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Analysis of Seasonal Water Characteristics and Water Quality Responses to the Land Use/Land Cover Pattern: A Case Study in Tianjin, China

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Abstract: As the second largest city in northern China, Tianjin has a unique geographical and social status. Following its rapid economic development, Tianjin is experiencing high levels of surface water pollution. The land use/land cover (LULC) pattern has a considerable impact on hydrological cycling and pollutant transmission, and thus on regional water quality. A full understanding of the water quality response to the LULC pattern is critical for water resource management and improvement of the natural environment in Tianjin. In this study, surface water monitoring station data and LULC data from 2021 to 2022 were used to investigate the surface water quality in Tianjin. A cluster analysis was conducted to compare water quality among monitoring stations, a factor analysis was conducted to identify potential pollution sources, and an entropy weight calculation was used to analyze the impact of the land use pattern on water quality. The mean total nitrogen (TN) concentration exceeded the class V water quality standard throughout the year, and the correlation coefficient of the relationship between dissolved oxygen (DO) and pH exceeded 0.5 throughout the year, with other water quality parameters showing seasonal changes. On the basis of their good water quality, the water quality monitoring stations near large water source areas were distinguished from those near areas with other LULC patterns via the cluster analysis. The factor analysis results indicated that the surface water in Tianjin suffered from nutrient and organic pollution, with high loadings of ammonia nitrogen (NH_3N), TN, and total phosphorus (TP). Water pollution was more serious in areas near built-up land, especially in the central urban area. The entropy weight calculation results revealed that water, built-up land, and cultivated/built-up land had the greatest impact on NH_3N, while cultivated land had the greatest impact on electrical conductivity (EC). This study discusses the seasonal changes of surface water and impact of land use/land cover pattern on water quality at a macro scale, and highlighted the need to improve surface water quality in Tianjin. The results provide guidance for the sustainable utilization and management of local water resources.

Keywords: surface water monitoring; land use; cluster analysis; factor analysis; water pollution source

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1. Introduction

Freshwater is one of the most important natural resources for human survival, and is also a strategic resource for national economic development [1–3]. Excellent water quality is essential to maintain ecosystem balance and enable sustainable human development. However, climate change, urbanization, industrialization, and agricultural production have had a negative impact on water quality in recent decades, leading to eutrophication, organic pollution, and black and odorous water [4,5]. Water quality deterioration has gradually emerged as an issue that threatens ecosystem function, agricultural production, food safety, and public health [6].

To prevent water quality deterioration and improve the aquatic environment, long-term monitoring of water quality is necessary in key areas [7]. Water quality parameters that are routinely monitored include electrochemical parameters, nutrients, organics, and ions, according to the Environmental Quality Standards for Surface Water of China (EQSSWC; standard number: GB3838-2002) [8–12]. By monitoring these parameters, the surface water quality of areas with different land uses can be characterized, and the main factors influencing surface water pollution can be effectively determined. According to the source and geographical scope, water pollution can be classed as either point or non-point source pollution [13,14]. Point source pollution refers to pollution sources with fixed discharge points, such as industrial wastewater and domestic sewage pollution, which are mainly affected by human activities. Non-point source pollution refers to pollution from non-specified places, which flows into the water bodies (rivers, lakes, reservoirs, bays, etc.) through runoff because of the precipitation and snowmelt scouring. Non-point source pollution is mainly affected by human activities and environmental factors (climate, soil, topography, etc.) [15,16]. Either point or non-point pollution present great challenges to water quality management. For effective water resource management and improvement of the natural environment, it is essential to comprehensively investigate regional water quality and water pollution sources.

Numerous studies have shown that climate, soil, terrain, land use/land cover (LULC), and human activities affect the water quality in river basins [17,18]. The LULC pattern has a considerable impact on the natural environment and water quality of river basins through non-point source pollution, which has increased in many river basins due to natural landscape fragmentation and increasing urbanization [19–22]. Land use/land cover refers to the long-term or periodic operation, management, treatment, and transformation of land by human beings according to a series of biological and technological means for specific economic and social purposes [23,24]. It can determine the pollution generated on land and transported to water bodies through runoff [25–27]. The allocation and proportion of LULC in a region are closely related to water quality, and LULC patterns impact local water quality. Generally, forests and grasslands enhance water quality by filtering particulate pollutants, such as nitrogen, phosphorus and suspended solids [28]. Watersheds covered with cultivated land tend to have poorer water quality than natural vegetation, with agricultural fertilizer being one of the main sources of water quality deterioration [29,30]. Due to impervious surfaces, such as roofs, roads, and parking lots, urban land accelerates the runoff process and increases pollutant transport to rivers, which has a negative impact on water quality, especially around residential areas [31]. It is important to clarify the relationship between the LULC pattern and water quality for the determination of water pollution sources, and for the ecological governance of rivers and lakes, because LULC has a significant long-term impact on water quality in river basins.

The Haihe River Basin covers six provinces, including Beijing and Tianjin, which are the largest and second largest cities in northern China, respectively. The Haihe River Basin plays an important role in Chinese politics and the national economy, and contains numerous, densely populated large- and medium-sized cities [32,33]. Tianjin, which is the largest coastal open city in northern China, is positioned on both banks of the Haihe River, and many rivers and canals flow through the urban area. The city is entirely located within the Haihe River Basin. Due to its important geographical location, the water quality in Tianjin has a large impact on the aquatic environment and ecological functions of the Haihe River Basin, as well as the inshore region of the Bohai Sea [34–36]. Some of the main rivers in the Tianjin area have been severely polluted and the water quality has deteriorated [37,38]. As a result of the shortage of water resources and discharge of sewage, the self-purification ability of the river water has been substantially reduced [39]. There is an urgent need to investigate the factors influencing water quality and determine the main pollutants in the surface water of Tianjin.

Most previous studies of Tianjin's aquatic environment focused on coastline changes, water quality parameter inversions, or interannual changes of water quality in rivers and lakes. There is a need to conduct annual analyses of surface water quality and land use patterns at a macro scale. Therefore, the main objectives of this study were to characterize the annual variation of surface water quality at water monitoring stations at the macro scale in Tianjin; identify factors affecting water pollution and sources in Tianjin; and clarify the response of surface water quality variables to the land use pattern in Tianjin.

2. Materials and Methods

2.1. Study Area

Tianjin (38°33′–40°15′ N,116°42′–118°03′ E) is located in the northern part of the North China Plain, downstream of the Haihe River Basin, and faces the Bohai Sea in the east and Yanshan Mountains in the north (Figure 1). It is the hub of the regional river network, and there are 19 first-level rivers in Tianjin (total length = 1095.1 km) and 79 secondary rivers (total length of 1363.4 km). Tianjin has a typical temperate monsoon climate with four distinct seasons. The lowest temperature is in January and the highest is in July; the mean annual temperature is 12–15 °C and the mean annual precipitation is 550–600 mm. There are distinct dry (September to June) and wet (July to August) seasons in Tianjin, with most of the precipitation occurring in the wet season.

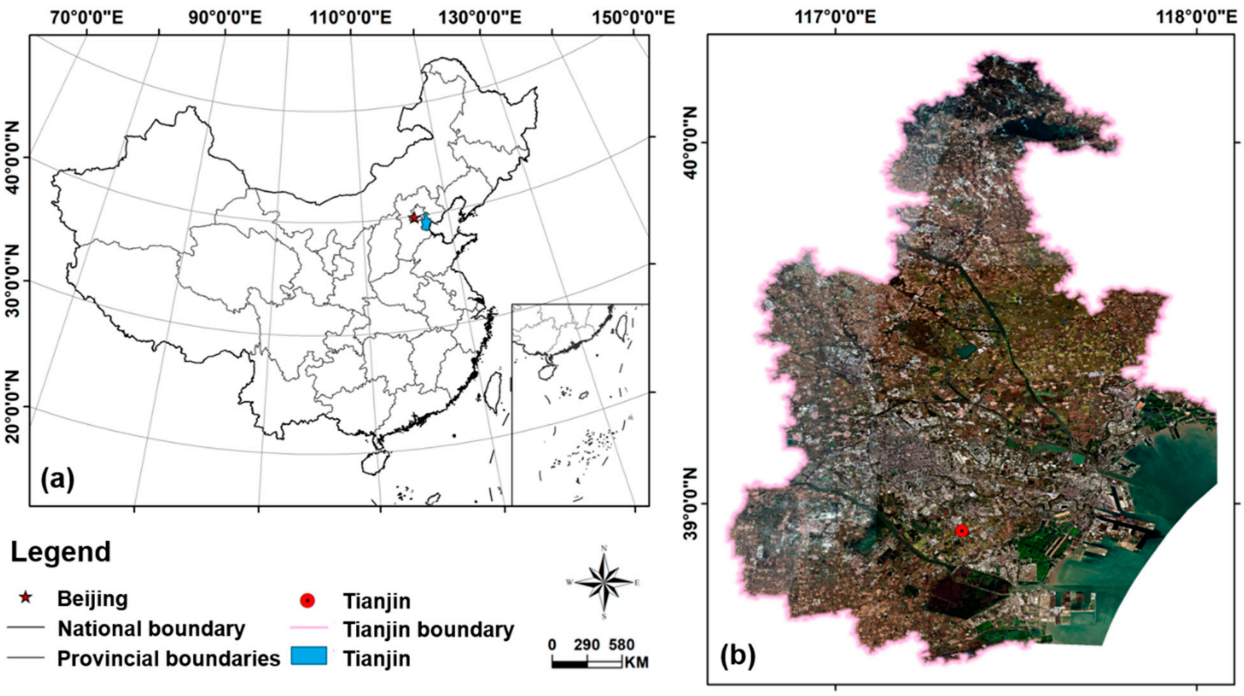

Figure 1. (**a**) Location of the study area in China. (**b**) A true-color image of Tianjin from Sentinel-2.

2.2. Dataset

2.2.1. Data Collection and Processing

Daily surface water quality data from 16 water quality monitoring stations in Tianjin for the period September 2021 to August 2022 were collected from the China National Environmental Monitoring Centre (http://www.cnemc.cn/, accessed on from 1 September 2021 to 31 August 2022). Daily surface water quality monitoring data were provided for nine water quality parameters: pH, temperature (°C), dissolved oxygen (DO, mg/L), electrical conductivity (EC, μS/cm), turbidity (Tur, NTU), permanganate index (COD_{Mn}, mg/L), ammonia nitrogen (NH_3N, mg/L), total nitrogen (TN, mg/L), and total phosphorus (TP, mg/L). The process and method of water quality monitoring in the National Surface Water Environmental Quality Monitoring Network are operated according to the Operation Instructions for Monitoring Tasks of the National Surface Water Environmental Quality Monitoring Network (Trial) issued by China. The pH, temperature, DO, EC and Tur were measured by electrochemical method. The COD_{Mn} was measured by laboratory analysis methods (GB/T 11892-1989, issued by China). The TP concentration were measured by ammonium molybdate spectrophotometric method (GB 11893-1989, issued by China). The TN concentration were measured by alkaline potassium persulfate digestion UV spectrophotometric method (HJ 636—2012, issued by China). The NH_3N concentration were measured by Nessler's reagent spectrophotometry (HJ 535-2009, issued by China). These indicators can reflect the surface water quality.

Water quality parameters were recorded every 4 h throughout the day at each water monitoring station. To ensure data consistency, the values at 12:00 am were selected to represent the water quality parameter values of the stations in the daytime, and the values at 12:00 pm represented the nighttime data. Due to the uncertainty in instrumental maintenance, data assurance, and quality control, surface water quality data had to be preprocessed by removing outliers and filling null values. The validity of the water quality data was determined according to the Environmental Quality Standards for Surface Water of China. The mean value was then calculated at 3-day intervals, such that each water monitoring station had nine groups of data in February and 10 groups in all other months (except for the station at the center of the Yuqiao Reservoir (Station 2), which freezes from December to March such that data were missing). A comparative analysis revealed that, as the daily variation in water quality at each station was small, only the daytime data were analyzed.

A detailed workflow of this study is presented in Figure 2. First, the water quality characteristics at Tianjin surface water monitoring stations were characterized at the macro scale by statistical analyses. Second, a hierarchical cluster analysis was conducted using Ward's method to compare the water monitoring stations. Third, factor analysis was used to determine the pollution parameters that had the largest effect on water quality, and to identify the monitoring station with the most severe pollution. Finally, the impact of the LULC pattern on water quality was analyzed using an entropy weight calculation.

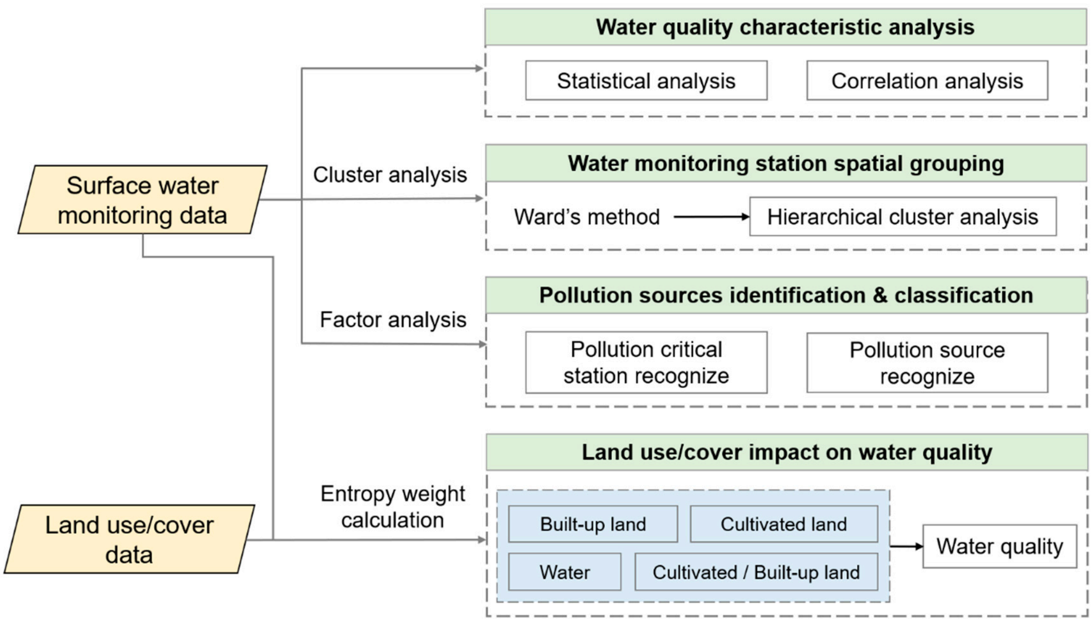

Figure 2. Study flowchart.

2.2.2. Land Use/Land Cover Data

Land use/land cover classification data were acquired from the European Space Agency (ESA) WorldCover 10 m 2020 product (https://zenodo.org/, accessed on 3 November 2022). in this study. The WorldCover product provides a global land cover map for 2020 at 10 m resolution based on Sentinel-1 and Sentinel-2 images. The product has 11 land cover/use classes: trees, shrubland, grassland, cropland, built-up land, barren/sparse vegetation, snow/ice, open water, herbaceous wetland, mangroves, and moss/lichen. They were reclassified into six classes after obtaining the LULC data for the study area according to the Chinese remote sensing monitoring LULC classification system: forest, grassland, cultivated land, water, built-up land, and other land.

2.3. Methods

2.3.1. Statistical Analysis

The Kolmogorov–Smirnov test was used to check the normality of the surface water quality data distribution [40]. One-way analysis of variance (ANOVA) was used to analyze data with a normal distribution ($p < 0.05$). The surface water characteristics were recorded as maximum, minimum, and mean $\pm$ standard deviation (SD) values. The associations among various water quality parameters were analyzed by Pearson correlation.

2.3.2. Cluster Analysis

A cluster analysis is an unsupervised learning method that divides data samples into several clusters according to certain rules. Similar samples are clustered together, while dissimilar samples are divided into different clusters; this enables analysis of the similarity between samples [41,42]. The clusters with the highest similarity are grouped first, and the Euclidean distance between them is the smallest. All clusters are ultimately grouped into one cluster as cluster similarity decreases. The number of clusters is determined by a dendrogram, and each cluster has its own characteristics. In this study, the water quality monitoring stations in Tianjin are mainly distributed near built-up land, cultivated land, large area of water, and the mix land of built-up and cultivated land. The cluster analysis was used to consider whether the stations can be grouped according to their water quality characteristics or not, and the Euclidean distance was used to determine the similarity of measurements from different water quality monitoring stations. The Euclidean distance is defined using Equation (1):

$$ED(x, y) = \sqrt{\sum_{i=1}^{n} (x_i - y_i)^2} \quad (1)$$

where $ED(x, y)$ is the Euclidean distance between x and y, $x = (x_1, x_2, \ldots, x_n)$, $y = (y_1, y_2, \ldots, y_n)$. The cluster analysis was performed and implemented using Python 3.7.

2.3.3. Factor Analysis

Factor analysis is a statistical method used to extract common factors from different groups. It assembles variables with the same characteristics into a single factor and therefore reduces the number of variables [43,44]. When performing factor analysis, Bartlett's test of sphericity and the Kaiser−Meyer−Olkin (KMO) test are first performed to evaluate the accuracy and sufficiency of the data. As an efficient means to decrease dimensionality, factor analysis can be used to detect the contribution of pollution and other parameters to water quality in a certain area. More illustration of the factor analysis is available in the paper of Surendra Kumar [45]. The factor analysis was written using Python 3.7.

2.3.4. Entropy Weight Calculation

The entropy weight method is commonly used to determine objective weights according to index variability. This method has been widely used in engineering, social economics, and other fields. The basic concept of the entropy weight method is to determine weights based on information entropy and the degree of index variability. The weight of each index is then modified according to the entropy weight to obtain a more objective index weight [46,47]. Generally, the smaller the information entropy of an index, the greater the variation of the index value, such that the index may be more important for comprehensive evaluation and is thus assigned a greater weight. In this study, the impact of LULC class on water quality was determined by an entropy weight calculation. The weighted entropy was calculated as Equations (2)–(6):

$$R_{ij} = \frac{X_{ij} - min_{X_{ij}}}{max_{X_{ij}} - min_{X_{ij}}} \tag{2}$$

$$P_{ij} = \frac{R_{ij}}{\sum_{j=1}^{n} R_{ij}} \tag{3}$$

$$E_j = -\ln(n)^{-1} \sum_{i=1}^{n} P_{ij} \times \ln(P_{ij}) \tag{4}$$

$$D_j = 1 - E_j \tag{5}$$

$$W_j = \frac{D_j}{\sum_{i=1}^{n} D_j} \tag{6}$$

where X_{ij} is the value of the jth index at the ith scheme, P_{ij} is the standardized data of the jth index at the ith scheme, E_j is information entropy of the jth index, D_j is the redundancy of the jth index, W_j is the weight of the jth index. The entropy weight calculation was performed using Python 3.7.

3. Results

3.1. Seasonal Variation of Water Quality Characteristics

Seasonal differences in water quality may occur due to the influence of climate, topography and land use/land cover, etc. [48]. Seasonal statistics for nine water quality parameters were calculated in this study, including maximum, minimum, and mean ± SD values, as shown in Table 1.

Table 1. Seasonal statistical characteristics of surface water in Tianjin.

		Temperature	pH	DO	EC	Tur	COD_{Mn}	NH_3N	TP	TN
Spring	Max	25.61	9.57	27.06	23,609.87	162.53	15.18	5.96	0.32	7.26
	Min	4.57	7.79	3.72	312.39	1.30	2.02	0.03	0.01	0.63
	Mean	15.43	8.45	10.87	3159.34	23.45	5.01	0.12	0.06	2.77
	SD	4.86	0.26	2.77	4428.14	25.25	2.47	0.29	0.04	1.82
Summer	Max	93.13	9.45	20.62	38,637.23	686.40	9.33	3.13	0.52	9.43
	Min	16.94	6.99	0.06	3.20	0.40	0.06	0.03	0.01	0.48
	Mean	26.51	8.08	6.37	2538.18	43.29	4.86	0.37	0.11	2.43
	SD	3.92	0.44	3.35	5100.55	74.63	1.51	0.51	0.07	1.61
Autumn	Max	24.58	10.66	21.77	10,088.90	716.56	12.44	4.09	0.52	12.12
	Min	6.34	7.13	1.03	2.94	2.43	0.87	0.03	0.01	0.59
	Mean	16.97	8.00	8.04	1871.64	40.46	4.90	0.46	0.10	3.92
	SD	5.11	0.34	3.22	1923.62	77.79	2.20	0.54	0.07	2.00
Winter	Max	10.74	9.22	29.42	13,144.17	314.21	14.57	1.96	0.27	13.78
	Min	1.26	7.68	4.52	408.53	1.35	0.34	0.03	0.01	0.37
	Mean	5.51	8.41	14.06	2532.39	15.50	5.10	0.25	0.06	4.50
	SD	1.97	0.31	4.01	2366.09	22.22	2.08	0.22	0.03	2.81

Note: DO, dissolved oxygen; EC, electrical conductivity, Tur, turbidity; COD_{Mn}, permanganate index; NH_3N, ammonia nitrogen; TP, total phosphorus; TN, total nitrogen.

Temperature is an important parameter because it regulates physical, chemical, and biological processes in water [49]. The distribution, transportation, and interaction of some contaminants have strong relationships with water temperature. The mean water temperature in this study displayed obvious seasonal differences, with a tendency to increase gradually from spring (15.43 ± 4.86 °C) to summer (26.51 ± 3.92 °C), and then decrease from autumn (16.97 ± 5.11 °C) until reaching a maximum in winter (5.51 ± 1.97 °C). The differences in water temperature may have been caused by differences in air temperature among seasons. Changes in LULC and water depth, and runoff disturbances, can also influence water temperature.

The pH value indicates the degree of acidity or alkalinity of water, which is one of the most important physical and chemical water quality parameters and is critical to the growth and survival of aquatic organisms [50]. Natural phenomena, chemical changes, and industrial processes that use aqueous solutions can all affect the pH value. For example, the pH value is related to the carbon dioxide (CO_2) concentration in the water, while the CO_2 concentration is related to the abundance and activity of plankton in the water [51,52]. The pH value in Tianjin was weakly alkaline throughout the study period, with lower mean values occurring in summer (8.08 ± 0.44) and autumn (8.00 ± 0.34) than spring (8.45 ± 0.26) and winter (8.41 ± 0.31). All values were suitable for aquatic organisms.

As a significant water quality parameter, DO influences the living conditions of aquatic organisms that require oxygen. Changes in human activities and environmental conditions can affect the DO concentration [12,53]. The DO concentration decreases with an increase in water temperature. The mean DO concentrations in Tianjin were highest in spring (10.87 ± 2.77 mg/L) and winter (14.06 ± 4.01 mg/L), with lower concentrations seen in summer (6.37 ± 3.35 mg/L) and autumn (8.04 ± 3.22 mg/L) in association with changes in water temperature.

Electrical conductivity refers to the ability of water to conduct a current, which is closely related to the mineral content of the water [50]; the lower the water conductivity, the purer the water. The mean EC value at the water quality monitoring stations in Tianjin was generally high. The mean EC values in spring, summer, autumn, and winter were 3159.34, 2538.18, 1871.64, and 2532.39 µS/cm, respectively. Electrical conductivity was highest in spring and lowest in autumn, which indicates that the water quality in autumn was relatively better than that in spring.

Turbidity is an optical property of water that depends on the amount of suspended solids therein [54]. Suspended solids reduce the incoming sunlight, which negatively impacts the photosynthesis of algae and phytoplankton. The Tur of surface water in Tianjin fluctuated substantially in summer and autumn, and there were relatively high mean values (43.29 ± 74.63 mg/L in summer, 40.46 ± 77.79 mg/L in autumn). The maximum value in summer was 686.40 mg/L and the minimum value was 0.4 mg/L. In autumn, the maximum and minimum values were 716.56 and 2.43 mg/L, respectively. The seasonal variation of Tur may be related to the precipitation received in the rainy season. High precipitation in the rainy season, especially in summer, would lead to a higher mean Tur.

The COD_{Mn} value indicates the quantity of organic matter that needs to be oxidized in water, as measured by a chemical method [12]. As an important indicator of organic pollution in water, the smaller the COD_{Mn} value, the less polluted the water. The mean COD_{Mn} value in Tianjin changed only slightly over the study period, with the highest value occurring in winter (5.10 ± 2.08 mg/L), followed by spring (5.01 ± 2.47 mg/L), and the lowest value occurring in summer (4.86 ± 1.51 mg/L); water pollution was relatively serious in winter.

The NH_3N concentration represents the sum of nitrogen in water in the form of free ammonia and the ammonium ion. Excessive NH_3N leads to water eutrophication, and is also a major oxygen-consuming pollutant in water. Therefore, the presence of NH_3N in water bodies is not conducive to the survival of fish and other aquatic organisms [55]. The mean NH_3N concentrations at Tianjin water quality stations were 0.12 ± 0.29, 0.37 ± 0.51, 0.46 ± 0.54, and 0.25 ± 0.22 mg/L in the spring, summer, autumn, and winter, respectively.

Total phosphorous is an important indicator of water eutrophication, and consists of all inorganic, organic, and dissolved forms of phosphorus in a water body [56]. Agricultural runoff and wastewater from sewage treatment plants are the main sources of phosphorus in surface water. The mean TP concentration at Tianjin surface water monitoring stations was similar between summer (0.11 $\pm$ 0.07 mg/L) and autumn (0.1 $\pm$ 0.07 mg/L), but was lower in spring (0.06 $\pm$ 0.04 mg/L) and winter (0.06 $\pm$ 0.03 mg/L); this may have been caused by the vigorous growth of plants and eutrophication. The mean TP concentrations in summer and autumn were significantly higher than in spring and winter, i.e., the TP concentration in the rainy season was higher than in the dry season, consistent with previous studies.

Total nitrogen is the total amount of inorganic and organic nitrogen in a water body. It is one of the most important indicators of water quality and can be used to evaluate the seriousness of water pollution. When the content of nitrogen and phosphorus in surface water increases, microorganisms will multiply and plankton will grow vigorously, resulting in eutrophication [57,58]. The mean TN concentration in Tianjin was highest in winter (4.5 $\pm$ 2.81 mg/L), followed by autumn (3.92 $\pm$ 2.0 mg/L), and was lowest in summer (2.43 $\pm$ 1.61 mg/L).

The various water quality parameters displayed different seasonal variations. For parameters indicating water pollution, such as TP and NH3N, the concentrations were highest in summer and autumn, which may be related to the higher precipitation in the rainy season. The EQSSWC categorize the water quality into five classes according to the environmental functions and protection objectives of the surface water area, which may be used to objectively evaluate water pollution. Class I water with the best quality, is used for source water and national nature reserves; class V is applicable to areas with agricultural and landscape requirements, with the worst quality. According to the categorization of water quality base on EQSSWC, the pH range of class I to class V is 6~9, the range of DO is 2~7.5 mg/L (class I $\geq$ 7.5 mg/L, class V $\geq$ 2 mg/L), the range of COD_{Mn} is 2~15 mg/L, the range of NH_3N is 0.15~2 mg/L, the range of TP is 0.02~0.4 mg/L and the range of TN is 0.2~2 mg/L. The mean value of pH in different seasons is about 8, and the water quality is weakly alkaline. The mean value of DO in spring, autumn and winter is greater than 7.5, reaching the standard of class 1 water, the water quality in summer is class 2. The mean value of COD_{Mn} in different seasons is 4~6 mg/L; the water quality of is class 3 from the index of CODMn. The mean value of NH_3N in different seasons is 0.1~0.5 mg/L and the water quality is class 2, while the maximum value far exceeds the class 5 water standard. The mean value of TP in different seasons is 0.06~0.11 mg/L, and the water quality is class 2. The annual average of TN is more than 2 mg/L, exceeding the class V water quality standard throughout the whole year, indicating that nitrogen pollution of the surface water in Tianjin is a serious concern. The nitrogen pollution can be reduced by tracing the source of pollutants, controlling the application of pesticides and fertilizers. In addition, the measures such as dredging water system, planting grass in river, and establishing vegetation buffer zone can be taken to improve the self-purification capacity of water bodies, thus reducing nitrogen pollution.

3.2. Correlations among Water Quality Parameters

Figure 3 shows the correlations among the water quality parameters in the different seasons. The correlation coefficient for the relationship between DO and pH exceeded 0.5 throughout the year, but those among the other water quality parameters varied seasonally. Temperature was negatively correlated with TN in spring (R = -0.6) and winter (R = -0.7), and was weakly correlated with DO. The pH value was positively correlated with DO in all seasons, and the correlation coefficient with COD_{Mn} was 0.6 in the autumn. The correlations between DO and other water quality parameters were not significant, with all positive and negative correlations having R values < 0.5. Electrical conductivity had a strong correlation with COD_{Mn} in the summer (R = 0.8) and autumn (R = 0.7), but the R value was low in spring and winter. The correlation between Tur and other water quality parameters was not strong, although the correlation coefficient for the relationship with TP was 0.6 in winter. The correlation coefficient between TP and NH_3N was 0.7 in spring and summer, and that with COD_{Mn} was 0.7 in winter. There were no obvious correlations in the other seasons.

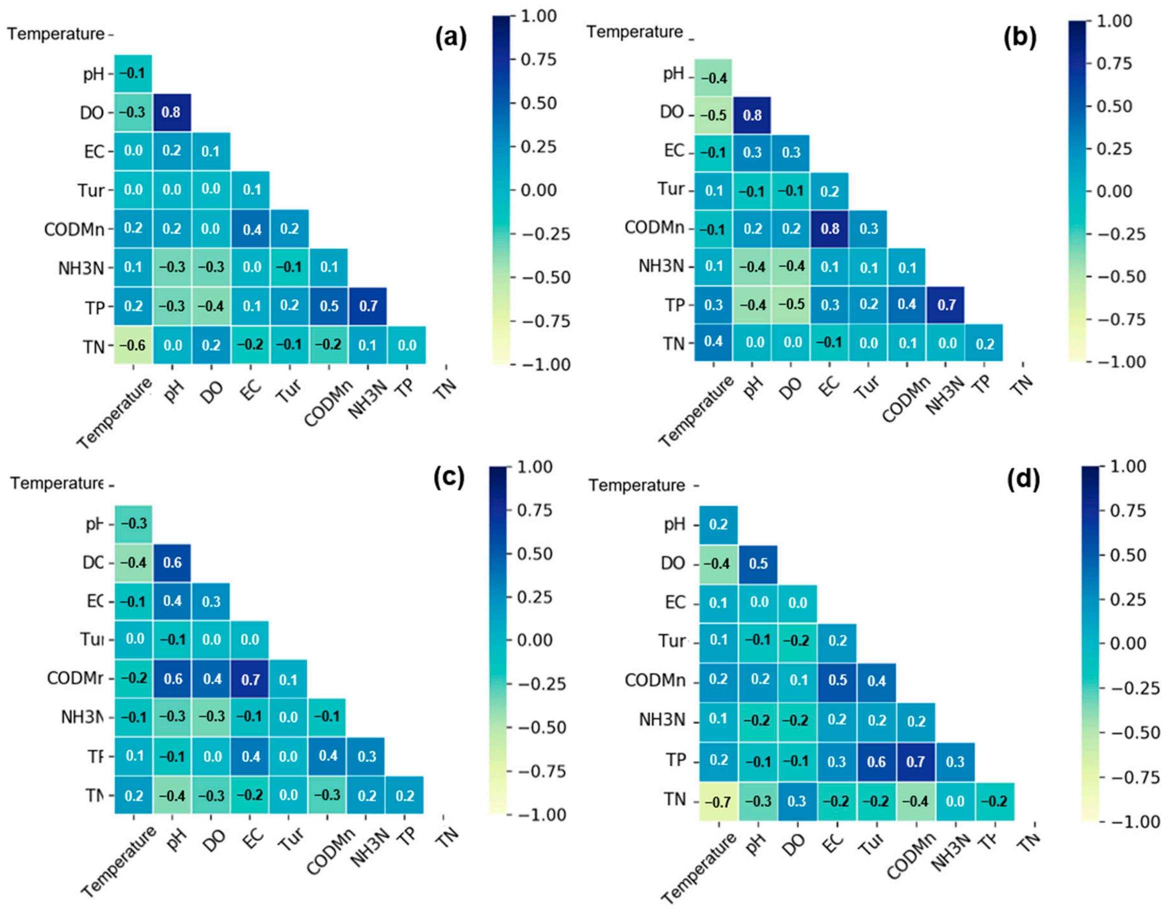

Figure 3. Seasonal correlations among water quality parameters. (**a**) spring; (**b**) summer; (**c**) autumn; (**d**) winter. DO, dissolved oxygen; EC, electrical conductivity, Tur, turbidity; COD_{Mn}, permanganate index; NH_3N, ammonia nitrogen; TP, total phosphorus; TN, total nitrogen.

3.3. Spatial Distribution of LULC Patterns

Based on Google Earth images, there were only slight changes in LULC patterns near the water quality monitoring stations during 2021–2022 compared with the pattern in 2020. Therefore, the land use classification in 2020 was used to represent the LULC pattern of Tianjin during the observation period. It can be seen from Figure 4 that cultivated land accounted for the largest land use in the Tianjin area, followed by built-up land, water, forest, and grassland. Forests were mainly distributed at high altitudes in the mountains to the north of Tianjin. Grassland was also mainly distributed to the north of Tianjin. Cultivated land was widely distributed throughout Tianjin, and residential areas were distributed in the central part of the city. As a coastal city, open water was distributed to the southeast of Tianjin. There were also several large reservoirs (e.g., Yuqiao Reservoir) in Tianjin, in addition to the Haihe River and other major rivers.

Cultivated land accounted for the largest proportion of the total LULC in Tianjin. Previous studies have shown that pesticides, fertilizers, and other chemicals used near agricultural land can enter water bodies in various ways, leading to an increase in the concentrations of TP, TN and other pollutants in the river, which adversely affects water quality near agricultural land [59,60]. Built-up land accounted for the second largest proportion of the total LULC in Tianjin. The intense human activities in residential areas are a source of pollutant release and have a large impact on the spread of pollutants. The water quality was likely affected by the residential population of Tianjin due to the limited bearing capacity of the sewage treatment system and presence of impermeable surfaces in the city [61–63]. Forest cover and grassland accounted for a small proportion of the total LULC. Generally, forests and grassland have a positive impact on water quality by maintaining water and soil, conserving water sources, and purifying water [28,64]. For example, forests can effectively purify and store water through a series of physical, chemical, and biological processes, such as filtration and adsorption. Grassland can intercept pollutants, promote water infiltration, recharge groundwater, and filter runoff to improve surface water quality. As shown in Figure 4, the water quality monitoring stations in Tianjin were mainly distributed around built-up land, cultivated land, and large areas of open water.

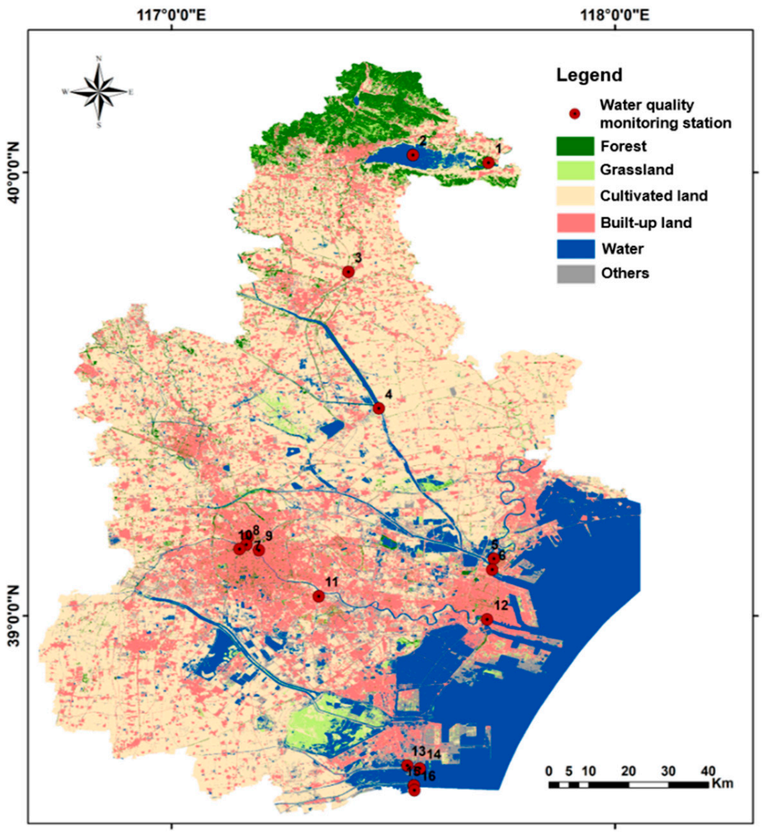

Figure 4. Land use/land cover (obtained from the European Space Agency WorldCover 10 m 2020 product) and the distribution of water quality monitoring stations in Tianjin.

3.4. Cluster Analysis of the Surface Water Quality Monitoring Stations

Principal component analysis (PCA) is an effective data dimension reduction method [65]. Prior to the cluster analysis, a PCA was conducted to reduce the dimensions of the water quality time series data from the 16 monitoring stations in Tianjin. The first five principal components (PCs) of each water quality parameter were obtained for each monitoring station and subjected to cluster analysis. Figure 5 shows the results of hierarchical cluster analysis of data from 16 water quality monitoring stations in Tianjin, with the blue line representing the location where the Euclidean distance was equal to 2.5. The Euclidean distance among all water quality monitoring stations was <6, and the 16 water quality monitoring stations were divided into six clusters based on the Euclidean distance.

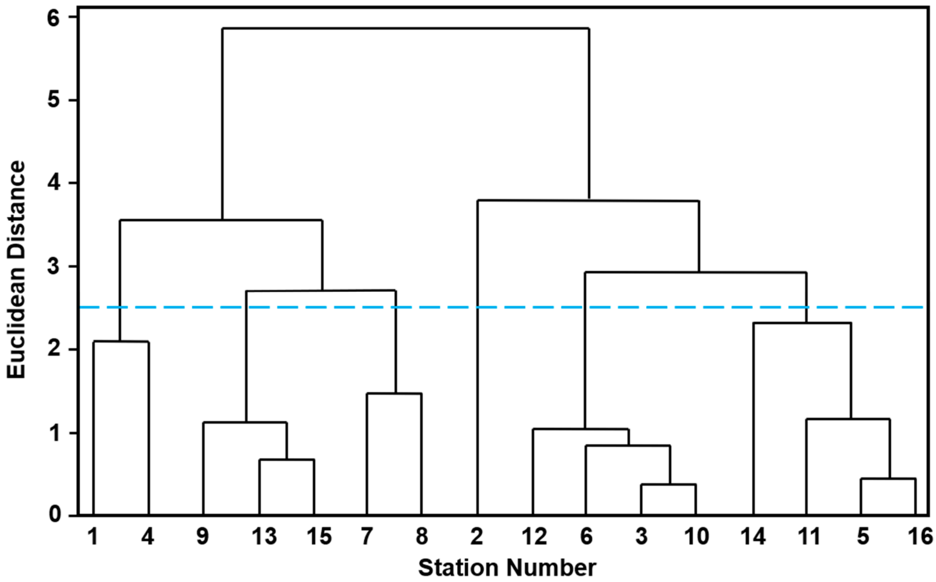

Figure 5. Hierarchical clustering results of the Tianjin water quality monitoring stations (the blue line represents the location where the Euclidean distance was equal to 2.5).

Figure 6 shows the locations of water quality monitoring stations and the surrounding LULC pattern, while the detailed location of the water quality monitoring stations is shown in Figure 4. Eight monitoring stations were located within built-up areas: stations 5, 6, 7, 8, 9, 10, 12, and 13. Monitoring stations 1, 3, 4, 14, and 16 were located near cultivated land. Monitoring station 2 was located in the center of the Yuqiao Reservoir, while monitoring stations 11 and 15 were located in the vicinity of both built-up and cultivated land.

Figure 6. The LULC pattern around Tianjin water quality monitoring stations. S1–S16 are water quality monitoring stations 1–16, respectively.

It can be seen from Figures 5 and 6 that cluster 1 included monitoring stations 1 and 4, and the Euclidian distance between the two stations was >2. Monitoring station 1 was located at the side of a river connected to Yuqiao Reservoir, while monitoring station 4 was located within cultivated land. Cluster 2 included monitoring stations 9, 13, and 15, which were near areas of built-up and cultivated land where water quality was affected by urban residents and agricultural discharges. Cluster 3 included monitoring stations 7 and 8, which were located on the banks of rivers that passed through residential areas and were surrounded by green belts. Cluster 4 only included monitoring station 2 in the center of Yuqiao Reservoir, which indicated that the water quality at the monitoring station was very different to that of the other monitoring stations. Cluster 5 included monitoring stations 3, 6, 10, and 12. Monitoring station 3 was surrounded by cultivated land and installed near trees. Monitoring station 6 was located near the middle of a river in a residential area. Monitoring station 10 was located in the middle of a river surrounded by built-up land. Monitoring station 12 was close to the sea and was surrounded by built-up land. Cluster 6 included monitoring stations 5, 11, 14, and 16. Station 5 was located on the river bank near built-up land. Station 11 was located in the middle of the river, with cultivated land and built-up land on both sides of the river. Stations 14 and 16 were surrounded by large areas of cultivated land.

4. Discussion

4.1. Analysis of the Water Quality Characteristics of the Clusters

The mean values of the different water quality parameters were calculated to evaluate and compare the water quality characteristics among clusters (Figure 7). The mean TN concentration in cluster 1 (5.56 mg/L) was significantly higher than that of the other clusters; therefore, the TN concentration was the main water quality parameter used to distinguish cluster 1 from the others. Cluster 1 included monitoring stations 1 and 4, which were located within a large area of cultivated land. The excessive TN concentration might be related to pesticide and fertilizer applications and the discharge of rural domestic sewage. The mean EC and COD_{Mn} values in cluster 2 were higher than those at other stations, especially EC (3858 µS/cm), which was significantly higher than that of clusters 1, 3, and 4; this indicates that the water quality monitoring stations in cluster 2 had a high level of pollution. The mean COD_{Mn} value was 5.79 mg/L in cluster 2, implying that the monitoring station in this cluster had more severe organic pollution than the other stations. The monitoring stations in cluster 2 were stations 9, 13, and 15. It can be seen from Figures 4 and 6 that there was both cultivated and built-up land around monitoring stations 9, 13, and 15. The discharge of agricultural wastewater and domestic sewage may explain the high EC and COD_{Mn} values of cluster 2. In cluster 3, the mean pH, Tur, COD_{Mn} and TN values were low, indicating low levels of organic pollution in stations 7 and 8.

Cluster 4 had the maximum mean temperature, pH value, and DO concentration, the minimum mean EC value and NH_3N and TP concentrations, and intermediate Tur, COD_{Mn}, and TN concentration values. The high DO and low EC, TP, and NH_3N indicated that the water body in cluster 4 had a strong self-purification ability, and fewer impurities and organic pollutants than the other clusters. This may explain why cluster 4 clearly differed from the other clusters. Cluster 4 only contained monitoring station 2, in the center of Yuqiao Reservoir, which is a large national reservoir. It is an important source of drinking water for Tianjin, and its water quality is, therefore, of great significance to human health and the natural environment. The mean water depth of the Yuqiao Reservoir is only about 4.5 m, and it is, therefore, classed as a shallow reservoir. More than 80% of the water stored in the reservoir originates from upstream areas where agricultural non-point source pollution is serious, especially TP and TN. Due to the pollution of the Yuqiao Reservoir, a series of measures have been implemented in Tianjin, such as water source protection, closed management, peripheral treatment, and ecological restoration, which have improved the natural environment of the reservoir and established a long-term mechanism for continuous improvement of water quality [66,67]. The water quality in Yuqiao Reservoir is regarded as stable to Class III and has improved after years of comprehensive treatment.

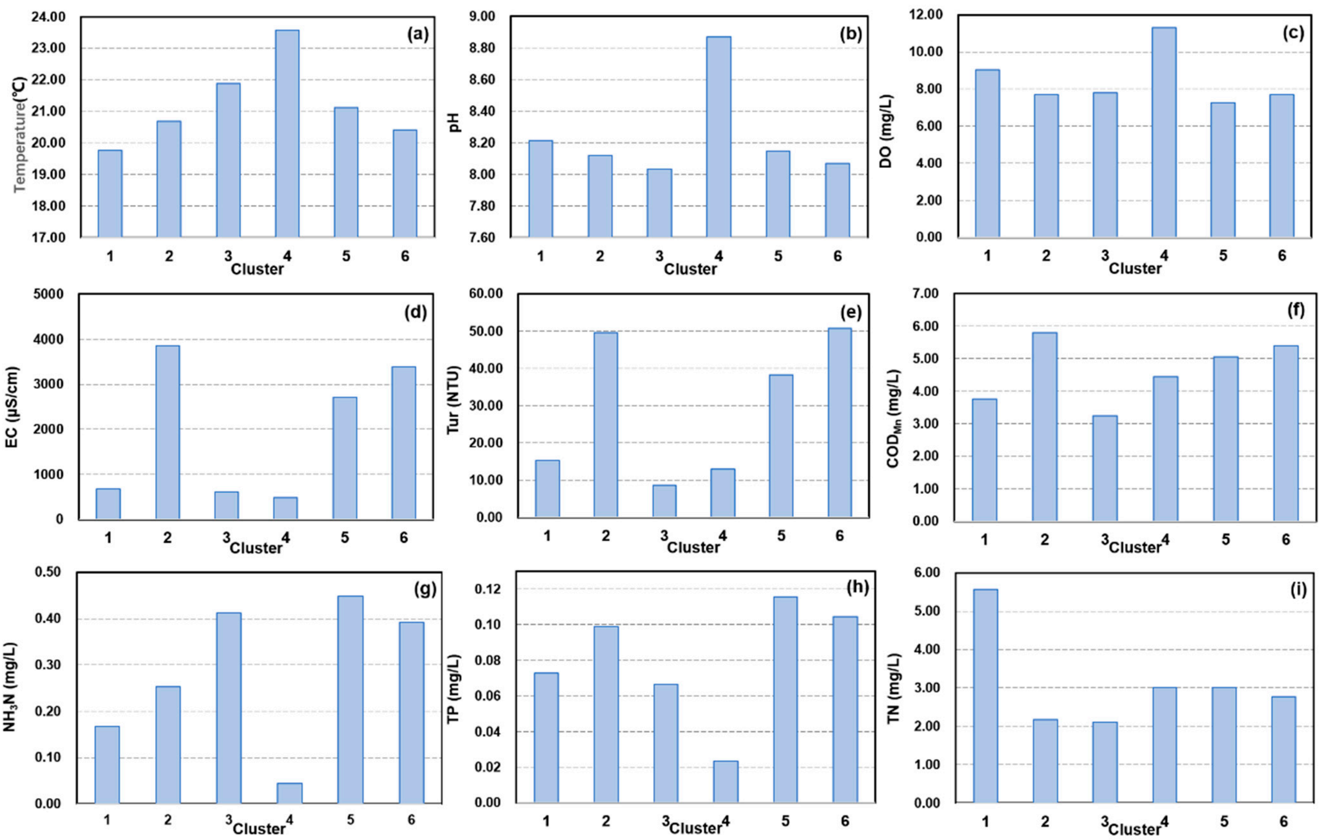

Figure 7. The mean values of the main water quality parameters in the different clusters identified in Tianjin. (**a**) temperature; (**b**) pH; (**c**) DO, dissolved oxygen; (**d**) EC, electrical conductivity, (**e**) Tur, turbidity; (**f**) COD_{Mn}, permanganate index; (**g**) NH_3N, ammonia nitrogen; (**h**) TP, total phosphorus; (**i**) TN, total nitrogen.

Cluster 5 included monitoring stations 3, 6, 10, and 12. The mean DO concentration was the lowest among all clusters and the mean NH_3N concentration was the highest, indicating that the monitoring stations included in this cluster had high levels of organic pollution. The mean Tur value (50.7 mg/L) in cluster 6 was the highest among all clusters, indicating that the mean suspended sediment content at monitoring stations 5, 11, 14, and 16 was higher than at the other stations. The average turbidity values of cluster 2 and cluster 6 are significantly higher than that of other clusters. According to DEM and Google image, these water quality monitoring stations included in these two clusters are located near flat the construction land and farmland, the accumulation of suspended sediment caused by topographic factors has few impacts on the turbidity of water quality. The phenomenon of high turbidity may be related to the Tur and self-purification capacity of the water bodies in the cluster.

4.2. Identification of Critical Water Parameters and Potential Sources of Water Quality Variation

The factor analysis results are presented in Table 2. The 16 variables were first subjected to a varimax rotation, and factor loading values were then extracted according to the eigenvalues and eigenvectors. The results showed that the cumulative variance explained exceeded 75% when five factors were selected; in other words, five factors adequately represented the water quality characteristics of the 16 monitoring stations. Therefore, the number of factors was set to five to ensure adequate representation of the water quality characteristics.

Table 2. Factor loadings of the water quality monitoring stations in Tianjin.

Factors	1	2	3	4	5
Temperature	−0.077	−0.048	**0.991**	−0.056	−0.012
pH	−0.192	**0.947**	0.043	0.001	−0.073
DO	−0.134	**0.893**	−0.062	−0.024	0.067
EC	−0.073	−0.091	−0.180	−0.281	−0.062
Tur	−0.106	−0.117	−0.180	**0.959**	−0.072
COD_{Mn}	0.293	0.017	−0.003	−0.007	**0.710**
NH_3N	**0.968**	−0.175	−0.031	−0.006	0.165
TN	**0.877**	−0.162	0.049	−0.003	0.416
TP	**0.621**	−0.107	−0.130	−0.030	0.059
% of variance	25.05	19.85	11.92	11.16	8.09
Cumulative	25.05	44.89	56.82	67.97	76.06

Note: DO, dissolved oxygen; EC, electrical conductivity, Tur, turbidity; COD_{Mn}, permanganate index; NH_3N, ammonia nitrogen; TP, total phosphorus; TN, total nitrogen.

Factor 1 explained 25.05% of the total variance. It had high loads of NH_3N, TP, and TN. These parameters indicate inorganic and organic pollution and have a large impact on water quality [17,68]. Factor 2 accounted for 19.85% of the total variance. This factor had high factor loadings for pH and DO. These water quality parameters reflect the pH and oxygen content in the water, which affect the growth of aquatic plants and animals [69,70]. Factor 3 accounted for 11.92% of the total variance. This factor had a high factor loading for temperature, which exerts an important influence on water quality (because it influences the DO concentration and growth of aquatic plants and animals) [69]. Factor 4 accounted for 11.16% of the total variance. This factor had a high loading for Tur, which can indicate whether the water quality has deteriorated. Factor 5 accounted for 8% of the total variance. High factor loadings were indicated by COD_{Mn}, which is a water parameter denoting organic pollution [71]. The water quality parameters with high loadings were all indicators of water pollution, implying that the Tianjin surface water was polluted, especially with nitrogen and phosphorus.

Figure 8 shows the factor analysis results for the 16 water quality monitoring stations. The factor scores extracted from the factor analysis represented pollution sources and critical sites. A higher factor analysis score corresponds to a greater impact of a given factor.

As can be seen from Figure 8, factor 1 was significant at monitoring stations 7–9. These monitoring stations are located in the center of Tianjin, where there is intensive industrial, agricultural, and residential activity and a large area of built-up land [19,72]. The water quality in these monitoring stations was probably affected more by domestic effluent and industrial wastewater. Factor 2 was significant at monitoring stations 2, 11, and 16. The factor score of factor 2 at station 2 was much higher than at stations 11 and 16. Station 2 is located in the center of Yuqiao Reservoir, which had good water quality due to the lack of domestic and agricultural pollution, as well as the operation of various water purification facilities. Factor 3 was significant at monitoring stations 6, 12, and 15, which are located near built-up land. This likely reflected the impact of domestic sewage and industrial wastewater from the urban infrastructure, and a range of residential activities occurring in the area. Factor 4 was significant at monitoring stations 10, 11 and 16, with station 10 having the highest score. Station 10 was also located in the main urban area of Tianjin, near residential and industrial areas with large pollution sources. As with factor 3, factor 5 was also significant at monitoring stations 6, 12, and 15. The factor score showed that water pollution was more serious at the monitoring stations near built-up land, especially at stations 7–10, which are located in the central urban area. The factor analysis results could be explained by the dense population, and by the industrial and commercial activities that occurred around the water quality monitoring stations.

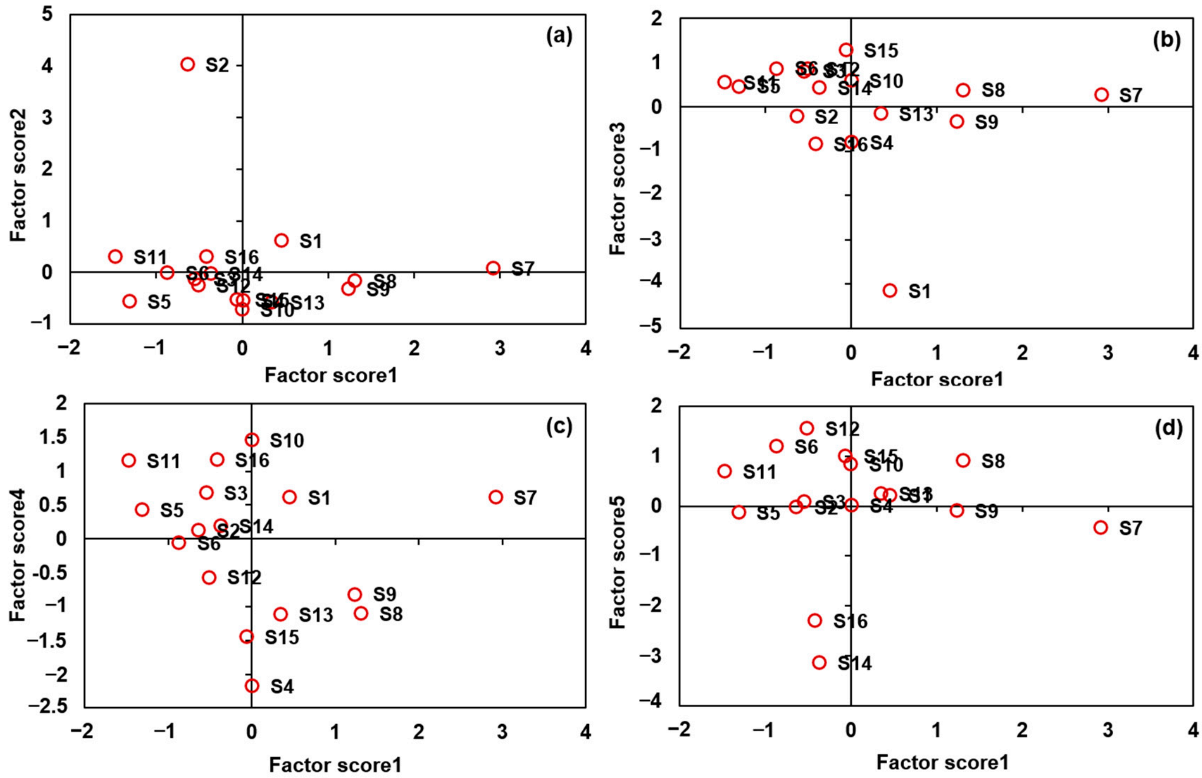

Figure 8. Factor scores for water quality monitoring stations in Tianjin. S1–S16 are water quality monitoring stations 1–16, respectively.

4.3. Impact of the LULC Pattern on Water Quality Characteristics

According to the LULC map (Figure 4) and the distribution of ground objects around the water monitoring stations (Figure 6), the locations of water monitoring stations could be divided into water, cultivated land, built-up land, and cultivated/built-up land. To determine the main parameters of the areas influenced by the LULC, the entropy weight of surface water quality parameters in each land use class were calculated, and the results are shown in Table 3.

Table 3. Entropy weights of water quality parameters for different LULC patterns in Tianjin.

Land Use/Cover	Water		Cultivated Land		Built-Up Land		Built-Up/Cultivated Land	
	H	W	H	W	H	W	H	W
Temperature	0.9688	0.0036	0.9665	0.0039	0.9701	0.0035	0.9636	0.0043
pH	0.9826	0.002	0.986	0.0016	0.9918	0.001	0.9792	0.0024
DO	0.9726	0.0032	0.9833	0.002	0.9795	0.0024	0.9794	0.0024
EC	0.9191	0.0095	0.8451	**0.0183**	0.9125	**0.0102**	0.9551	0.0052
Tur	0.9166	0.0097	0.8908	0.0129	0.9232	0.0089	0.8921	**0.0126**
COD_{Mn}	0.9861	0.0016	0.9902	0.0012	0.9861	0.0016	0.9897	0.0012
NH_3N	0.8814	**0.0138**	0.8742	0.0148	0.9101	**0.0104**	0.8689	**0.0153**
TP	0.9586	0.0048	0.9744	0.003	0.9614	0.0045	0.9581	0.0049
TN	0.9758	0.0028	0.9714	0.0034	0.9782	0.0025	0.9753	0.0029

Note: H is information entropy and W is weight. DO, dissolved oxygen; EC, electrical conductivity, Tur, turbidity; COD_{Mn}, permanganate index; NH_3N, ammonia nitrogen; TP, total phosphorus; TN, total nitrogen.

The highest weight was obtained for the NH_3N concentration. This indicates that it should have a large weight in the comprehensive evaluation of large reservoirs, and should be able to effectively distinguish among water bodies when determining the overall water pollution status of an area. Cultivated land had an effect on water quality, as indicated by the EC, Tur, and NH_3N concentration, and the highest weight was obtained for EC.

The high weights of these water quality parameters indicated that the water quality under the current LULC pattern was characterized by high Tur and low water purity, with severe pollution occurring due to the application of nitrogen fertilizer. This was consistent with the reported water quality characteristics in the vicinity of cultivated land [19,73]. In built-up land, EC, Tur, and NH_3N had a large influence on water quality, especially for EC and NH_3N. The wastewater and sewage discharges in built-up areas, as well as the accumulation of pollutants on the impervious surfaces, result in a decline in water quality over time, especially in residential areas [20]. The results also showed that the mixed land use pattern of cultivated and built-up land had an impact on water quality, as shown by the temperature, EC, Tur, NH_3N, and TP. The intensive human activities and high nutrient concentrations in water bodies from agriculture may be the reason for this phenomenon [20,74,75]. The NH_3N concentrations had the highest weight in water, built-up land, and cultivated/built-up land, indicating serious nitrogen pollution in the water monitoring stations of Tianjin.

5. Conclusions

The natural water environment of Tianjin has a considerable impact on the ecology and economy of northern China due to the significant geographical location of the city. In this study, nine water quality parameters were analyzed at the macro scale based on water quality data from surface water monitoring stations in Tianjin. A cluster analysis, factor analysis, and entropy weight calculation were conducted to determine the potential pollution sources in the surface water near the monitoring stations, as well as the response of surface water quality to the LULC pattern in Tianjin. Three main conclusions were drawn. First, the surface water quality parameters of Tianjin displayed seasonal variation and were affected by organic pollution. In particular, the mean TN concentration exceeded the class V water quality standard throughout the whole study period. There was a strong correlation ($R > 0.5$) between pH and DO over the whole year, whereas there were no obvious correlations among the other water quality parameters. Second, as the main water source in Tianjin, Yuqiao Reservoir had excellent water quality, while Tianjin's surface water quality was affected by organic pollution. The NH_3N, TN and TP concentrations had high loadings and water pollution was most serious near built-up land, especially in the central urban area, indicating that the intensive human activities in the central city had a negative impact on water quality. Third, the water quality response to the LULC pattern was mainly reflected in the NH_3N, EC, and Tur. Water, built-up land, and cultivated/built-up land had the largest response to NH_3N, and cultivated land had the largest response to EC, in Tianjin. This study focus on discussion on the seasonal changes of surface water and impact of land use/land cover pattern on water quality in Tianjin, and highlighted the need to improve surface water quality in Tianjin; the results provide a research basis and guidance for the sustainable utilization and water resources management in Tianjin. Further studies will incorporate more land use and landscape pattern indicators to better explain the complicated relationship between water quality and the surrounding environment.

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Abbreviations

NH_3N	Ammonia nitrogen
DO	Dissolved oxygen
EC	Electrical conductivity
EQSSWC	Environmental Quality Standards for Surface Water of China
LULC	Land use/land cover
COD_{Mn}	Permanganate index
TN	Total nitrogen
TP	Total phosphorus
Tur	Turbidity

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