

Original Research

Ecological Remediation of Blocked Urban River by Integrated Physical-Biological Approaches

Yifan Lin¹, Junrui Cheng¹, Doudou Gao², Ying Zhang¹, Yang Wang¹, Minhui Guo³, Guangming Jiang⁴, Tianhao Li¹, Yuanjie Zheng⁵, Kan Wang^{1**}, Jie Yu^{1,6*}

¹Department of Civil and Environmental Engineering, Ningbo University, Ningbo 315211, China

²Ningbo Municipal Engineering Construction Group Co. Ltd, Ningbo 315000, China

³Department of Environmental Engineering, Zhejiang University, Hangzhou 310058, China

⁴Engineering Research Center for Waste Oil Recovery Technology and Equipment, Ministry of Education, Chongqing Technology and Business University, Chongqing 400067, China

⁵Ningbo Shuixin Internet of Things Technology Co. Ltd, Ningbo 315033, China

⁶Environmental Technology Innovation Center of Jiande, Hangzhou 311607, China

Received: 29 May 2023

Accepted: 8 July 2023

Abstract

Urban rivers were often cut off during engineering construction in regions with dense river network, causing severe deterioration of the river eco-system. Due to little research conducted on the blocked river remediation, this study applied integrated engineering measures including aeration, planted floating beds, fiber biofilm carriers, and microbial reagents to remediate a blocked river in-situ. The concentrations of NH₃-N, total phosphorus (TP), and COD_{Mn} of the blocked river were markedly reduced, with removal efficiencies of 50.5-94.7%, 15.8-78.2%, and 30.4-78.7% after 3-months remediation, respectively. Negative correlations were found between NH₃-N and temperature, pH, between TP and pH, probably due to season and/or pH dependent biological processes. Positive correlation between COD_{Mn} and dissolved oxygen suggests the efficiency of artificial aeration in COD elimination. The biofilms developed on fibers showed temporal and spatial variations in quantity and extracellular polymeric substances (EPS) composition. The biofilm EPS was dominated by humic acid-like compounds with low freshness, while the dissolved organic matter in the river mainly consisted of aromatic proteins and fulvic acid-like compounds with high freshness which may attributed to the microbial reagents. No secondary pollution from sediment was observed. Results suggest integrated ecological remediation as a feasible strategy for the blocked river remediation.

Keywords: blocked river, ecological remediation, biofilm, aeration, planted floating bed

*e-mail: yujie@nbu.edu.cn

**e-mail: wangkan@nbu.edu.cn

Introduction

Urban rivers are significant to human beings survival and development, as they serve many functions that relate closely with people's life, like water supply, agricultural production, and transportation [1]. However, rapid and excessive exploitation and urbanization led to the breakdown of ecological balance of the river system [2]. Large amount of nutrients and organic matter derived from industrial, agricultural, and human activities were discharged into urban rivers, causing the contamination of river, which would greatly hinder the economic development and threaten human health [3]. Furthermore, the urban rivers were often cut off during engineering construction in regions with dense river network, followed by stagnation of the water flow, depletion of oxygen, and reduction of water self-purification capacity, influencing the rivers functions such as flood control and deteriorating the rivers ecosystem severely. The promotion of effective remediation measures is thus urgent to restore the damaged river eco-system, especially the blocked river system.

Several ecological remediation technologies, including physical, chemical, and biological-ecological methods, have been increasingly developed and applied for the river water purification and the ecosystem rebuilding [1]. Physical methods mainly include sediment dredging or covering, algae removal by mechanical methods, and artificial aeration [1, 4]. Sediment dredging is controversial as the pollutants tend to re-accumulate in the sediment after a certain time, and the artificial aeration is effective in reducing the secondary pollution and improving the oxygen content and transparency of the river water [4, 5]. Chemical methods involve the chemicals addition (e.g., flocculant, algacide, and lime) into the river to remove chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), total phosphorus (TP), NH_3-N , and algae. Though fast and effective, this type of method may cause secondary pollution and toxic effects on aquatic organisms [1].

Biological-ecological methods, such as biofilm reactor, bio-manipulation, constructed wetland, and planted floating bed system, exploit the potential of microorganisms, aquatic animals, and macrophytes in eliminating pollutants within micro-ecosystems [2, 4, 6]. Biofilms, known as aggregates of microorganisms, are often found in biofilm reactors and other substrata in river water and serve as important recipients and consumers of pollutants [1, 2]. In particular, extracellular polymeric substances (EPS) of biofilms that are mixture of high molecular weight polymers from the organisms secretion, cellular lysis, and macromolecules decomposition, provide significant and unique structural and functional benefits to the biofilms [7]. Bio-manipulation restores the ecological balance through regulating the fish community structure and improving the efficiency of zooplankton grazing on phytoplankton in the water body [1]. Macrophytes are the main units

of constructed wetland and planted floating bed, and the economic and environmental benefits and the capacity of nutrients removal were widely acknowledged [1, 3].

A single method is sometimes not effective in practical application for remediation of heavily polluted river, and integrated approaches are thus more favorable [3]. Combinations of two or more ecological remediation methods, such as macrophyte combined with artificial aeration, hybrid engineering approach of aeration, microorganisms, biological aerated filtration, artificial biofilms, and planted floating beds, integration of constructed wetlands, sediment dredging, hydrophytes, and planted floating beds, have been applied in field to restore contaminated river water and proven to overcome restrictions of the single method [5, 8]. However, there is little report concerning the remediation of the blocked river, which is a bit different from the common polluted rivers since the water flow is completely stagnated. It is thus of importance to seek feasible approaches to address the blocked river issue that usually occurred in regions with dense river network and intensive human activities.

Restoration of the blocked river system involves the increase of oxygen content, improvement of water flow, activation of microbes, and promotion of contaminants removal, which would be probably achieved by integrated remediation technologies. Thus, comprehensive engineering measures were designed in this study for in-situ ecological remediation of a blocked river in Ningbo, China: (1) artificial aeration to increase the dissolved oxygen content and promote the water flow, (2) planted floating beds acting as both micro phytoremediation sites and biofilm carriers, (3) fiber materials for biofilm growth, and (4) microbial reagents to strengthen the microorganisms activities, and the water quality, the biofilm and sediment properties were evaluated, aiming to gain a further understanding of the river system responses towards the remediation engineering and offer a possible approach for blocked urban rivers remediation.

Experimental

Study Site

The Niulang River is located in Ningbo (a coastal city with dense river network) in southeastern China (29.52°N, 121.35°E). The river connects Mingyi River in the west and Houxi River in the east, and has an approximate area of 13421 m² (822 m in length and 16 m in width) (Fig. 1a). The major land use in the region is constructed land, and the river water quality was mainly influenced by human activities and non-point source pollution from rainwater runoff. The river was cut off due to the subway construction in 2017, and the water became highly anoxic, black, and odorous.

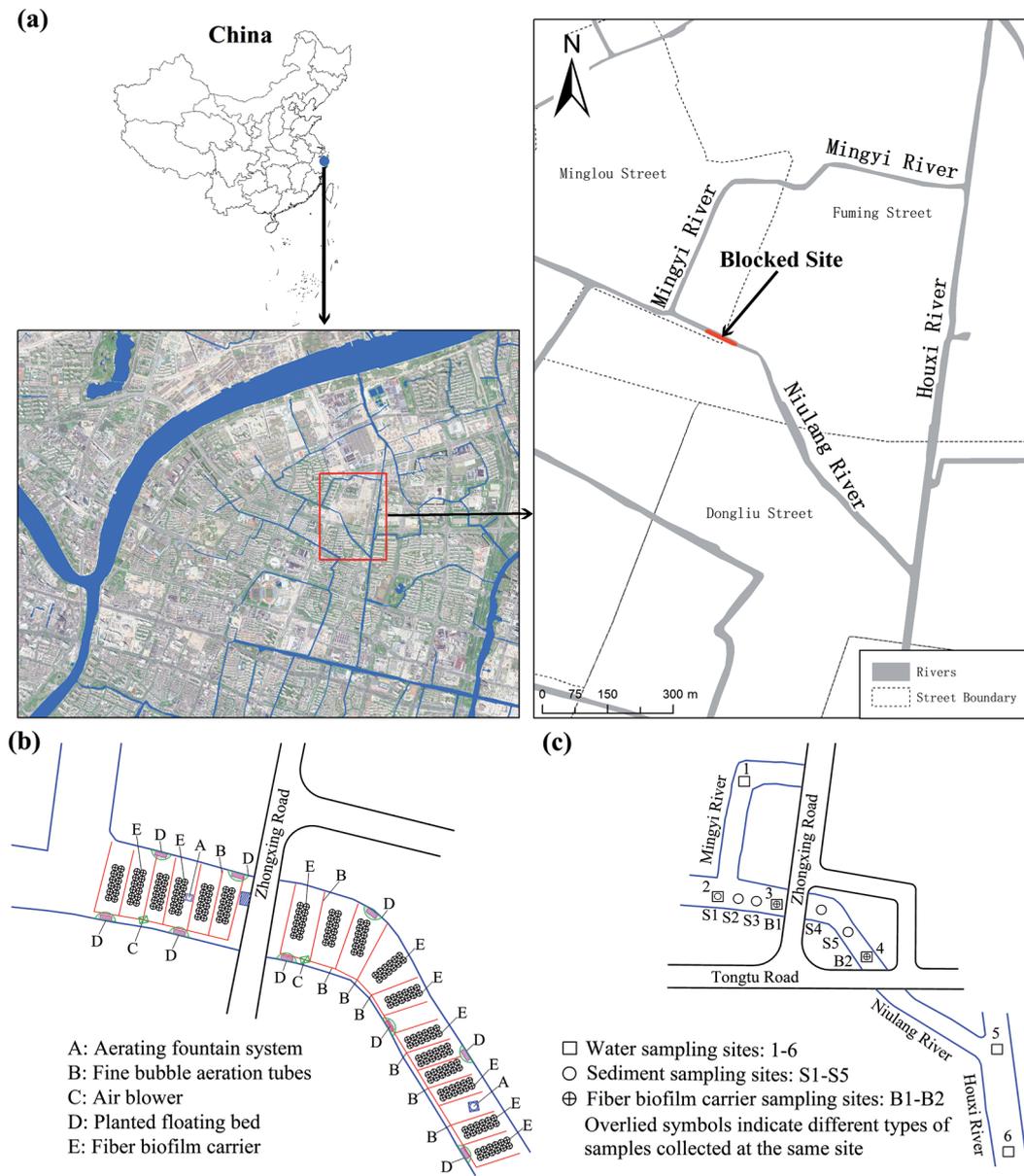


Fig. 1. Locations of the blocked Niulang River a), the integrated ecological remediation project b), and the sampling sites of the river water, sediment, and biofilm c).

In-situ Ecological Remediation

An integrated ecological remediation system was constructed in the blocked river, as presented in Fig. 1b). Two kinds of aerators were set to improve the water flow and the oxygen transfer efficiency: (1) two aerating fountain systems (1.5 kW) installed at each side of the blocked site (type A in Fig. 1b), (2) fine bubble aeration tubes set at an interval of 8 m along the river (type B in Fig. 1b) powered by two air blowers (flow rate: 2.34 m³/min, power consumption: 2.2 kW, type C in Fig. 1b), with a running time of 12 h per day for both aerators. Planted floating beds were placed along the river bank (type D in Fig. 1b), which are 1-2 m in width and 4-8 m in length, planting hydrophytic plants (*Canna indica* L., *Iris pseudacorus* L., *Hydrocotyle verticillata*,

Sagittaria trifolia L., and *Pontederia cordata* L.) on buoyant polymeric materials. The fiber biofilm carrier (0.15 m in diameter, 1 m in height, and 250 m²/m³ in specific surface area) was hanged vertically in the river for microorganisms attachment and growth (type E in Fig. 1b). Microbial reagents containing photosynthetic bacteria, bacillus, phosphorus-accumulating bacteria, nitrifying bacteria, lactic acid bacteria, and yeast were added into the river every two months at a dosage of 0.5 mg/m² to enhance the activity of microbes.

Sampling and Analysis

Before remediation, the river water was sampled in November, 2017 from 5 sites (sites 2 to 6 in Fig. 1c) located at both sides of the blocked site of Niulang River,

the intersections with the Mingyi and Houxi River, and the Houxi River for pH, dissolved oxygen (DO), $\text{NH}_3\text{-N}$, and COD_{Mn} measurements. After the operation of the remediation project, one additional sampling site was set at the Mingyi River (site 1 in Fig. 1c). The river water was collected every half a month except rainy days from March, 2018 to December, 2018, and pH, DO, and water temperature were measured immediately using a HACH sensION5 portable meter (Hach Company, Colorado, US). Other water quality parameters, including $\text{NH}_3\text{-N}$, TP, and COD_{Mn} were determined within 7 d according to the Chinese standard methods. The concentration of $\text{NH}_3\text{-N}$ was measured at 420 nm using a U-3900 spectrophotometer (Hitachi, Japan) after reaction with Nessler reagent (HJ 535-2009). The water samples were digested with potassium persulfate in an autoclave for 30 min at 120°C, followed by addition of ascorbic acid, ammonium molybdate, and detection at 700 nm for TP determination (GB 11893-89). The COD_{Mn} was determined from the consumption of potassium permanganate during chemical oxidation of organic matter in the water sample (GB 11892-89). Three-dimensional excitation-emission matrix (3D-EEM) fluorescence spectra of the water samples collected in November, 2018 were obtained using an F-4600 fluorescence spectrophotometer (Hitachi, Japan) which scanned from 280 to 550 nm at 1.0 nm increment for the emission spectra and from 200 to 400 nm with 5.0 nm interval for the excitation spectra at a scan speed of 2400 nm/min [9].

The fiber biofilm carrier was collected once a month in October and November, 2018 at sites B1 and B2 (Fig. 1c). The carrier was cut into three pieces, rinsed twice with pure water to remove impurities, and the dry weight of the carrier was measured as W_1 after drying at 80°C. The attached biomass was separated by adding the dry carrier into 200 mL pure water and sonicating for 20 min. The carrier was dried at 80°C again (weight: W_2) and the quantity of biomass was calculated using Eq. (1):

$$\text{Biomass quantity} = \frac{W_1 - W_2}{W_2} \quad (1)$$

The biomass solution was centrifuged at 10000 g for 20 min and the supernatant was collected as EPS after filtering through 0.45 μm membrane. The 3D-EEM fluorescence spectra of the EPS were characterized following the procedures used for water samples. Three fluorescence indices, including humification index (HIX), fluorescence index (FI), and freshness index ($\beta : \alpha$), were calculated, representing the humification degree, precursor source, and freshness of the fluorescent materials. The HIX was estimated by dividing areas under the emission curve at 435-480 nm by the sum of areas in the emission range of 300-345 nm and 435-480 nm at an excitation wavelength of 255 nm. The FI was the ratio of emission intensity at 470 nm and 520 nm

excited at 370 nm. The freshness index was obtained by dividing emission intensity at 380 nm by the maximum emission intensity at 420-435 nm at 310 nm excitation wavelength [10].

The sediment was collected once a month in October, November, and December, 2018. The $\text{NH}_3\text{-N}$, TP, total organic carbon (TOC), and pH of the sediment were measured using the Chinese standard methods. The $\text{NH}_3\text{-N}$ in the sediment was extracted by potassium chloride, and measured at 630 nm after reacting with hypochlorite and phenol (HJ 634-2012). The TP was determined at 700 nm after melting the sediment with NaOH at 400 and 720°C for 15 min and reacting with ascorbic acid and ammonium molybdate (NY/T 88-1988). The TOC was calculated from the consumption of potassium dichromate during chemical oxidation of organic carbon in the sediment at 170-180°C for 5 min (LY/T 1237-1999). The pH was measured after solubilizing the sediment in 0.01 mol/L calcium chloride solution (LY/T 1239-1999).

Statistical analysis of the data was performed by SPSS Statistics 20.0 using one-way analysis of variance, multiple comparisons (LSD test), and Pearson correlation analysis.

Results and Discussion

Purification Performance of the Integrated Ecological Remediation

Water Quality of the Blocked River

The water quality parameters of the blocked Niulang River before the implementation of the remediation project are presented in Table 1. The concentrations of $\text{NH}_3\text{-N}$, TP, and COD_{Mn} increased as the sampling point approached the blocked site (from site 2 to 3 and from site 6 to 5 and 4), indicating the severe deterioration of the water quality due to the blockage. And the concentrations of $\text{NH}_3\text{-N}$, TP, and COD_{Mn} at site 3 were almost twice of those values at site 2 and 4, which suggests a more severe damage of the river eco-system at the western segment. In terms of overall pollution level, the blocked river is similar to a reported heavily polluted river in China (Dihe River, prior to remediation) [10].

$\text{NH}_3\text{-N}$ Removal

Post-project investigation shows a significant improvement of the water quality (Fig. 2). The $\text{NH}_3\text{-N}$ concentration decreased sharply from 18.72 (prior to remediation, November, 2017) to 2.86-9.42 mg/L (post-remediation, March to December, 2018) and from 11.23 to 0.59-8.68 mg/L for sites 3 and 4 (Fig. 2a), resulting in removal efficiencies of 49.7-84.7% and 22.7-94.7%, respectively (Fig. 2d). The monthly changes of the $\text{NH}_3\text{-N}$ concentration of the water sampled at the same

Table 1. Water quality parameters of the blocked Niulang River before the implementation of the comprehensive ecological remediation project.

Parameters	Sampling sites				
	2	3	4	5	6
NH ₃ -N (mg/L)	10.75±0.53	18.72±0.90	11.23±0.56	8.21±0.40	7.11±0.33
TP (mg/L)	0.72±0.03	1.24±0.06	0.57±0.02	0.46±0.02	0.41±0.01
COD _{Mn} (mg/L)	10.94±0.50	17.86±0.88	9.54±0.40	5.53±0.20	4.62±0.23
pH	6.96±0.02	6.99±0.02	6.93±0.04	6.95±0.04	6.95±0.05
DO (mg/L)	1.20±0.06	0.89±0.03	3.00±0.10	3.50±0.10	3.80±0.20

side of the blocked site followed a similar trend, and the NH₃-N concentration of sites 3 and 4 was statistically lower ($p < 0.05$) or had no statistically significant difference compared with that of other sites on the same side in most cases during remediation, suggesting that the integrated ecological remediation measures are effective in enhancing the NH₃-N purification ability of the blocked river.

The best performance of NH₃-N removal was mainly achieved in summer and autumn, and Pearson

correlation analysis further confirms that the NH₃-N concentration had a negative and weak correlation with water temperature (-0.389) and a negative and moderate correlation with pH (-0.462) at the 0.01 significance level (Fig. 3). Biological processes, such as plants growth and microorganism activities, would be strengthened as the temperature increased (Fig. 2g), inducing a higher removal rate of NH₃-N in summer and autumn [5]. Moreover, increase of pH values (from 7.12-7.37 in March and April to 7.20-8.24 in summer and

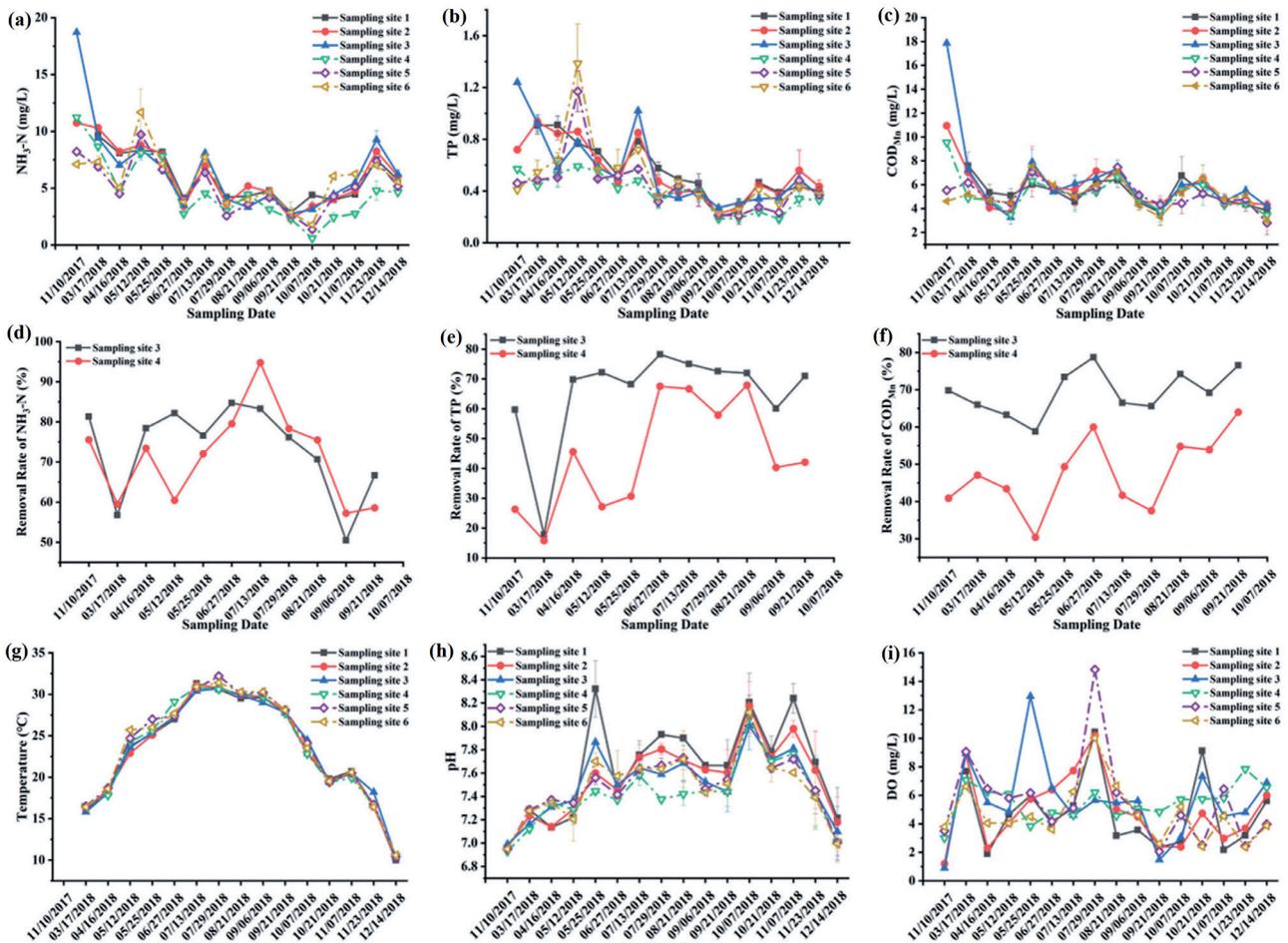


Fig. 2. Variations and removal rates of NH₃-N (a and d), TP (b and e), COD_{Mn} (c and f) and variations of temperature (g), pH (h) and DO (i) of the river during remediation (prior to remediation: November, 2017, post-remediation: March to December, 2018).

autumn, 2018) which may resulted from algal activity was favorable for nitrification process during which nitrifying bacteria consumed $\text{NH}_3\text{-N}$ (Fig. 2h) [11].

TP Removal

The TP was markedly removed due to the ecological remediation, reducing from 1.24 (prior to remediation) to 0.27-1.02 mg/L (post-remediation) and from 0.57 to 0.18-0.48 mg/L for sites 3 and 4 after three months operation (Fig. 2b), corresponding to removal efficiencies of 17.7-75.8% and 15.8-68.4%, respectively (Fig. 2e). The temporal fluctuation of TP was similar to that of $\text{NH}_3\text{-N}$ (a positive and very strong correlation of 0.815, Fig. 3), inferring that $\text{NH}_3\text{-N}$ and TP were primarily from the same source, i.e., the non-point rainwater runoff [12]. Compared with sites 1 and 2, the TP of site 3 had no statistically significant difference or was statistically lower ($p < 0.05$) in most cases during remediation, similar to that of site 4 when compared to sites 5 and 6, indicating the effectiveness of the integrated remediation project in the TP removal and the ecological system restoration of the blocked river.

Similar to $\text{NH}_3\text{-N}$, there was a negative and moderate correlation (-0.434) between TP and pH at the 0.01 significance level (Fig. 3), indicating that a slight alkalinity is beneficial for TP removal, probably due to the promotion of phosphorus-accumulating organisms growth and phosphate precipitation reaction under alkaline conditions [13]. However, no significant correlation was observed between TP and temperature, which is consistent with a former study reporting

an optimal water temperature of about 20°C for TP removal in constructed wetlands [14]. Too high or low temperatures might induce low TP removal efficiency.

COD Removal

The COD_{Mn} of the blocked river water was reduced significantly from 17.86 (prior to remediation) to 3.26-7.91 mg/L (post-remediation) and from 9.54 to 3.44-7.41 mg/L for sites 3 and 4 (Fig. 2c), with removal efficiencies of 55.7-81.7% and 22.3-63.9%, respectively (Fig. 2f). Unlike $\text{NH}_3\text{-N}$ and TP, the COD_{Mn} fluctuated with no seasonal trend during the post-remediation investigation. Little statistically significant difference was obtained between site 3 and sites 1, 2, between site 4 and sites 5, 6 during remediation, suggesting the promotion of the blocked river purification ability.

The blocked river water was hypoxic with DO concentrations of 1.2 and 0.89 mg/L for sites 2 and 3 (less than 2 mg/L) before remediation, respectively, and turned into saturated or supersaturated due to the artificial aeration (most of the observed values were between 2 and 7 mg/L, Fig. 2i) [11]. The DO concentration had a positive and moderate correlation (0.407) with COD_{Mn} at the 0.01 significance level (Fig. 3), indicating that increase of the DO concentration by the aeration promoted the oxidation reaction in the water and changed the flow regime, which contributed to the restoration of the eco-system and the fleet COD_{Mn} reduction of the blocked river during the initial remediation period [15].

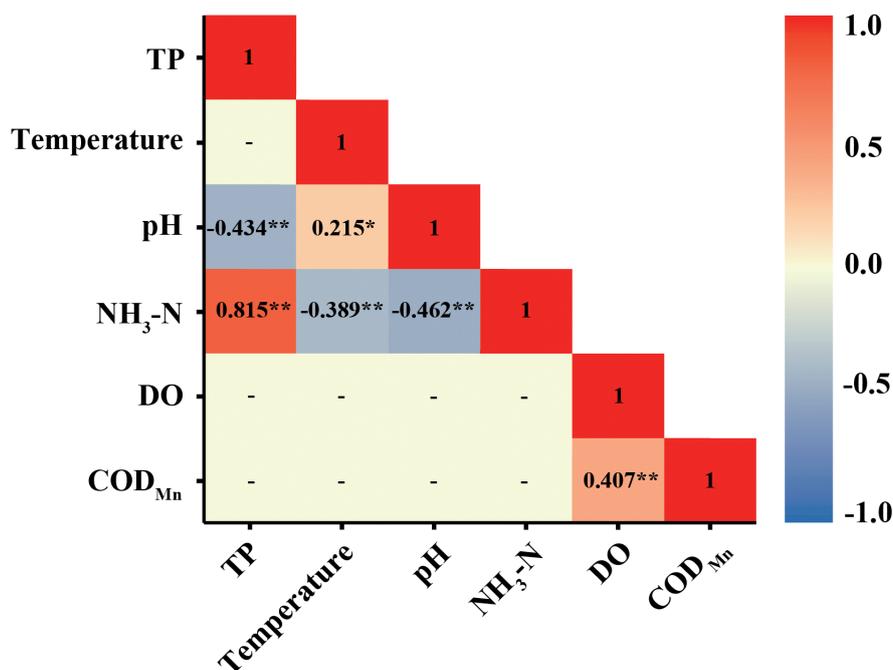


Fig. 3. Pearson correlation analysis of the water quality parameters during remediation. **: a significant correlation at the 0.01 level (2-tailed); *: a significant correlation at the 0.05 level (2-tailed). Correlation coefficient (absolute value): 0.8-1.0: very strong correlation; 0.6-0.8: strong correlation; 0.4-0.6: moderate correlation; 0.2-0.4: weak correlation; 0.0-0.2: very weak correlation.

Biofilm Developed on Fiber Biofilm Carrier

Fluorescence Properties of Biofilm

Biofilm could develop on any submerged surfaces during the river restoration process, and is efficient in absorbing, immobilizing, and degrading various pollutants like heavy metals and organic contaminants [16]. Due to the limited proportion of environmental matrices that can be occupied by biofilms, fiber biofilm carrier was employed providing vast surface area for biofilm attachment and growth [17]. Dark brown biofilms with uneven thickness were developed on the fiber biofilm carrier, as shown in Fig. 4a). Biofilm was reported as a non-uniform structure with variable thickness and various pores and channels in the biofilm interior [18]. The biomass quantities collected in October and November, 2018 were 6.56±0.58 and 6.91±0.01 mg/g (site B1), 7.38±2.93 and 5.49±0.29 mg/g (site B2), respectively, suggesting the temporal and spatial variation of the biofilms, consistent with a former study [19]. The biomass quantities were lower than the

reported values of biofilms attached on fiber biofilm carrier hanging beneath a river planted floating bed, and the difference in hydrological condition, water quality, and temperature may account for this [20].

The EPS participate directly in binding of contaminants and protecting organisms against environmental shocks [9, 17]. The EPS were extracted from the biofilms grown on the fiber biofilm carrier for 3D-EEM fluorescence spectra characterization, and several typical fluorophores were identified, as presented in Fig. 4b). The fluorescence spectra of biofilm EPS showed a strong temporal variation. Only one peak was identified in the EPS sampled in October, 2018: excitation/emission wavelength (Ex/Em) = 350-355/434 nm, which could be attributed to humic acid-like compounds, while more diverse components were detected in the EPS sampled in November, 2018, that is, peaks located at Ex/Em = 230/339-358 nm, 285/334-357 nm, 230-240/391-423 nm, and 310-345/412-437 nm, which could be described as aromatic proteins, soluble microbial by-product-like proteins, fulvic acid-like compounds, and humic acid-like compounds,

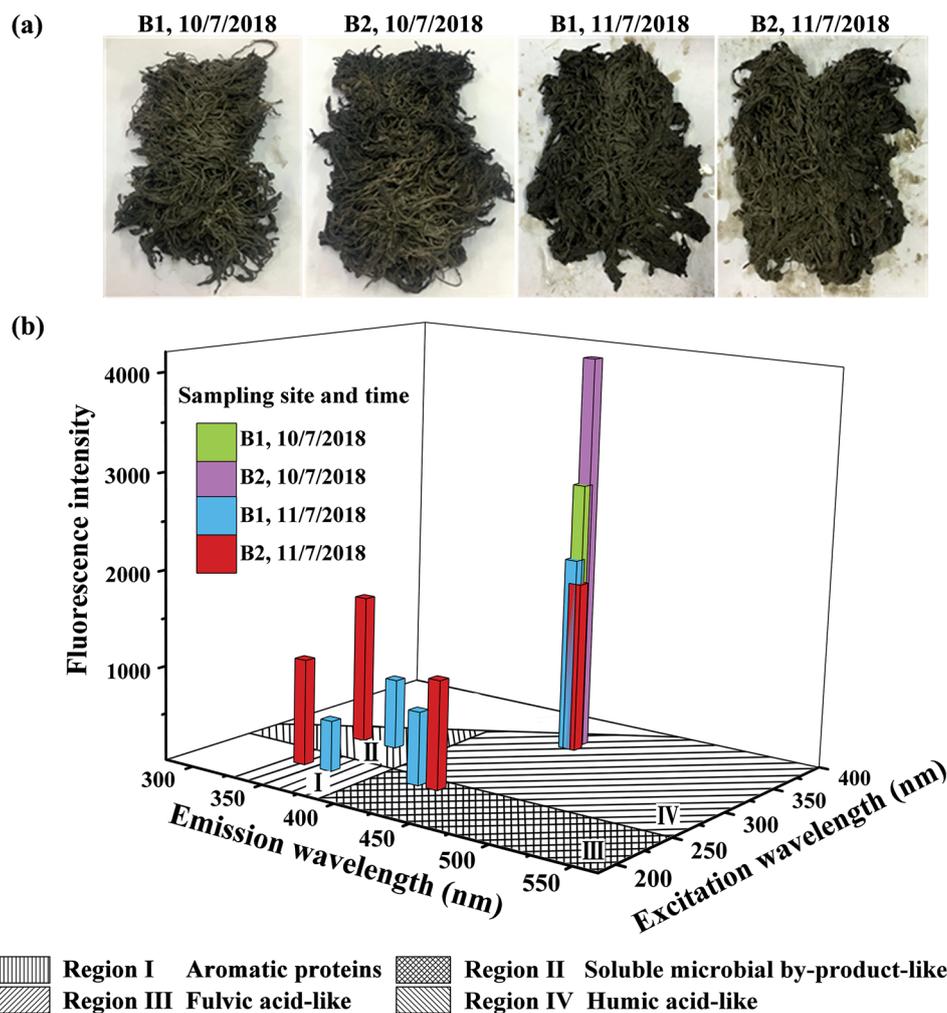


Fig. 4. Images of biofilms on fiber biofilm carriers a) and fluorescence intensities of fluorophores in biofilm EPS b) during the river remediation.

respectively. The high fluorescence intensity of humic acid-like compounds suggest the dominance of humic acid-like compounds in biofilm EPS.

Fluorescence indices, including HIX, FI, and $\beta:\alpha$, reveal the compositional variation and source of the biofilm EPS (Fig. 5). The HIX of EPS sampled in November, 2018 (0.64-0.80) were slightly lower than that sampled in October, 2018 (0.80-0.97) (Fig. 5a), suggesting a declined degree of humification and less humified materials, which is in accordance with the fluorescence results in Fig. 4b [10]. Fluorescence index, which indicates the terrestrial (FI \approx 1.3) or microbial (FI \approx 1.8) origin of organics, was in the range of 1.68-2.03 for biofilm EPS (Fig. 5b), suggesting that the EPS were mainly derived from microbial activity and had low aromaticity [10, 21]. The freshness indices (0.57-0.70) were lower than the reported ones (0.68-1.16) (Fig. 5c), suggesting the low proportion of freshly produced EPS which might be influenced by the growth period of microbes [17]. Generally, the biofilm EPS was primarily produced by the microbial processes, with a certain degree of humification.

Comparison between Biofilm EPS and Dissolved Organic Matter (DOM) in the River

Biofilms exchange materials and energy with the water body, and the fluorescence properties of biofilm EPS and DOM in the river (both sampled in November 7, 2018) were compared (Fig. 6). The type and relative abundance of the fluorescent DOM in the river varied from those of biofilm EPS. One more fluorescence peak were observed in the fluorescence spectra of the river DOM, i.e., tyrosine-like proteins at

Ex/Em = 225-230/305-309 nm. Unlike the dominance of humic acid-like compounds in biofilm EPS, the fluorescence intensities of aromatic proteins and fulvic acid-like compounds were much higher than those of other fluorescent compounds in the river water, suggesting the major presence of aromatic proteins and fulvic acid-like compounds. The varied biological processes in between the biofilm and river water may account for the difference in the fluorescence properties [22].

The HIX and FI values of the river DOM (0.67-0.77 and 1.81-1.99, respectively) were similar to those of biofilm EPS (Fig. 5a and b), indicating their similar humification degree and source, while the freshness indices (0.85-1.01) were slightly higher compared to those of biofilm EPS (Fig. 5c), inferring the higher proportion of freshly produced DOM and stronger microbial activity in the river water, which were probably due to the addition of microbial reagents. Microbial reagents could increase the diversity and abundance of the microbial community, strengthening the microbial activity in transforming DOM and degrading contaminants [15].

Sediment

Sediment acts as sink and source of a wide variety of contaminants including nutrients and heavy metals [23, 24]. The physico-chemical properties of sediment during the ecological remediation are presented in Fig. 7. $\text{NH}_3\text{-N}$ is the dominant speciation of nitrogen in sediment as the anoxic environment promotes the $\text{NH}_3\text{-N}$ formation (Fig. 7a) [23, 25]. The contents of $\text{NH}_3\text{-N}$ ranged from 5.63 to 177 mg/kg during post-project investigation, which were lower than reported values of polluted river sediments [6, 25]. The TP concentrations were in the range of 209-1830 mg/kg (Fig. 7b), most of which were higher than the average background value of local river sediment (239 mg/kg), but much lower compared to a heavily polluted river sediment in China (3514 mg/kg) [25, 26]. The TOC contents of sediments (12.6-103.2 g/kg, Fig. 7c) were 3-25 times of the average background value of local river sediment (4.2 g/kg), but similar to the reported values of the polluted river sediments [6, 23, 26]. The pH values of sediments were neutral (6.87-7.84, Fig. 7d), which are favorable for the stabilization of the contaminants in sediment [27]. Results suggest that the blocked river sediment was moderately polluted in terms of nutrients accumulation compared to other heavily polluted river sediments.

Positive and strong correlations were observed between $\text{NH}_3\text{-N}$ in water and sediment (Pearson correlation coefficient: 0.747), between TP in water and sediment (0.693), and between COD_{Mn} in water and TOC in sediment (0.758) at the 0.05 significance level (Fig. 7e), indicating the synchronous change of these pollutants in between the water and sediment. Tang and co-workers [24] reported opposite variation trends

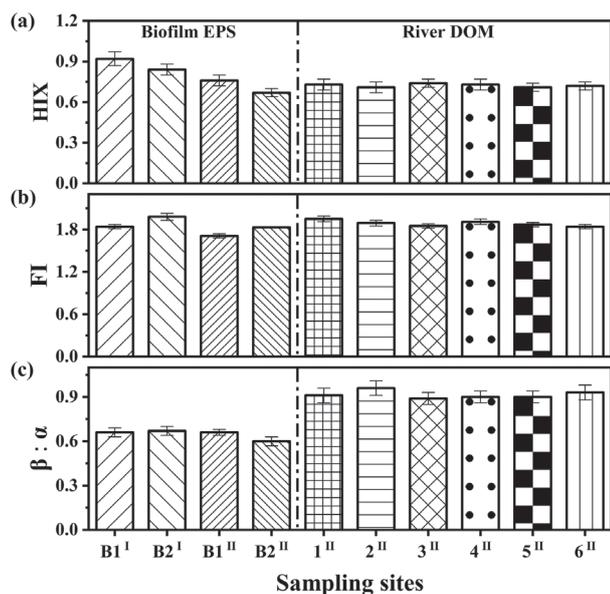


Fig. 5. Fluorescence indices (a: HIX, b: FI, c: $\beta:\alpha$) of the biofilm EPS and DOM in the river. (I: sampled at 10/7/2018, II: sampled at 11/7/2018).

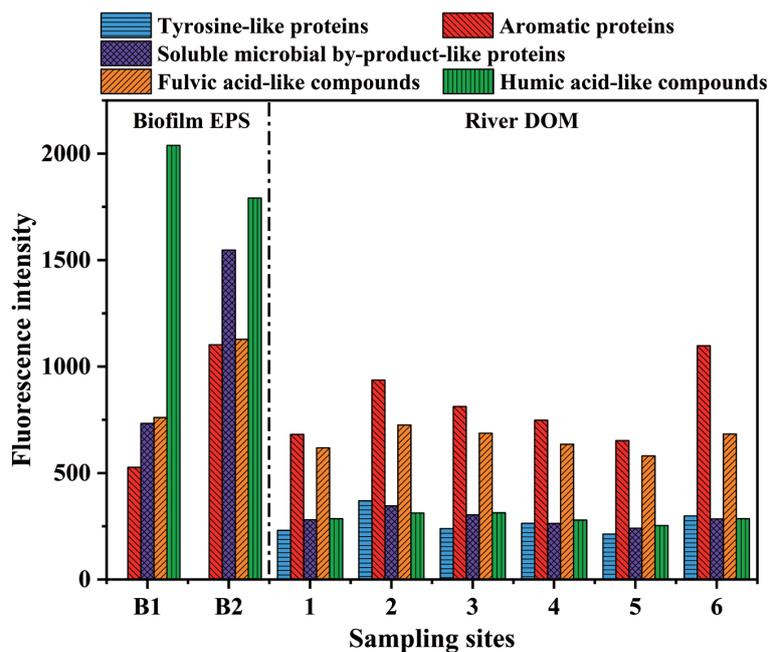


Fig. 6. Fluorescence intensities of fluorophores in biofilm EPS and river DOM sampled in November 7, 2018. Data for biofilm EPS same as data provided in Fig. 4.

of nitrogen and organic matter contents in between the overlying water and sediment during remediation, which was attributed to the migration of these pollutants. The ecological remediation project here may have increased the microbial activity in the sediment and enhanced the contaminants removal, avoiding the secondary pollution from the sediment.

Discussion

$\text{NH}_3\text{-N}$, TP, and COD_{Mn} are the key pollution indicators of urban rivers and the blocked river. The preliminary achievements in the blocked Niulang river suggest that the integrated ecological remediation is a feasible strategy for the blocked river remediation. During the remediation, the elimination of $\text{NH}_3\text{-N}$ and TP can be attributed to the hydrophytic plants absorption and microorganisms decomposition [5, 28]. Hydrophytic plants such as *Canna indica* L. and *Hydrocotyle verticillata* were reported to have high absorption ability for N and P through the plants roots entrapping and consuming N and P as nutrition [5, 6]. The fiber biofilm carriers and plants roots provided interfacial micro-environment for oxygen, N, and P transfer, promoting the activities of nitrifying, denitrifying, and polyphosphate-accumulating bacteria and enhancing the N and P removal efficiencies [28]. These biological processes are usually season and/or pH dependent, and thus induced the significant correlation of $\text{NH}_3\text{-N}$ with water temperature and pH and TP with pH (Fig. 3) [5].

However, the correlation of $\text{NH}_3\text{-N}$ and TP with temperature and/or pH suggests declined removal rates of $\text{NH}_3\text{-N}$ and TP in winter (low temperature and pH),

which had been previously reported [5, 28]. Integrated measures are thus essential to compensate for the deficiency. Other strategies, like adding adsorbents (zeolites, sponge iron, red mud, activated carbon, etc.) in the floating bed system, are also suggested to strengthen the nutrients removal during winter [3, 28].

Aeration is a popular physical engineering approach for pollutants degradation in urban rivers, and was successfully applied to improve the water quality of several rivers in Europe, US, and China [3]. Results here suggest its effectiveness in COD elimination in the blocked river through maximizing the oxygen transfer and accelerating the water flow. While effective, artificial aeration is cost intensive: the power consumption of the aerators was 88.8 KWh per day, i.e., 91 CNY, accounting about half of the total operation cost of the remediation project. Further strategies such as model simulation, intermittent aeration, and intelligent control, are suggested to help engineers to balance the operation cost and the pollutants removal.

The biofilms developed on the fiber biofilm carriers and other submerged surfaces are considered as huge reactors for pollutants adsorption and decomposition. The biofilms assemble different microbes that are capable of degrading contaminants through various metabolic pathways [16]. Furthermore, humic acid-like compounds dominated in biofilm EPS have strong affinity to organic pollutants due to van der Waals interaction, electrostatic interaction, and hydrophobic effect [29]. In the future, more extensive study of the relationship among the biofilms microorganisms, EPS, and pollutants removal is needed for better management of the contaminated river.

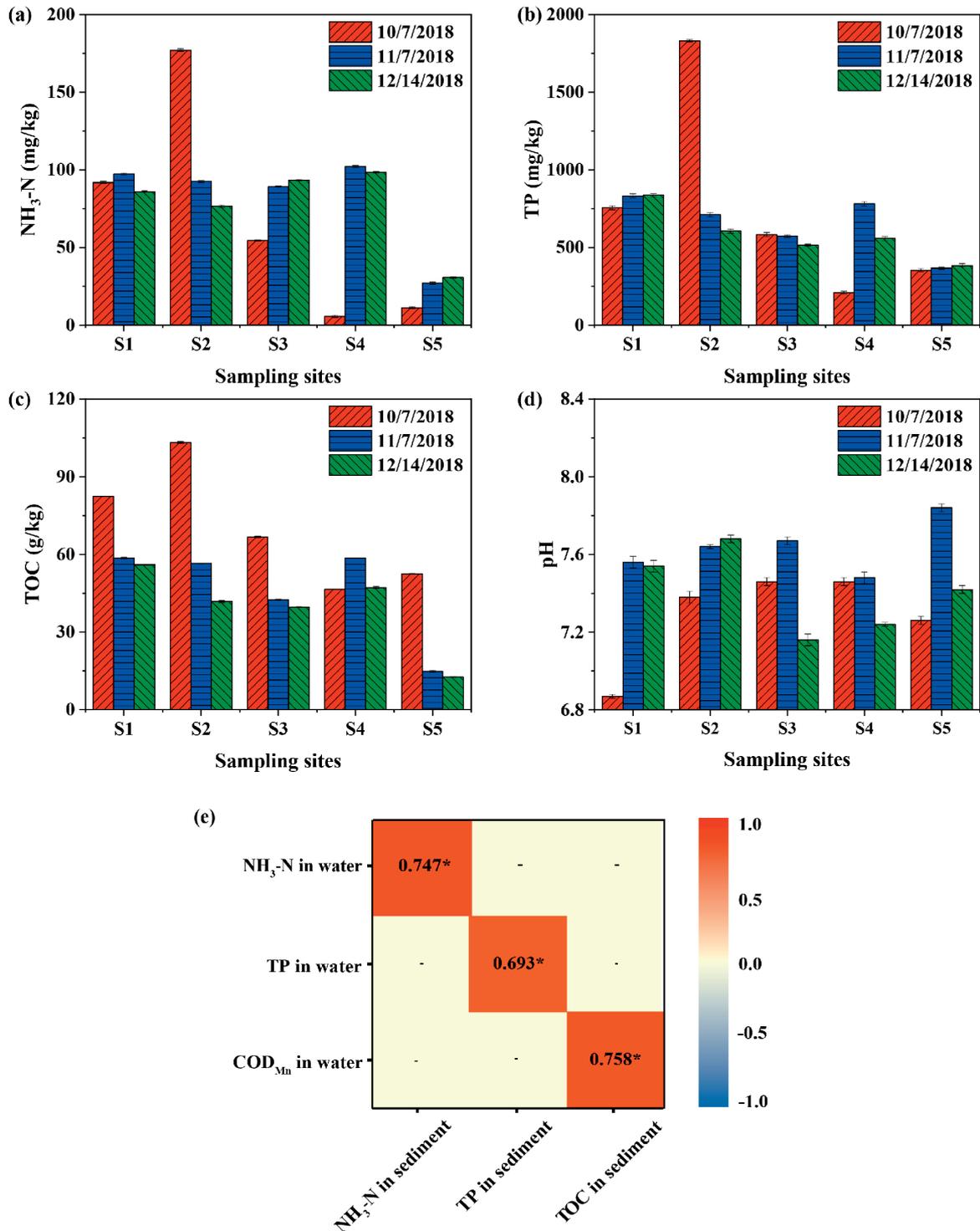


Fig. 7. Physico-chemical properties of the sediment in the blocked river during the ecological remediation (a: NH₃-N, b: TP, c: TOC, d: pH) and Pearson correlation analysis of the parameters between the blocked river water and sediment sampled at the same time and site e). *: a significant correlation at the 0.05 level (2-tailed).

Conclusions

Integrated ecological remediation involving artificial aeration, planted floating beds, fiber biofilm carriers, and microbial reagents were successfully applied for in-situ restoration of the blocked river. The water quality

was markedly improved, with little potential risk of secondary pollution from the sediment. The biological processes, including hydrophytic plants absorption and microorganisms decomposition, probably account for the NH₃-N and TP elimination, while artificial aeration promoted the COD removal. The biofilm

quantity and EPS composition showed strong temporal variations, with humic acid-like compounds dominated in EPS. The microbial reagents may account for the varied composition and higher freshness of river DOM compared with biofilm EPS. This work suggests the further development of integrated ecological remediation techniques as a feasible measure for restoring and managing the blocked river system.

Acknowledgements

This work was supported by the Science and Technology Innovation 2025 Major Project of Ningbo [2022Z212, 2020Z100], the National Natural Science Foundation of China [51978343], the Natural Science Foundation of Ningbo [2016C51035], the Scientific Research Project of Agriculture and Social Development of Hangzhou [2017NF19], the Joint Funds of the Zhejiang Provincial Natural Science Foundation of China [LZJWY23E090007], and Houniao Project of Jiande.

Conflict of Interest

The authors declare no conflict of interest.

References

- PAN B.Z., YUAN J.P., ZHANG X.H., WANG Z.Y., CHEN J., LU J.Y., YANG W.J., LI Z.W., ZHAO N., XU M.Z. A review of ecological restoration techniques in fluvial rivers. *International Journal of Sediment Research*, **31** (2), 110, **2016**.
- LI M., LI P., DU C.U., SUN L.Q., LI B.A. Pilot-Scale Study of an Integrated Membrane-Aerated Biofilm Reactor System on Urban River Remediation. *Industrial & Engineering Chemistry Research*, **55** (30), 8373, **2016**.
- MD ANAWAR H., CHOWDHURY R. Remediation of Polluted River Water by Biological, Chemical, Ecological and Engineering Processes. *Sustainability*, **12** (17), 7017, **2020**.
- WANG W., TANG X.Q., HUANG S.L., ZHANG S.H., LIN C., LIU D.W., CHE H.J., YANG Q., Segolz M. Ecological Restoration of Polluted Plain Rivers Within the Haihe River Basin in China. *Water, Air, & Soil Pollution*, **211** (1-4), 341, **2010**.
- FANG T., BAO S.P., SIMA X.F., JIANG H., ZHU W.T., TANG W. Study on the application of integrated eco-engineering in purifying eutrophic river waters. *Ecological Engineering*, **94**, 320, **2016**.
- NING D.L., HUANG Y., PAN R.S., WANG F.Y., WANG H. Effect of eco-remediation using planted floating bed system on nutrients and heavy metals in urban river water and sediment: a field study in China. *The Science of the total environment*, **485**, 596, **2014**.
- LYU Y., YU J., GUO M.H., WANG K., YU Z.X., ZHANG L.X., ZHANG Y., CHEN L.L. New insights into interaction of proteins in extracellular polymeric substances of activated sludge with ciprofloxacin using quartz crystal microbalance with dissipation. *Chemosphere*, **263**, 128044, **2021**.
- GU D.G., XU H., HE Y., ZHAO F., HUANG M.S. Remediation of Urban River Water by *Pontederia Cordata* Combined with Artificial Aeration: Organic Matter and Nutrients Removal and Root-Adhered Bacterial Communities. *International Journal of Phytoremediation*, **17** (11), 1105, **2015**.
- YU J., GAO D.D., ZHANG Y., YU X.B., CHENG J.R., JIN L.Z., LYU Y., DU Z.M., GUO M.H. Multiple roles of Ca²⁺ in the interaction of ciprofloxacin with activated sludge: Spectroscopic investigations of extracellular polymeric substances. *Science of The Total Environment*, **751**, 142246, **2021**.
- LAVONEN E.E., KOTHAWALA D.N., TRANVIK L.J., GONSIOR M., SCHMITT-KOPPLIN P., KÖHLER S.J. Tracking changes in the optical properties and molecular composition of dissolved organic matter during drinking water production. *Water Research*, **85**, 286, **2015**.
- WANG C., SAMPLE D.J., DAY S.D., GRIZZARD T.J. Floating treatment wetland nutrient removal through vegetation harvest and observations from a field study. *Ecological Engineering*, **78**, 15, **2015**.
- ZHONG F., WU J., DAI Y.R., XIANG D.F., DENG Z.F., CHENG S.P. Responses of water quality and phytoplankton assemblages to remediation projects in two hypereutrophic tributaries of Chaohu Lake. *Journal of Environmental Management*, **248**, 109276, **2019**.
- FILIPPE C.D., DAIGGER G.T., GRADY C.P. Effects of pH on the Rates of Aerobic Metabolism of Phosphate-Accumulating and Glycogen-Accumulating Organisms. *Water Environment Research*, **73** (2), 213, **2001**.
- WU H.M., ZHANG J., LI C., FAN J.L., ZOU Y.N. Mass Balance Study on Phosphorus Removal in Constructed Wetland Microcosms Treating Polluted River Water. *CLEAN - Soil, Air, Water*, **41** (9), 844, **2013**.
- SHENG Y.Q., QU Y.X., DING C.F., SUN Q.Y., MORTIMER R.J.G. A combined application of different engineering and biological techniques to remediate a heavily polluted river. *Ecological Engineering*, **57**, 1, **2013**.
- MITRA A., MUKHOPADHYAY S. Biofilm mediated decontamination of pollutants from the environment. *AIMS Bioengineering*, **3** (1), 44, **2016**.
- WANG L.F., CHEN W., SONG X.C., LI Y., ZHANG W.L., ZHANG H.J., NIU L.H. Cultivation substrata differentiate the properties of river biofilm EPS and their binding of heavy metals: A spectroscopic insight. *Environmental Research*, **182**, 109052, **2020**.
- STEWART P.S., MURGA R., SRINIVASAN R., DE BEER D. Biofilm structural heterogeneity visualized by three microscopic methods. *Water research (Oxford)*, **29** (8), 2006, **1995**.
- TIEN C., LIN M., CHIU W., CHEN C.S. Biodegradation of carbamate pesticides by natural river biofilms in different seasons and their effects on biofilm community structure. *Environmental Pollution*, **179**, 95, **2013**.
- ZHANG Z.S., DONG B., XU G.D., CHEN J.H., XI D.L., Dynamic pilot study on biofilm characteristics of fiber padding in enhanced ecological floating raft. *Technology of water treatment*, **35** (09), 37, **2009**.
- YANG Y.R., QIN J.J., QI T., ZHOU X.M., CHEN R.Z., TAN J.H., XIAO K., JI D.S., HE K.B., CHEN X.T. Fluorescence characteristics of particulate water-soluble organic compounds emitted from coal-fired boilers. *Atmospheric Environment*, **223**, 117297, **2020**.

22. HANSEN A.M., KRAUS T.E.C., PELLERIN B.A., FLECK J.A., DOWNING B.D., BERGAMASCHI B. A. Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. *Limnology and Oceanography*, **61** (3), 1015, **2016**.
23. LIU X.N., TAO Y., ZHOU K.Y., ZHANG Q.Q., CHEN G.Y., ZHANG X.H. Effect of water quality improvement on the remediation of river sediment due to the addition of calcium nitrate. *Science of The Total Environment*, **575**, 887, **2017**.
24. TANG Y.Q., LI M., ZOU Y.N., LV M.Y. SUN J.M. Mechanism of aerobic denitrifiers and calcium nitrate on urban river sediment remediation. *International biodeterioration & biodegradation* , **126**, 119, **2018**.
25. YIN H.B., ZHU J.C., TANG W.Y. Management of nitrogen and phosphorus internal loading from polluted river sediment using Phoslock® and modified zeolite with intensive tubificid oligochaetes bioturbation. *Chemical Engineering Journal*, **353**, 46, **2018**.
26. WANG Q.H., DONG Y.X., ZHENG W., ZHOU G.H. Soil geochemical baseline values and environmental background values in Zhejiang, China. *Geological Bulletin of China*, **26** (05), 590, **2007**.
27. WU Y.H., WEN Y.J., ZHOU J.X., WU Y.Y., Phosphorus release from lake sediments: Effects of pH, temperature and dissolved oxygen. *KSCE journal of civil engineering*, **18** (1), 323, **2014**.
28. WANG W.H., WANG Y., LI Z., WEI C.Z., ZHAO J.C., SUN L.Q. Effect of a strengthened ecological floating bed on the purification of urban landscape water supplied with reclaimed water. *Science of The Total Environment*, **622**, 1630, **2018**.
29. CHIANESE S., FENTI A., IOVINO P., MUSMARRA D., SALVESTRINI S. Sorption of Organic Pollutants by Humic Acids: A Review. *Molecules*, **25** (4), 918, **2020**.