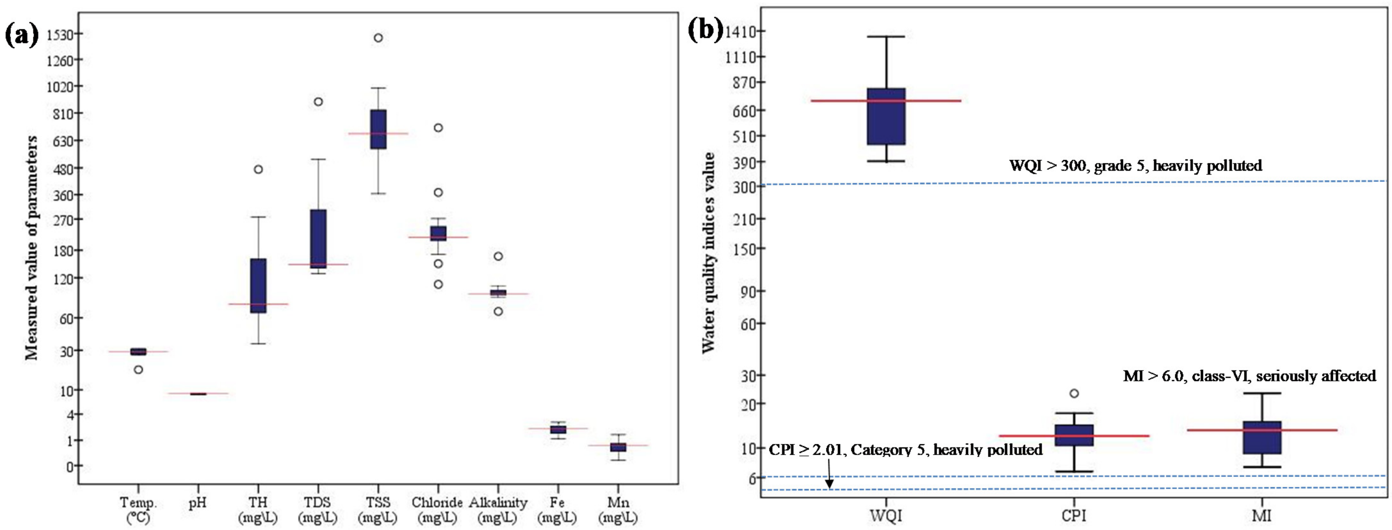

Figure 2. Boxplots for (**a**) descriptive statistics and (**b**) water quality indices.

Total hardness (TH) is influenced by contents of carbonate, bicarbonate, sulfate, and chloride salt of calcium and magnesium that decrease the water softness for cleaning, heating, and boiler systems. The WHO and national guideline for the total hardness of water is 500 mg/L, and the average observed concentration of 120.6 mg/L is lower (Table 1). The maximum and minimum concentration of total hardness was 472.6 and 34.8 mg/L at sampling station PS-20 and PS-9, respectively (Table 1). BNS Mongla (PS-20) was affected by the discharge of calcium and magnesium from household and industrial waste.

Total dissolved solids (TDS) consist of dissolved inorganic ions and suspended matter, and Bangladesh has recommended a maximum concentration of 1000 mg/L. The average concentration of TDS in the study area was 241.8 mg/L (Table 1) and the median was 147.2 mg/L (Figure 2a). The maximum and minimum concentration of TDS were 893.3 and 127.7 mg/L at sampling sites PS-20 and PS-4, respectively. TDS in the study area comes from domestic and industrial waste such as detergents, chloride, bicarbonate, fluorides, sulfate, and other ions. The chloride concentration range in samples was 108.2 to 708.9 mg/L with an average of 243.9 mg/L. The average is within the WHO and national standards (Table 1). The median value of chloride (214.6 mg/L) was also within the WHO standard limit (Figure 2a). The concentration of chloride in sampling locations PS-3, PS-12, PS-16, and PS-20 exceeded the WHO standard limit, whereas the chloride concentration of PS-11 exceeded the WHO and national guidelines of Bangladesh. Thus, the concentration of TDS and chloride at some locations did not exceed the permissible limits. A possible reason for this is the significant runoff of stormwater during the rainy season in the study area (129–322 mm) that can dilute the polluted water.

Total suspended solids (TSS) were calculated from dissolved suspended and colloidal materials that increase surface water's turbidity. TSS can affect surface water quality. Excess concentration of TSS affects light transmission and aquatic life. The standard limit of TSS should be maintained below 10.0 mg/L, which is recommended by the Bangladeshi standard (DoE). However, the average TSS concentration was 737 mg/L (Table 1). The median concentration of TSS was 671 mg/L and much higher than national standard value (Figure 2a). Maximum and minimum concentration of TSS in the river water was 1482 and 363 mg/L at the Omera Petroleum Industrial area (PS-3) and Laudobe ghat area (PS-14), respectively. All sampling sites displayed a higher TSS than permissible levels (Table 1). This is probably due to the discharge of large volumes of industrial waste and wastewater from nearby industry and local urban bazaars to the river without any treatment.

Total alkalinity is related to the contents of carbonate, bicarbonate, and hydroxyl ions in the water. The average concentration of total alkalinity in the samples was 96.2 mg/L. Maximum and minimum concentrations were 165.3 and 67.7 mg/L at sampling points PS-20 and PS-11 (Table 1), respectively. At PS-20, the total alkalinity concentration was higher than other sampling points due to alkaline household and industrial waste discharged into the river without treatment.

Iron is a common metal in surface water that may dissolve from surface sediments and suspended matter. Dissolved iron in the surface water is usually not a health hazard, but it may create a bitter taste, stain, and discolor laundry. In addition, high iron contents are not suitable for heating systems and boilers. According to the WHO standard, iron concentrations should be below 0.30 mg/L. However, the average concentration of iron in the samples was 1.91 mg/L (Table 1). The median value of Fe was 2.0 mg/L, and much higher than the standard limit (Figure 2a). The maximum and minimum concentration of iron in river water was 2.75 and 1.13 mg/L at sampling sites PS-11 and PS-4, respectively. High iron concentrations probably stem from suspended matter and industrial waste (Table 1). Thus, it can be concluded that the river water is not fit for use in household activities and industrial purposes without treatment. Iron forms several sulfides in nature, such as pyrite (FeS_2), marcasite (FeS_2), pyrrhotite ($Fe_{11}S_{12}$), troilite (FeS), and numerous other more complex compounds. Iron exists naturally in rivers; it may also be released to water from natural geologic deposits. Iron at average temperature is usually deposited from solutions such as hydrous sesquioxide, carbonates, sulfides or hydrous silicates of iron and potash known as glauconite. Anthropogenic sources such as untreated industrial effluents, improper disposal of domestic waste, and agricultural runoff are the main contributors to iron pollution in the Pasur River.

Manganese is an essential natural element in surface water but may adversely affect aquatic ecosystems [48]. The manganese concentration should be below about 0.1 mg/L according to the WHO and Bangladeshi standards for water. The average manganese concentration in the study area was 0.66 mg/L. The median value was 0.68 mg/L, and consequently much higher than recommended standards (Figure 2a). The maximum and minimum manganese concentration in the study area was 1.41 and 0.19 mg/L at sampling points PS-11 and PS-10, respectively (Table 1). The concentration of metals in the water of the Pasur River is compatible with that of surface water of other aquatic systems in Bangladesh and worldwide [29,49–51]. The manganese concentration in the Pasur River is alarming for aquatic environments, most likely caused by dissolved, suspended solids and industrial waste. Manganese sources can be geogenic or anthropogenic. Manganese forms two sulfides, alabandite (MnS) and hauerite (MnS_2). Both minerals are scarce and so unstable that they rapidly oxidize on exposure. Alabandite is the less rare form and usually occurs as a subordinate constituent of metalliferous veins or allied deposits. The anthropogenic sources of Mn are industrial effluents, runoff from agricultural activities, and uncontrolled release or leakage from landfill sites. The Sela River at Sundarbans area, an ecologically important river like the Pasur River, has drawn global attention after an oil spill accident in December 2014, when about 94,000 gallons of heavy fuel were released into the river, causing instant damage to the mangrove habitat and wildlife. Thus, chemical accidents or disasters in adjacent rivers are also sources of physicochemical and toxicological pollution.

3.2. Water Quality Indices

The water quality indices in the analyzed water were expressed by box plots. The three water quality indices are shown in Figure 2b. The *WQI* was within the range of 391–1336. The median was 725 (Figure 2b) and greatly exceeded the maximum limit of 300, which indicates the pollution status of grade 5. Thus, water in all locations falls under the "very poor water" and "likely not suitable for drinking purposes" categories. The highest *WQI* was found at PS-11 (Table 2). The metal contamination in this location is very high, which is a major concern. The high *WQI* in the study area is due to both geogenic sources of pollutants and discharge of municipal wastewater and industrial effluents, fishing boats, agricultural runoff, loading–unloading, and construction activities in the Mongla seaport area.

The *CPI* was applied to understand the overall status of Pasur River water pollution. This varied between 6.7–23.1, with an average of 12.8 (Table 2), and a median of 12.1 (Figure 2b). The median *CPI* (12.1) indicates high pollution levels. All sampling locations exceeded the maximum limit of $\geq$2.0, indicating Category 5 and heavy pollution. The highest *CPI* was recorded at PS-3. The reason is discharge of domestic waste, sewerage, and septic waste. At the same time, metals are generated from garages, vehicle battery maintenance shops, and other adjacent industries.

To assess and evaluate the combined effects of metals, *MI* was used. The *MI* ranged from 7.2–23 with a median of 13 (Figure 2b). The median exceeded the maximum limit of 1 (*MI* > 1 is a threshold of warning). All sampling locations were clearly above the maximum limit of >6.0 (class-VI, seriously affected). Highest *MI* was found at PS-11 (Table 2).

The source of metals may be anthropogenic or geogenic. Anthropogenic sources of metal contamination are probably due to industrial wastewater from workshops and garages, vehicle batteries, paints and pigment, fishing boats, fuel stations, and agrochemicals.

3.3. Spatial Distribution of Water Quality Indices

GIS analysis was applied to improve the understanding of the spatial distribution of the different water quality indices (*WQI*, *CPI*, and *MI*) (Table 2). The QGIS (version 2.18.2) was used for this purpose [52]. The distribution maps, thus, show the concentration variation of water quality parameters within the region. Lower values of quality indices are represented by light red color while deep red indicates a polluted area (Figures 3–5).

Table 2. Water quality index (*WQI*), Comprehensive Pollution Index (*CPI*), Metal Index (*MI*), and pollution status.

Sample ID	*WQI*	*CPI*	*MI*	Pollution Level
PS-1	466.4	10.80	8.93	High
PS-2	746.6	13.72	14.30	High
PS-3	638.8	23.13	11.23	High
PS-4	466.1	7.62	8.37	High
PS-5	744.8	12.73	14.00	High
PS-6	440.2	9.65	8.50	High
PS-7	826.5	16.58	14.77	High
PS-8	750.6	14.46	13.67	High
PS-9	391.3	9.64	7.23	High
PS-10	399.9	15.99	9.33	High
PS-11	1336.1	17.24	23.27	High
PS-12	875.6	12.09	16.33	High
PS-13	1008.1	13.96	18.40	High
PS-14	447.9	6.71	8.20	High
PS-15	706.1	11.82	13.00	High
PS-16	967.9	14.39	17.43	High
PS-17	807.5	10.82	15.20	High
PS-18	808.9	12.13	15.20	High
PS-19	582.9	10.05	10.90	High
PS-20	641.9	11.65	11.83	High
Average	702.7	12.76	13.0	High

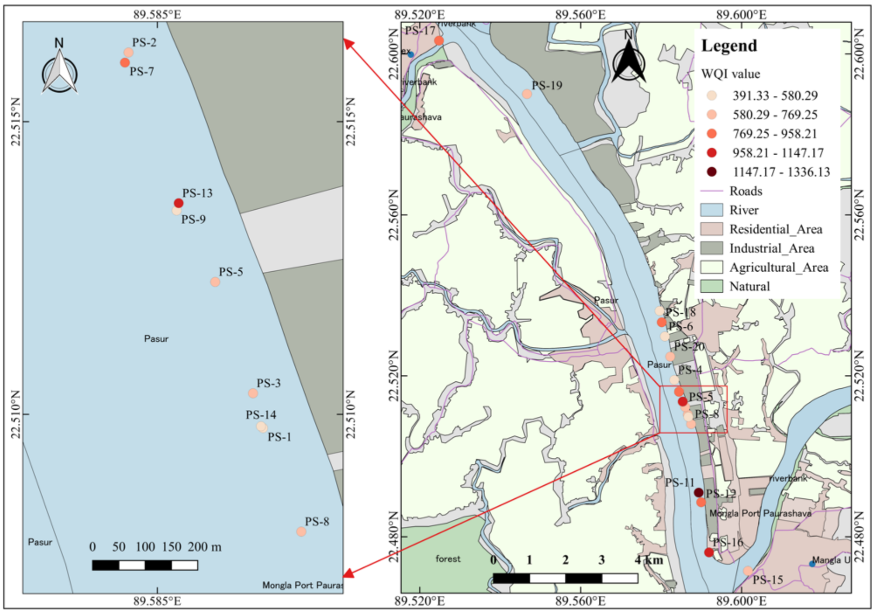

Figure 3. Spatial distribution of Water Quality Index (*WQI*).

The spatial variation of *WQI* is shown in Figure 3. The *WQI* ranged from 391 to 1336, calculated using pH, TDS, chloride, total hardness, TSS, Fe, and Mn. It can be concluded that the southeast part of the study area had the highest values. The sampling points were close to the Mongla Seaport associated with intense urban activities, including trunk roads with many landfills, garbage dumps, and municipal waste. Probably these are the primary pollution sources responsible for increasing the pollution and hence *WQI*. The lowest *WQI* was at the center of the area and decreasing when moving from south to north. High *WQI* is probably related to domestic waste, effluents from industry and nearby local markets, and agricultural runoff. Tidal processes and rainy period stormwater runoff are likely important for the transport characteristics of *WQI* pollutants. Runoff can also wash away topsoil particles and contribute to riverbank erosion. As the flow rate increases, resuspension can mobilize bottom sediments, further raising TSS concentrations.

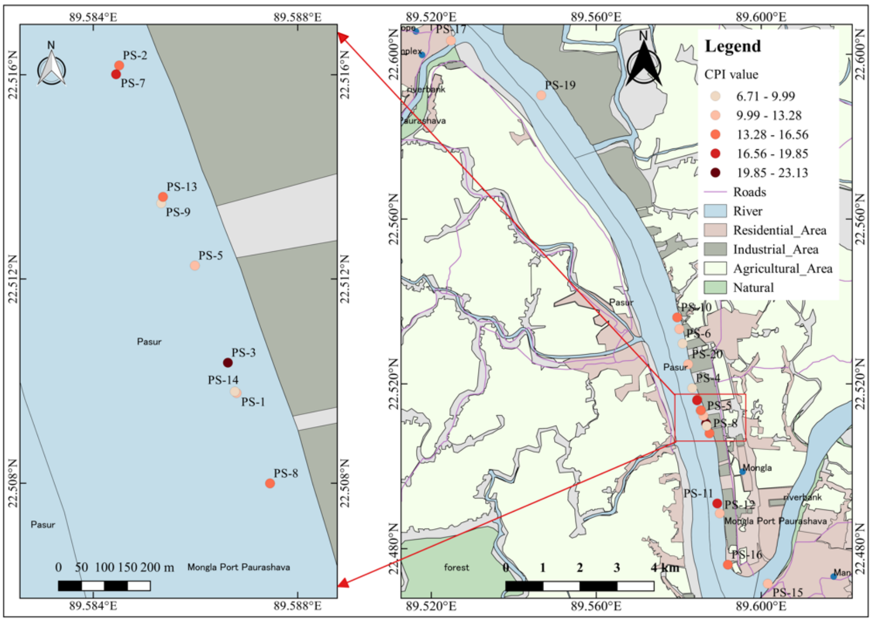

Figure 4. Spatial distribution of Comprehensive Pollution Index (*CPI*).

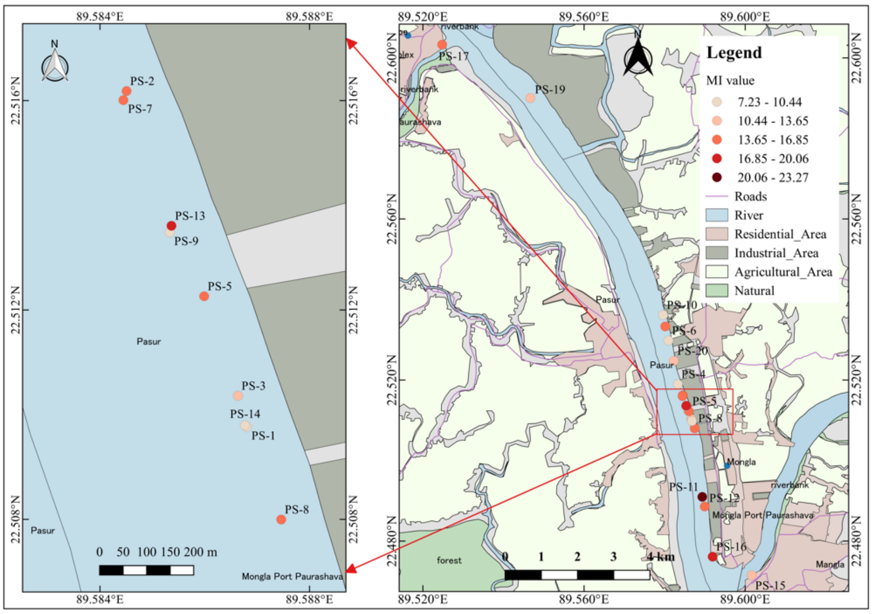

Figure 5. Spatial distribution of Metal Index (*MI*).

The spatial distribution of *CPI* is shown in Figure 4. The trend of *CPI* distribution is somewhat similar to the distribution for *WQI*. The *CPI* gradually decreases from south to north in the study area. Highest *CPI* was found in the south and south-eastern parts, whereas the north region is associated with low *CPI* (Figure 4). The sites with high pollution load are densely populated urban areas including a trunk road, bazaars, shops, car washing garages, and many small and heavy industries situated beside the bank of Pasur River. The pollution from industrial effluents, urban and agricultural waste, municipal and household waste in some rivers in Bangladesh has reached alarming levels. High water temperature and hardness increase the heavy metal toxicity.

The spatial variation of *MI* is shown in Figure 5. The spatial distribution indicates a trend with increasing concentrations from north to south. The southern study area thus indicates higher pollution pressure (Figure 5). The southern region is close to Mongla Seaport and urban areas with heavy industries. The highest value of *MI* was found in sampling location PS-11, which is closely associated with the Mongla seaport area. Many ships gather here for extensive loading and unloading activities. This may be the probable reason for higher metal pollution at this site. The *MI* index exceeded the standard limit ($MI > 1$) for all sampling points. Thus, it can be concluded that the entire study area is seriously threatened by metal pollution. Rivers transport large amounts of domestic sewage, industrial wastewater, and seasonal runoff from agricultural fields. The high *MI* is probably due to industrial, seaport, and construction activities, fishing boats, and domestic waste.

3.4. Multivariate Analysis

3.4.1. Pearson's Correlation Matrix

Pearson correlation was used to study relationships between surface water contaminants with significance levels at $p < 0.01$ and $p < 0.05$ [53–55]. Table 3 presents the Pearson correlation for physicochemical parameters. Parameters that correlated positively with one another included Mn with Fe ($r = 0.757$), $p < 0.01$); total hardness (TH) with alkalinity ($r = 0.739$, $p < 0.01$) and TDS ($r = 0.992$, $p < 0.01$), and TDS with alkalinity ($r = 0.735$, $p < 0.01$). TSS was moderately correlated with Fe ($r = 0.483$) and chloride was moderately related to Fe ($r = 0.641$, $p < 0.05$). Higher correlation between variables may indicate common sources, mutual dependence, and similar or nearly identical metal accumulation properties in surface water.

Table 3. Pearson's correlation matrix.

Parameter	Temp.	pH	TH	TDS	TSS	Chloride	Alkalinity	Fe	Mn
Temp.	1								
pH	0.344	1							
TH	0.104	0.292	1						
TDS	0.137	0.365	0.992 **	1					
TSS	−0.259	−0.097	−0.022	−0.021	1				
Chloride	0.068	0.328	0.32	0.287	0.165	1			
Alkalinity	0.015	−0.062	0.739 **	0.735 **	−0.159	−0.123	1		
Fe	0.127	0.2	0.133	0.146	0.483 *	0.391	−0.205	1	
Mn	0.239	0.391	0.226	0.236	0.17	0.641 **	−0.227	0.757 **	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

The strong correlation between total hardness with alkalinity indicates a common source of contamination. Hardness is mainly caused by calcium and magnesium salts. These salts are dissolved from geologic deposits through which water travels. Most alkalinity in surface water comes from calcium carbonate, $CaCO_3$, being leached from rocks and soil. The anthropogenic sources for both are industrial effluents, municipal wastewater discharge, or excessive application of lime to the soil in agricultural areas. The strong correlation between TDS and alkalinity indicates a similar source. TDS in surface water may come from agricultural and residential (urban) runoff, leaching of soil contamination, and point source water pollution discharge from industrial or sewage treatment plants.

Fe and Mn were strongly correlated. Both have a similar geogenic source. Carbonates of Fe and Mn are isomorphous with each other, hence a possible cause of their association, such as is seen in almost all manganiferous spathic iron ores, whether these ores are formed by direct precipitation or by replacement of carbonate of lime. The oxidation of such a mixture would give a combined iron and manganese ore of the common form. Common anthropogenic sources of Fe and Mn are industrial effluents and local urban wastewater discharge. TSS did not show a strong correlation with any variable. Thus, the source is probably different as compared to other pollutants.

3.4.2. Principal Component Analyses

The sources of pollutants were further investigated using PCA and HCA. The results of the PCA are shown in Table 4. The total number of components (common factors) in the PCA was determined based on the Kaiser criterion [56]. Under this criterion, the only component with eigenvalues ≥ 1 should be accepted as a possible source of variance in the data, with the highest priority ascribed to components with the highest eigenvector sum. Scree plots were used to identify the number of PCs to be retained to comprehend the underlying data structure [57]. This indicated that the first three components capture the most significant variation in the data. Thus, three PCs were extracted. The eigenvalues for these PCs ranged from 1.16 to 3.29, explaining 76.1% of the total variance. PC 1, PC 2, and PC 3 explained 36.6, 26.6, and 12.8% of the total variance, respectively (Table 4).

Table 4. Results of principal component analysis.

	PC 1	PC 2	PC 3
Temperature	0.57	0.10	0.24
pH	0.48	0.10	−0.70
TH	0.81	−0.54	0.06
TDS	0.81	−0.54	0.02
TSS	0.14	0.43	0.63
Chloride	0.63	0.38	−0.22
Alkalinity	0.38	−0.83	0.25
Fe	0.59	0.63	0.30
Mn	0.70	0.59	−0.12
Eigen values	3.29	2.40	1.16
% of variance	36.59	26.65	12.84
Cumulative %	36.59	63.23	76.07

PC 1, accounting for 36.6% of the total variance, had positive loadings for all parameters but especially high loading for total hardness, TDS, Mn, and chloride (r = 0.63–0.81), and moderately associated with pH, alkalinity, temperature, and Fe. The Pearson correlation matrix showed that total hardness was strongly correlated with TDS. These pollutants have similar geogenic and anthropogenic sources such as untreated industrial effluents, agricultural runoff, municipal waste, and landfills from nearby urban areas. PC 2 was strongly associated with Fe, Mn, and TSS also confirmed from the correlation matrix. The strong association between Fe and Mn indicates that similar sources are at hand. PC 3 had high association with TSS and pH (Table 4).

3.4.3. Hierarchical Cluster Analysis (HCA)

The HCA was based on Ward's method with squared Euclidean distance [58,59] and performed on standardized data based on the three PC scores outlined above. The 20 samples were classified into four distinct groups, clusters A, B, C, and D. The average concentration of each cluster group is shown in Table 5. The table shows that cluster A was not strongly related with any parameters. Cluster B was related to high TSS, Fe, and Mn. Cluster B contained higher indices values (*WQI*, *CPI*, and *MI*) than cluster A and D. Cluster C and D, in which only one sample was classified of each. High TSS, pH, chloride, Fe, and Mn were classified in cluster C. Cluster C was ranked as the most polluted area among the four clusters with respect to *WQI*, *CPI*, and *MI*. Cluster D was related to pH, TDS, and chloride. This cluster's *WQI*, *CPI*, and *MI* values were lower than cluster B and C but higher than cluster A. The decreasing order of indices was cluster C > cluster B > cluster D > cluster A (Table 5). Thus, cluster C was most polluted, and cluster A the least.

Table 5. Average concentration of water quality parameters in each cluster group.

	Cluster A	**Cluster B**	**Cluster C**	**Cluster D**
No. of samples	5	13	1	1
Temperature (°C)	26.2	29.34	29.67	31.0
pH	8.71	8.71	8.97	8.8
TH (mg/L)	67.92	109.74	173.47	472.64
TDS (mg/L)	140.56	224.19	326.18	892.27
TSS (mg/L)	516.65	813.36	926.84	652.45
Chloride (mg/L)	208.49	212.10	708.93	368.87
Alkalinity (mg/L)	92.66	94.5	67.67	165.33
Fe (mg/L)	1.26	2.11	2.75	1.72
Mn (mg/L)	0.40	0.71	1.41	0.61
WQI	442.4	758.8	1336.1	641.9
CPI	8.88	14.0	17.2	11.7
MI	8.25	14.14	23.3	11.8

The scatter plot of the 20 samples described by principal components (A: PCs 1 and 2; B: PCs 1 and 3; C: PCs 2 and 3) and classified into four clusters is shown in Figure 6. If a PC score is greater than 0, the water quality parameter characteristics influence the component at the site. Conversely, if a PC score is less than 0, it means that the component was not significantly affected by the water chemistry at the site [60,61]. In PC 1, cluster C and D are separated from cluster A, and B. PC 1 has smaller scores for cluster A indicating that it had less concentration of the quality parameters than cluster B, C, and D. Thus, it can be confirmed that samples of cluster A were less polluted than others. Cluster B contained higher PC 1 scores than cluster A. In addition, due to positive PC 2 scores of cluster B compared to cluster A, samples of this cluster had a higher concentration of water quality parameters than cluster A. The higher concentrations are due to geogenic and anthropogenic sources such as untreated industrial wastewater, domestic and municipal wastewater discharge from the urban areas, and agricultural runoff. Both cluster C and the majority sample of cluster B showed a positive score for PC 1 and 2, indicating that both clusters contained high concentration pollutants from industrial, agricultural, and urban areas. This is also confirmed from the average *WQI*, *CPI*, and *MI* value of Table 5. Both cluster C and cluster B showed positive scores for PCs 1 and 2, but cluster C was more affected than cluster B (Figure 5). PC 3 revealed that cluster B is significantly more influenced than cluster D. Thus, the sample of cluster B was more affected and polluted than cluster D.

The spatial distribution of each cluster can be observed in Figure 7. Cluster C is generally located nearer the Sundarban mangrove forest in the west part of the study area and the southeast region in the urban area. Cluster C is the study area's most contaminated sampling point containing the highest metal contamination and water quality indices (*WQI, CPI, MI*). The location of cluster C is associated with Mongla Seaport. Many ships and vessels are taking part in loading and unloading activities for different types of goods. Sometimes they discharge waste, including used oil and oily substances, coal, asbestos, and chemicals directly into the river. The high TSS may come from local bazaars in urban areas and municipal wastewater and landfills.

Cluster B is located south to north at different study area sites (Figure 7). The samples of this cluster contained high metal concentrations and high water quality indices (*WQI, CPI, MI*), indicating a metal contamination area. The contamination of this area is higher than for cluster D and cluster A. Sample of cluster D is in the southeast region and near the residential area. The sample of these points contained high calcium and magnesium carbonates, bicarbonates and sulfates, and combined content of all inorganic and organic substances present in a liquid in molecular, ionized, or micro-granular (colloidal sol) suspended form. For this reason, it contains the highest value of total hardness and TDS.

The source of these pollutants is agricultural runoff and residential (urban) runoff. This area had high metal contents and TSS.

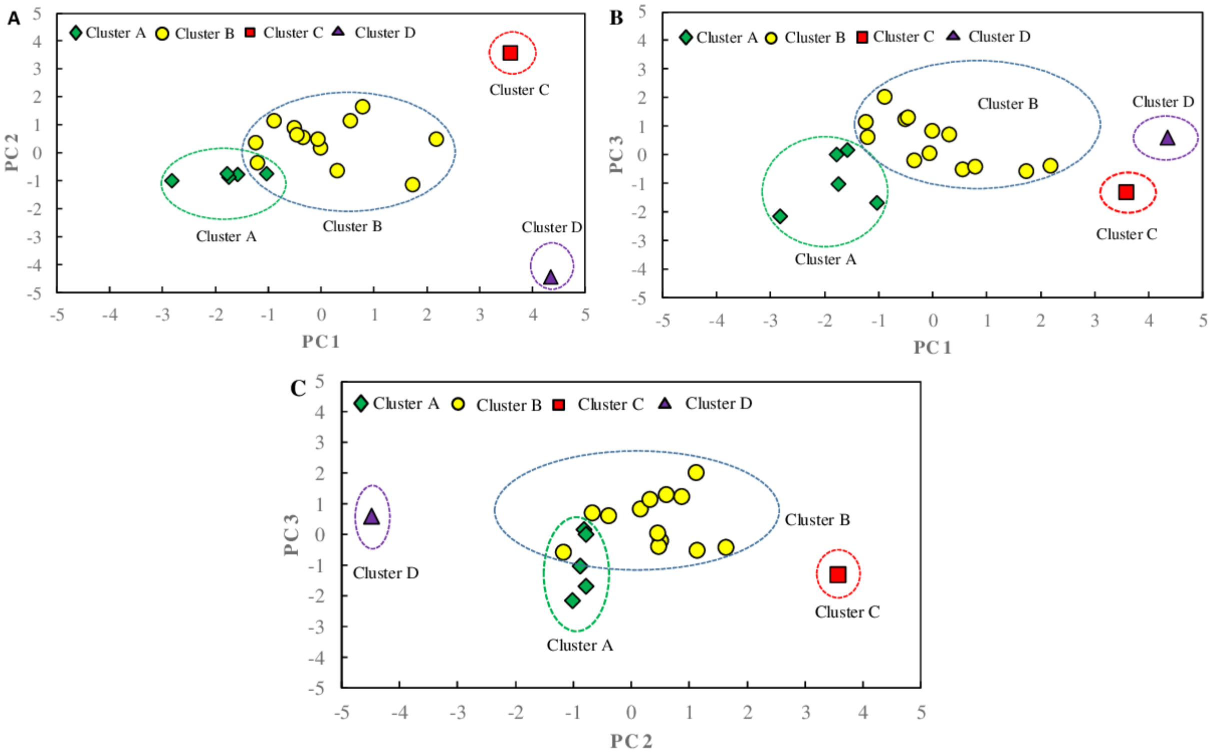

Figure 6. Scatter plots for two principal components with respect to clusters; (**A**) PCs 1 and 2, (**B**) PCs 1 and 3, and (**C**) PCs 2 and 3.

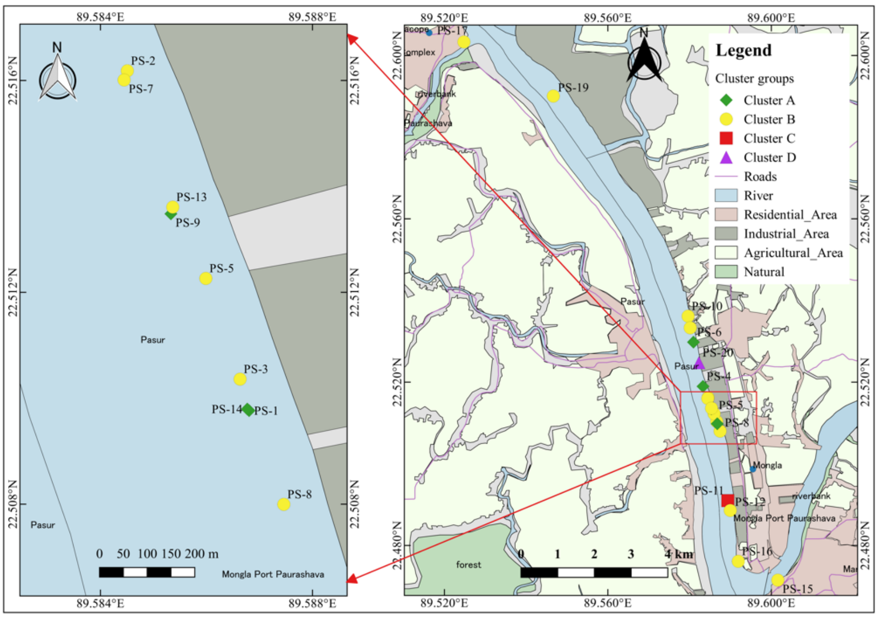

Figure 7. Distribution of each cluster in the study area.

All cluster A samples are in the southeast area but far from cluster C. Samples of cluster A contain the lowest value of metals and other physicochemical parameters. Thus, these samples were less polluted than other clusters. To conclude, this study shows that the pollution level of the study area is divided into four main areas.

4. Conclusions

Rivers are essential sources of water supply for humans and environment with critical conditions for water quality. This study concluded that iron, manganese, total suspended solids, chloride at some locations, and pH had much higher concentrations in the river water than recommended by WHO and Bangladesh Environmental standards (DoE) and thus are not safe for household use or aquatic ecosystems. We used water quality indices, spatial distribution, and multivariate statistical analyses to evaluate the pollution level and source determination. Multivariate analysis was used to improve the knowledge regarding the source of pollution. Based on the PCA results, four distinct groups were obtained by HCA. The concentration of different water quality parameters was different regarding land use and the importance of the three PC scores. The cluster groups revealed that the sample of cluster C was most polluted, and the samples of cluster A were the least polluted in the study area. The severe enrichment of pollutants in this area is primarily due to anthropogenic sources related to industrial, agricultural, urbanization, and fishing activities.

Mongla Seaport Authority, Mongla Export Processing Authority, Mongla Municipal Corporation, District Administration, and the Department of Environment can take the initiative to protect the river water from pollution and untreated industrial and municipal waste. Monitoring of coastal activities is essential to save the coastal ecosystems. This monitoring system can give policymakers and stakeholders an interest in the coastal environment and resources. A systematic and periodic inspection of each industry located beside the river should be performed before certificates of compliances are issued by the Department of Environment (DoE), Bangladesh. Short- and long-term scientific studies should be immediately started to assess the impacts of industrial activities on coastal water, soil, and fishery resources, as well as human health. Thus, this study recommends that continuous monitoring of the pollution level of the Pasur River as well as adjoining agricultural areas should be assessed regarding the risk for human health and ecosystems in the vicinity of the river. To avoid and alleviate environmental contamination, effective approaches for extracting harmful heavy metals from sewage and industrial effluents are urgently needed before the effluent is released into the environment. As well, traditional treatment techniques are necessary for water used for domestic purposes. Finally, public awareness of the impacts and remedies of pollution should be raised so that they can play a key role in pollution reduction.

Author Contributions: Conceptualization: M.S.I. and M.A.G.; Methodology: M.S.I. and M.A.G.; Formal analysis and investigation: M.S.I., M.A.-A.-M. and A.S.K.; Visualization; M.S.I. and K.N.; Writing—original draft preparation: M.S.I. and K.N.; Writing—review and editing: K.N., R.B., and M.S.I.; Resources: M.S.I.; Supervision: K.N. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors wish to express their sincere thanks to Department of Chemistry at "Jashore University of Science and Technology" for the laboratory support to complete this research and the "Asian Arsenic Network" laboratories for their generous cooperation in analyzing samples for elemental analysis by AAS.

Conflicts of Interest: The authors declare that they have no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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