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ASSESSMENT OF THE IMPACTS OF PHYTO-REMEDIATION ON WATER QUALITY OF THE LITANI RIVER BY MEANS OF TWO WETLAND PLANTS (*Sparganium erectum* and *Phragmites australis*)

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Abstract: Water pollution from human activities is largely a result of the discharge of wastewater and industrial waste into rivers. Phytoremediation, the technique that uses plants to remove pollutants from the polluted waters, is a growing field of research because of its various environmental advantages. This study aims at evaluating the efficiency of a constructed wetland in removing pollutants and treating the polluted waters of the Litani River in Lebanon, by means of two aquatic plants, *Phragmites australis* and *Sparganium erectum*. Results showed that the levels of the physico-chemical and biological parameters measured on water samples at downstream of the wetland were lower than those obtained at upstream. Results revealed that average removal efficiency was 41% for chemical oxygen demand (COD), 54% for biological oxygen demand (BOD5), 97% for nitrate (NO3-), 40% for nitrite (NO2-), 67 % for phosphate (PO43-), while it was negative (-62 %) for sulfate (SO42-), indicating an increase in sulfate content in the treated effluent returning to the River. On the other hand, most of the effluent chemical and biological characteristics were within the provisional discharge limits of effluent to water body set by the Ministry of Environment (MoE) and Lebanese Wastewater Reuse Guidelines of the Food and Agricultural Organization of the United Nations (FAO). Statistical analyses also showed significant variations ($P<0.5$) among the two sampling sites along the wetland. Our findings clearly demonstrate that phytoremediation is a viable solution to remove pollutants in a competitive environment, and improve the quality of contaminated waters by acting as a sink for various contaminants. The gained experience may be scalable to other sites and environments across the country.

Keywords: Water pollution; Litani River; Constructed wetland; Biological Oxygen Demand; Chemical Oxygen Demand; Pollutants removal

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1. Introduction

Constructed Wetlands are an alternative, promising technology for water/wastewater treatment and pollution mitigation (Stefanakis, 2020). They belong to the wider category of natural treatment systems, which are designed and constructed to utilize the natural processes involving wetland vegetation, soils, and the associated microbial assemblages to assist in treating wastewaters (Mustafa et al., 2009; Mustafa, 2013; Vyamazal, 2013). In addition, this environmentally friendly and sustainable technology provides multiple economic, ecological, technical and societal benefits, not only for domestic, municipal and industrial wastewater treatment, but also for treating agricultural runoff and agro-industrial wastewater (Mustafa and Haydar, 2020). Endowed with the advantages of cost-effectiveness and low energy consumption, the wetland technology places the overall context of the need for reliable and sustainable solutions to managing agricultural runoff and agro-industrial wastewater (Wang *et al.*, 2018).

Phytoremediation using constructed wetlands has become a logical solution to improve the quality of contaminated waters by acting as a sink for various contaminants (Herath and Vithanage, 2015). Phytoremediation is a technique for which aquatic plants are highly useful in removing pollutants in wastewater, by absorbing organic and inorganic pollutants in a competitive environment (Garad, 2022; Ali, 2022 Anning et al., 2013). Multiple water contaminants can be eliminated by using renewable and biological processes offered by constructed wetlands, requiring limited maintenance and external energy inputs (US-EPA, 2016).

The most important advantage of this system is that it is a green technology that uses plant and microbe natural resources, lowers degradation of the environment and safeguards ecosystems. Other benefits include the fact that both organic and inorganic pollutants are effectively removed by aquatic plants, making them suited for the treatment of mixed types of pollutants (Ali et al., 2022). However, a critical assessment of the performance and effectiveness of wetland systems for removing various contaminants, for which the design parameters and operational conditions affecting the efficiency of contaminant removal (Wang et al., 2018).

Plants are the primary components of a constructed wetland, as they can influence the wetland treatment performance by several processes (Wang *et al.*, 2015), either for enhancing the abundance and diversity of microorganisms in the rhizosphere by increasing available surface area for bacterial attachment and growth (Menon *et al.*, 2013), or exuding a range of degradable organic compounds (including sugars, organic acids, and amino acids), which can especially provide a continuing supply of carbon for denitrification bacteria in wetland systems (Dong *et al.*, 2016). In addition, wetland plants absorb nutrients into their tissues directly (Liu et al., 2014), and other contaminants, such as heavy metals and micro-pollutants (Teuchies *et al.*, 2012; Huang *et al.*, 2012). Wang *et al.* (2015) demonstrated that plant roots improve oxygen conditions, thereby supporting the aerobic processes in constructed wetlands in flooded conditions. On the other hand, the existence of plants is thought to increase and stabilize hydraulic conductivity in constructed wetlands (Zhang *et al.*, 2014). Lama et al. (2022) demonstrated that the interaction between water flow and *Phragmites australis* plants significantly affects flow dynamics, hydraulic conveyance, and water quality of vegetated water bodies.

The Litani River is Lebanon's largest river and most important water resource, suffering from widespread sewage disposal, direct drainage of unregulated industrial wastewater from urban areas, lack of river bed protection and illegal diversion. Today, the river is becoming a threat to public health as water contamination extends to soils, crops and wildlife, as well as hinders the socio-economic growth and well-being of riparian ecosystems. In an attempt to address the deteriorating water quality of the Litani River, the Litani River Basin Management Support (LRBMS) has constructed a wetland system between 2012 and 2013 in a publicly owned site by the Litani River Authority (LRA), to contribute to reducing the high pollution rates of the River’s waters. The objectives of the present study were to (i) assess the performance of a constructed wetland using two aquatic plants, *Sparganium erectum* and *Phragmites australis*, in treating the contaminated waters of the Litani River, and (ii) (ii) determine the efficiency of these two plants in removing pollutants and improving the quality of the polluted waters of the River.

2. Materials and methods

2.1. Climatic characteristics of the wetland site

The climate of South Bekaa Valley is sub-Mediterranean, with hot and dry season between April and September and cold and wet season for the rest of the year. Average yearly rain and potential evapotranspiration are 696 mm and 1314 mm, respectively, based on data of the EU-SUPROMED Project (Sustainable Production in Water Limited Environments of Mediterranean Agro-Ecosystems, 2019-2022) for the calculation of Typical Meteorological Year (TMY) for South Bekaa Valley, during the period from 1994 through 2018 (Karam et al., 2022). About 95% of the rain occurs from November to March. Ambient weather data (solar radiation, air temperature, wind speed at 2m height, air temperature at dew point and relative humidity) were recorded on an hourly basis from an automated weather station (METOS Compact, PESSL Instruments, Austria) 80 m apart from the wetland site. The weather station is established within a standard meteorological park (40 m N–S×40 m W–E) cultivated with rye grass (*Lolium perenne*), and is automatically linked to a built-in data logger, which discharges at 10-min interval the registered meteorological data via GPRS (General Packet Radio Service) standard wireless communication into a computer situated in the weather monitoring unit of the research station. Data was used to compute potential evapotranspiration according to Penman–Monteith equation (Allen *et al.*, 1998) (Figure 1).

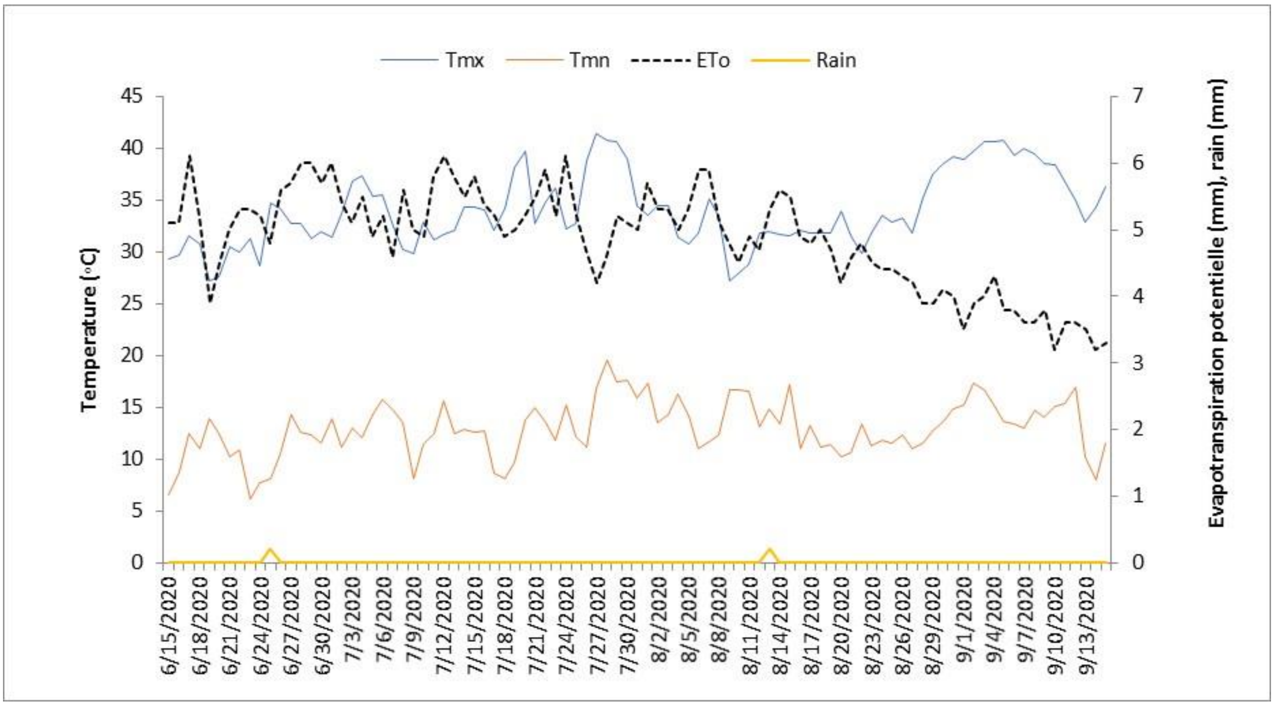


Figure 1. Daily precipitation (P, mm), maximum (Tmax, ºC) and minimum (Tmin, ºC) air temperature and potential evapotranspiration (ETo, mm day-1) recorded at the wetland site during the sampling period.

2.2. Characteristics of the constructed wetland

The designed wetland is a Free Water Surface (FWS) wetland established in 2013 by the Litani River Basin Management System (LRBMS), on a public-owned property, in the southern plains of the Bekaa Valley. The site is within Khirbet Kanafar Agricultural and

Extension Center of the Litani River Authority, and 10 km away from Lebanon's only remaining natural wetland "Ammiq Wetland" (UNESCO biosphere reserve), offering significant potential for environmental education, wetland habitat restoration, and other additional benefits. The constructed wetland area boundary is generally flat, with elevations ranging from 861.5 m above the sea level (a.s.l) at the top of the surrounding berms, to 860.0 m a.s.l in the shallow basins cultivated with *Phragmites australis* and *Sparganium erectum,* to 857.5-858.5 m a.s.l in the deep ponds (Figure 2). The wetland is approximately 3.5 ha in size, with an inner wet area (shallow basins and deep ponds) of 2.5 ha in size. It consists of three main parts:

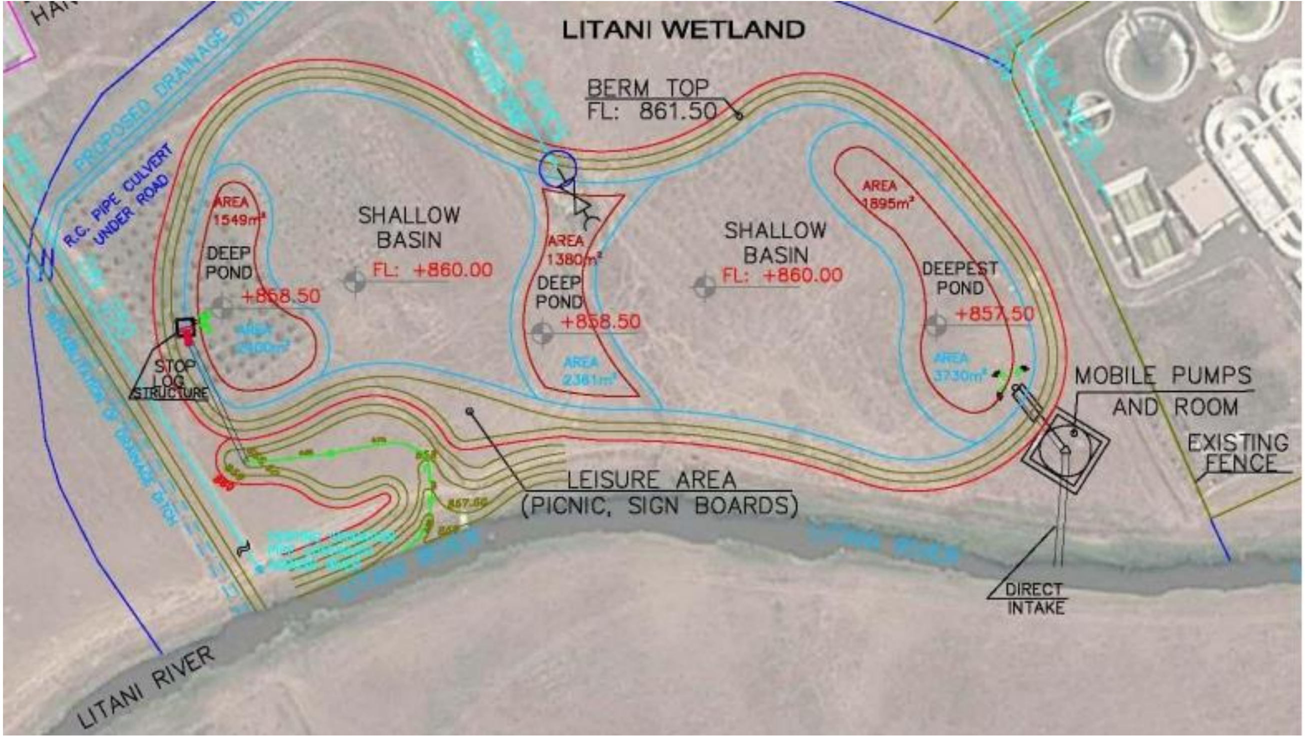


Figure 2. Overview of Litani River constructed wetland (LRBMS, 2012).

- Inlet structure, including piping and pumping station, constructed near the river bank, conveys inflow water from the river to the wetland. The pumping station consists of three electrical pumps, two of which are 60 l/s capacity each, and one 30 l/s capacity, impelling water directly from the bottom of the river, and conveying it into the wetland by means of a 16-inch galvanized iron pipe buried in the soil.
- An oval-shaped basin, 240 m average length (north-south) and 125 m average width (east-west), with an average outer area, including berms, of 35,000 m^2, and inner wet area of 25,000 m^2. The inner area consists of an alternation of three deep ponds (2-3 m deep) and two shallow areas (30-50 cm deep), with a ratio of 2:1 (2/3 deep ponds *versus* 1/3 shallow areas). The deep ponds were designed to promote mixing and uniform flow, and the shallow areas to promote growth of emergent wetland vegetation, which provides a biologically and chemically diverse environment, where much of the pollutant removal occurs.
- Adjustable outlet structure, made of a concrete weir, piping and outlet earth channel to convey the treated water back to the Litani River. The discharge channel features initial and terminal narrow stream channels whose banks are seeded with the same mix of plant species as the outside of the wetland berms. The bed of the discharge channel ends with a large rock weir structure. The discharge channel has been sized to accommodate a normal flow

of 20-60 l/s, based on expected outflows from the constructed wetland system. This corresponds to a channel width of approximately three to five meters with the exception of the widened, flattened central area.

The wetland has been designed to provide 5-day residency time for effluents, and treat as much as 100% of the River waters during the dry season. From the inlet pipe to the outlet pipe, water in the wetland spends 5-6 days for treatment purposes. This interval has been designed as the time period needed for water residency in the wetland, which corresponds to BOD five days (BOD_5). With a pumping capacity of 60 l/s, total daily pumped water 5184 m^3. With a storage capacity of 30,000 m^3, the residency time is then 30,000 m^3/5184 m^3 per day = 5.72 days. This water residency-time inside the wetland corresponds to BOD_5, or the amount of oxygen needed for the biological degradation of organic substances in water. From hydraulic point of view, a wetland is considered a water catchment surface, conceptualized as a 'Reservoir' with inflows (upstream contributions) and outflows (evaporation, infiltration, surface runoff and final drainage discharge. The storage within the wetland is conceptualized as the difference between inflows and outflows:

$$Q_{in} - Q_{out} = \frac{dV}{dt} \tag{1}$$

Where Q_{in} is inflow (m^3/s), Q_{out} outflow (m^3/s), V storage (m^3) and t time.

The constructed wetland has a dense coverage of emergent vegetation in its shallow zones with species adapted to constant flooding. *Phragmites australis* (common reed) and *Sparganium erectum* are native to Lebanon and a robust emergent marsh plant species that provides habitat for a variety of bird species. Moreover, they are commonly found near the site at Ammiq wetland, and are readily propagated by planting its rhizomes (root structures). In the deep, open water areas of the constructed wetland, both floating and submerged plants will serve to enhance biodiversity and the treatment effectiveness for certain pollutants. *Nymphaea alba*, or water lily are planted in the wetlands for this purpose.

3. Methodology used

For quality assessment, water samples were collected weekly during 10-week period from 21 June through 29 August 2020, from both the wetland inflow and outflow ponds. Water sampling method was the extendable sampling pole method, which is fully described in the 'Climate Change Indicators in the United States' (US-EPA, 2000 and 2016) and the 'Monitoring and Sampling Manual' of the Department of Environment and Science Government of the State of Queensland, Australia (DES, 2018). Samples were collected directly into the laboratory supplied containers at each water sampling date to reduce the risk of contamination. As described by US-EPA and DES, also UN-HABITAT (2008), direct sample collection is the preferred procedure if the environment is safe, *e.g.*, during low flow conditions, and sample bottles do not contain preservative. Collected water samples using the extendable sampling pole is recommended in isolated pools, so as not to disturb the substrate. A full description of the sampling method is available in the Monitoring and Sampling Manual of the Department of Environment and Science, State of Queensland (DES, 2018). Physicochemical and biological parameters were analyzed at the soil and water Laboratory of Kherbet Kanafar Agricultural and Extension Center of the Litani River Authority, 100 m apart from the constructed wetland. Physicochemical parameters included Total dissolved solids (TDS) and electrical conductivity (EC), which were determined by a tracer pocket tester (JENWAY 470 conductivity meter), pH by a portable pH meter (HI-83141), and nitrate (NO_3^-), nitrite (NO_2^-), phosphate

(PO_4^{3-}), and sulfate (SO_4^{2-}) by spectrometer (Thermo Helios Aquamate 2000E). Biological parameters included Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD_5), and Dissolved Oxygen (DO). The ratio of BOD_5/COD was then calculated. DO was measured directly on site by a dissolved oxygen meter (MILWAUKEE). COD was determined by using COD reagent tubes containing dichromate solution, 2 mL of water samples were added to the tubes, and then were placed in a heating reactor (VELP- Scientifica, Spain) at 150 °C for 2 hrs. After that, COD concentration was determined by a spectrometer (Thermo Helios Aquamate 2000E). For BOD_5 measurement, 250 ml of water sample were poured in glace bottles, a stirring bar, sodium hydroxide and nitrification inhibitor were added to the bottles that were closed by a VELP BOD sensor and placed in a BOD System 6–FTC 90–r Refrigerated incubator (VELP- Scientifica, Spain) for 5 days at 20 °C. Sampling was made regularly at weekly basis starting from the week of 21-27 June 2020, through the week of 23-29 August 2020. The influent samples were collected on Monday of each week of the sampling period, while the effluent samples were collected on Friday, to abide the 5-day interval of water time-residency between the two samplings days, so that the time needed for BOD_5 is respected.

3.1. Pollutants removal efficiency

The reduction efficiency (RE, in %) of the concentration of pollutants was assessed according to the International Water Association (Sperling, 2007) which proposed an equation for this intent (Singh, 2013). The efficiency of the wetland in terms of the removal percentage of pollutants (COD, BOD_5, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-}) was computed using the following formula:

$$\text{RE (\%)} = \frac{Ci-Ce}{Ci}\, x\, 100 \qquad (2)$$

Where, C_i and C_e are the average influent and effluent concentrations, respectively (in mg/L).

3.2. Statistical analyses

Statistical analyses of the physicochemical and biological parameters data obtained from water sampling at the wetland inflow and outflow during the study period were conducted by paired t-test using STATISTICA, Software version 10, which provides all the tools needed for statistical analysis (Hill and Lewicki, 2007; Statsoft Inc., 2011). The Student's t-test was used to detect how significant the differences between the two water sampling groups, inflow and outflow, are in terms of pollutant's concentration, and how the differences were repeatable for the whole sampling period.

4. Results and Discussion

4.1. Comparative influent and effluent water quality

Minimum, maximum and mean values of chemical oxygen demand (COD), dissolved oxygen (DO), biological oxygen demand (BOD_5), phosphate (PO_4^{3-}), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), water temperature (T), total dissolved solids (TDS), electrical conductivity (EC), and pH, measured on water samples from the wetland influent and effluent are found in Tables 1 and 2, respectively, alongside the Environmental limit values for surface water based on MoE Decision 8/1 of the Ministry of Environment (MOE, 2001) and the Lebanese Wastewater Reuse Guidelines (Food and Agricultural Organization of the United Nations, 2010 and 2016). In addition, Table 3 presents the results of standard deviation and p value of the removal efficiency of contaminants calculated according to Eqn. (2) on water samples from the two sites along the wetland.

Table 1. Minimum, maximum and mean value of water quality parameters collected from the wetland influent compared to recommended limits.

Parameters	**Wetland Influents**			**Environmental limit values for surface water based on MoE Decision 8/1 (MoE 2001)**	**Lebanese wastewater reuse guidelines (United Nations - Food and Agricultural Organization, 2010)**		
	Min	Max	Mean		Water Category I	Water Category II	Water Category III
Temperature (◦C)	21.0	27.5	25.1	30	-	-	-
EC (µs/m)	530.0	993.0	782.5	-	-	-	-
TDS (mg/L)	318.5	595.5	469.5	-	-	-	-
DO (mg/L)	2.0	5.6	3.9	-	-	-	-
pH	7.5	8.4	7.8	6 - 9	6 - 9	6 - 9	6 - 9
Phosphate (mg/L)	3.5	8.2	5.8	5	-	-	-
Nitrite (mg/L)	NQ*	0.35	0.1	-	-	-	-
Nitrate (mg/L)	NQ*	44.6	14.3	90	30	30	30
Sulfate (mg/L)	20.8	46.2	35.8	1000	-	-	-
BOD_5 (mg/L)	28.0	159.5	69.4	25	25	100	100
COD (mg/L)	59.0	377.5	262.1	125	125	250	250

* Not quantifiable.

Table 2. Minimum, maximum and mean value of water quality parameters collected from the wetland effluent compared to recommended limits.

Parameters	**Wetland effluents**			**Environmental limit values for surface water based on MoE Decision 8/1 (MoE 2001)**	**Lebanese wastewater reuse guidelines (United Nations - Food and Agricultural Organization, 2010)**		
	Min	Max	Mean		Water Category I	Water Category II	Water Category III
Temperature (◦C)	24.0	28.0	26.3	30	-	-	-
EC (µs/m)	561.3	1000.0	753.3	-	-	-	-
TDS (mg/L)	335.0	671.5	467.5	-	-	-	-

DO (mg/L)	4.0	6.9	5.3	-	-	-	-
pH	7.8	8.9	8.2	6-9	6 - 9	6 - 9	6 - 9
Phosphate (mg/L)	0.6	4.5	1.9	5	-	-	-
Nitrite (mg/L)	0.0	0.3	0.04	-	-	-	-
Nitrate (mg/L)	3.3	0.0001	0.37	90	30	30	30
Sulfate (mg/L)	15.6	181.1	57.9	1000	-	-	-
BOD$_5$ (mg/L)	5.4	99.8	31.7	25	25	100	100
COD (mg/L)	29.0	280.0	154.7	125	125	250	250

Table 3. Mean values of water quality parameters and variation percentages of the inflow and outflow of the constructed wetland of the Litani River.

Parameter	Number of samples	Inflow	Outflow	Removal Efficiency (%) *	*p* value
Temperature (◦C)	10	25.02 ± 2.68	26.29 ± 1.23	-5.06	0.072
EC (μs/m)	10	782.48 ± 127.1	753.31 ± 179.1	3.73	0.407
TDS (mg/L)	10	469.51 ± 75.9	467.51 ± 142.6	0.43	0.952
DO (mg/L)	10	3.96 ± 1.16	5.3 ± 1.05	-33.8	**0.032**
pH	10	7.82 ± 0.28	8.22 ± 0.35	-5.12	**0.006**
Phosphate (mg/L)	10	5.84 ± 1.49	1.90 ± 1.19	66.9	**0.000**
Nitrite (mg/L)	10	0.08 ± 0.1	0.04 ± 0.09	40.27	0.456
Nitrate (mg/L)	10	14.30± 20.44	0.37 ± 1.09	97.39	0.078
Sulfate (mg/L)	10	35.86 ± 8.26	57.99 ± 49.32	-61.67	0.202
BOD (mg/L)	10	69.45 ± 39.5	31.71 ± 26.8	54.3	**0.027**
COD (mg/L)	10	262.09 ± 130.3	154.72 ± 119.5	41	**0.012**

* Values were obtained by applying Equation (2).

4.2. Time course evolution of physicochemical parameters

4.2.1. EC, TDS, pH and T

Figures 3a and 3b illustrates time course evolution of electrical conductivity (EC) and total dissolved solids (TDS), respectively, during the sampling period from June through August 2020, in inflow and outflow samples. Electrical conductivity has been shown to decrease in the wetland outflow compared to the inflow. The value of EC of the influent ranged from 530 to 993 μSm^{-1}, with an average value of 782.5 μSm^{-1}, while the range in the effluent ranged from 561.3 to 1000 μSm^{-1}, with an average value of 753.3 μSm^{-1} (Tables 1 and 2). This slight decrease of the EC level at the downstream of the wetland may be due to the absorption of ions such as Ca^{2+} and Mg^{2+}, combined with sulfate and phosphate salts, by the wetland plants. Concerning TDS, the concentration of this indicator of water turbidity along the wetland did not mark a remarkable variation, as its concentration ranged from 469.5 mg·L^{-1} at the upstream to 467.5 mg·L^{-1} at the downstream. Natural water sources typically have a certain level of TDS, but human activity, such as irrigation, urbanization, can greatly raise the TDS level in surface water (Rosli and Seca, 2010). The same implies for EC, where large variations in conductivity may be due to either natural flooding, evaporation or man-made contamination which may be very harmful to the quality of the water (Mihir *et al.*, 2015). The World Health Organization (WHO) considers a TDS concentration less than 1000 mg L^{-1} as acceptable, and a range of 10 to 1000 µSm^{-1} for EC is acceptable in freshwater (WHO, 2006). Therefore, the results obtained in both the wetland inflow and outflow samples presented in Tables 1 and 2 satisfy the standards set by WHO.

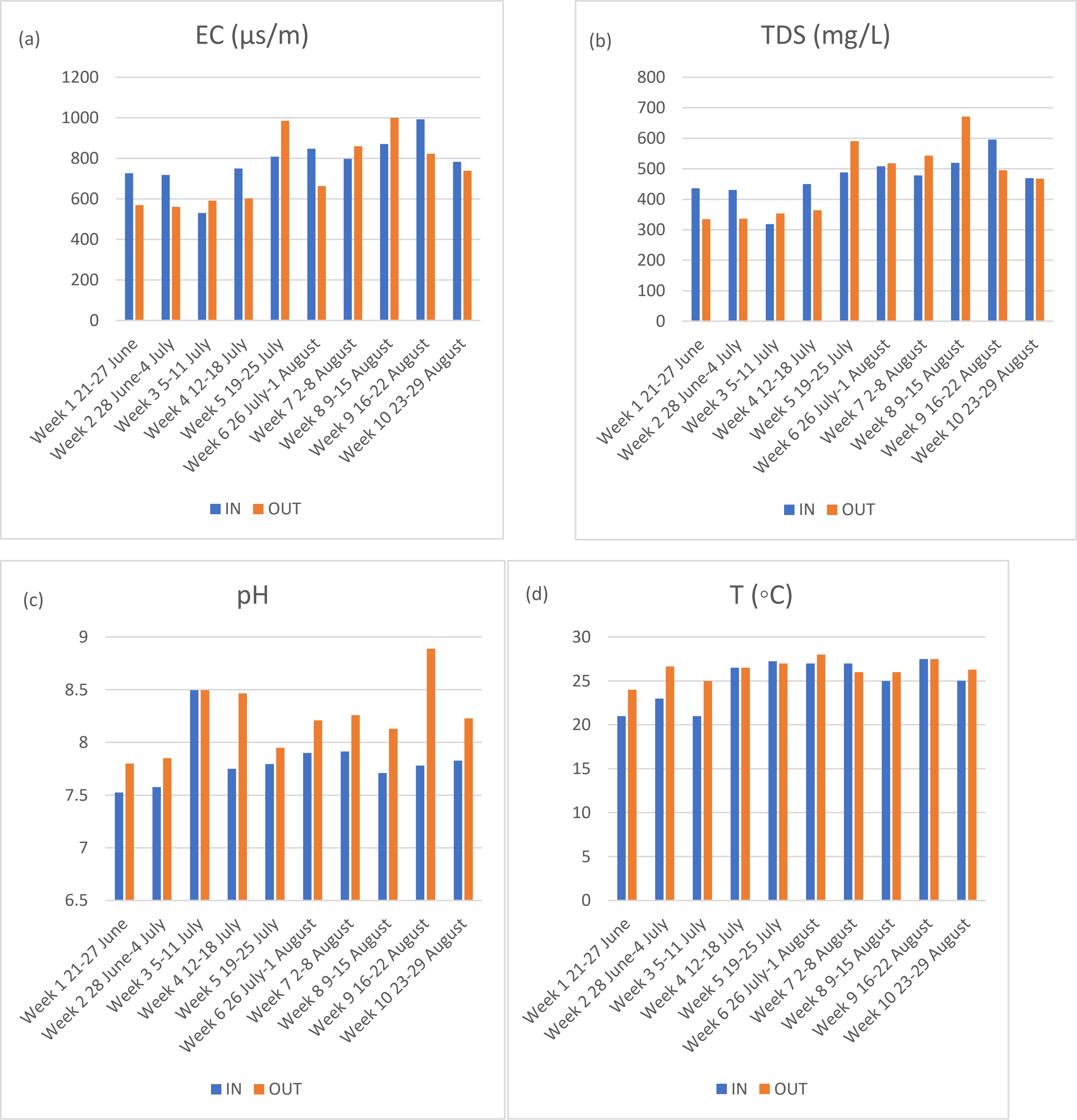


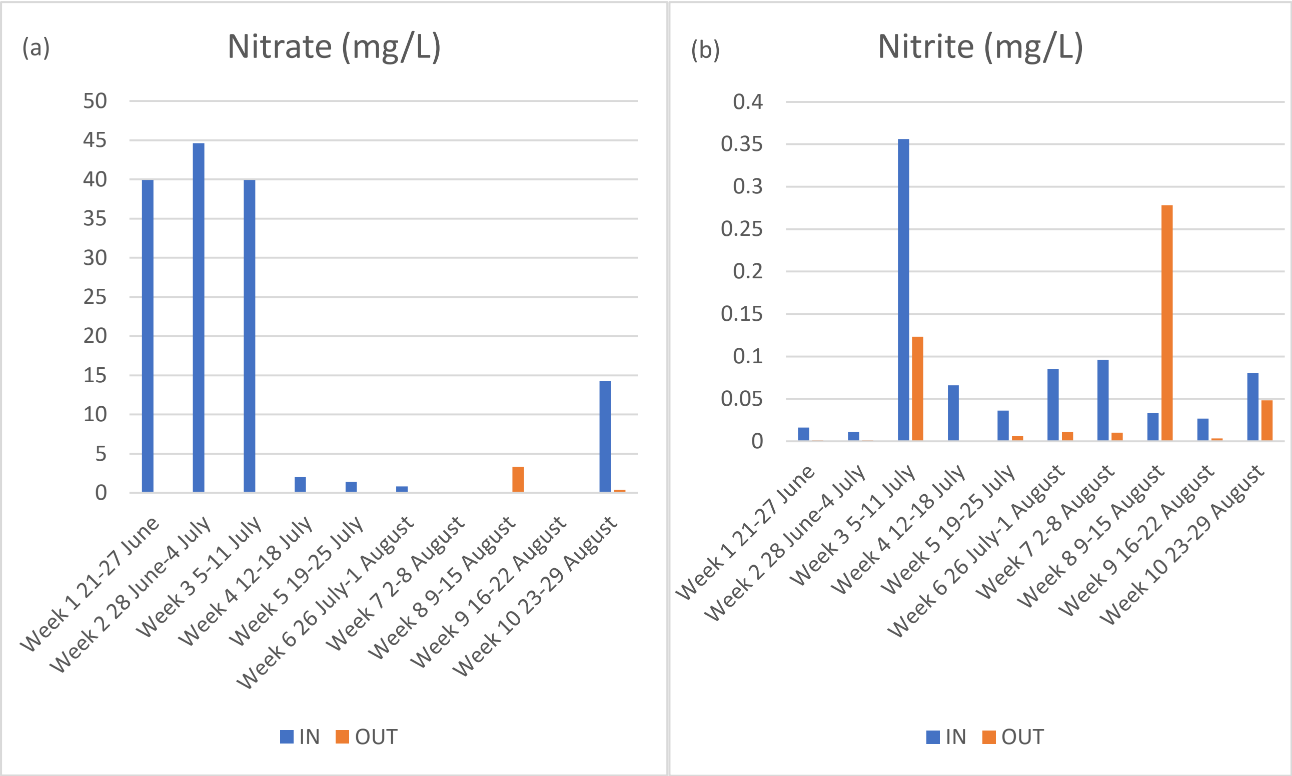
Figure 3. Time course evolution of electrical conductivity (3a), total dissolved solids (3b), pH (3c) water temperature (3d).

On the other hand, average pH along the wetland ranged from 7.8 at the inlet to 8.2 at the outlet (Figure 3c), and this range is within the environmental limits for surface water set by Decision 8/1 of the Ministry of Environment and FAO guidelines for wastewater reuse in Lebanon, while water temperature was found to steadily vary between the two sampling sites across the wetland from 25.0 ℃ to 26.3 ℃ (Figure 3d).

4.2.2. Nitrate and Nitrite

The evolution of nitrate and nitrite during the sampling period from the wetland inflow and outflow are presented in Figures 4a and 4b, respectively. Data shows a peak in the inflow concentration of nitrate at the beginning of the sampling period (Figure 4a). The mean level of nitrate (NO_3^-) in the downstream site of the wetland (0.37 mg L^{-1}) was much lower than the level obtained from the upstream site of the river, which is 14.3 mg L^{-1}, thus showing a high removal efficiency by the wetland. The high level of NO_3^- found at the upstream site of the wetland is mainly due to agricultural activities in the plains near the Litani River, for which overestimation of irrigation needs of sprinkler-irrigated potatoes may have led significant loads of nitrate by surface runoff to the river.

For nitrite, the concentrations along the wetland trail ranged from an average value of 0.35 mg L^{-1} at the inflow site to 0.30 mg·L^{-1} at the outflow site, with a removal efficiency of 40% ($P<0.456$). However, the values of NO_3^- and NO_2^- differed significantly among the different sampling dates, as marked in Figures 4a and 4b. This variation might be attributed to several components, as the Litani River effluents contain excessive amounts of nitrogen, as a result of the agricultural runoff and agro-industrial wastewater typical of the Litani River Basin.



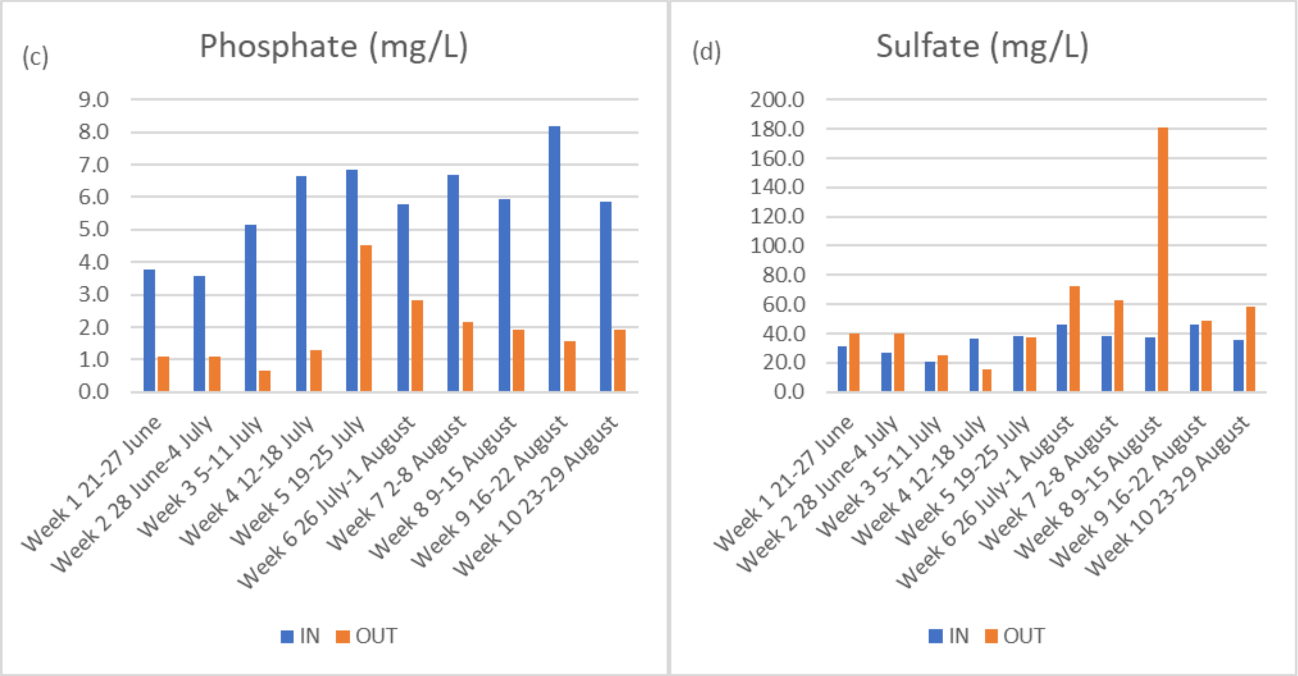


Figure 4. Time course evolution of Nitrate (4a), Nitrite (4b), Phosphates (4c) and Sulfates (4d).

Despite substantial variability in the degree and rate of nitrogen cycling under the influence of several variables, such as air temperature, level of dissolved oxygen, pH and other environmental conditions, the probable elimination mechanisms of nitrate and nitrite include plant and microbial assimilation, nitrification/denitrification phase and potential release of volatile ammonia gas to the atmosphere (Lee *et al.*, 2009).

The inflow NO_3^- concentrations (Table 1) fall within the range of the environmental limit values for surface water based on MoE Decision 8/1 (MoE, 2001). Furthermore, the levels of NO_2^- found in the inflow samples were found to be lower than the guideline levels for protecting sensitive aquatic animals during short-term exposures (Camargo and Alonso, 2006). On the other hand, outflow concentrations for both nitrate and nitrite remained relatively constant throughout the study, demonstrating high removal efficiency for nitrate (97.39 %, $P<0.078$) and nitrite (40%, $P<0.456$). This was expected given the strong dependency of microbial denitrification on temperature, which converts NO_2^-/NO_3^- to NO_x and N_2 gases (Kadlec and Wallace, 2009).

4.2.3. Phosphate

Figure 4c presents time course evolution of phosphate in water samples from both the wetland inflow and outflow during the sampling period. A significant decrease in phosphate concentration measured in the outflow was observed, compared to the inflow, with a removal efficiency of 67% (Table 3). Average concentration of phosphate along the wetland upstream and downstream ranged from 5.8 mg L^{-1} to 1.9 mg·L^{-1}, respectively (Tables 1 and 2). The level of phosphate in the influent at all sampling dates were higher than the discharge limit of 5 mg L^{-1} set by the Ministry of Environment (MoE, 2001). Indeed, the concentrations of phosphates at the downstream site of the wetland ranged from 0.6 to 4.5 mg·L^{-1}, and were higher as compared to the values obtained from the upstream site. This indicates that the river is in increasing level phosphate as the result of its direct discharge into its waters.

Phosphate in water is primarily due to the natural decomposition of rocks and stones, agricultural runoff, flooding, sewage and industrial waste. Phosphorous can increase the growth of algae and aquatic vegetation contributing to eutrophication of the aqueous environment (Sperling, 2007). On that note, Box et al. (2021) found that changes in the riverine environment, such as vegetation growth associated with altered flow regimes, increased sediment loads and eutrophication. In order to prevent eutrophication, the environmental limit value for phosphate concentration in surface water based on MoE Decision 8/1 (MoE, 2001) is < 5 mg/L. The constructed wetland treatment system has achieved effluent quality that satisfies these requirements in terms of PO_4^{3-} in all samples. The removal mechanism of phosphate occurs as a result of several physical, chemical and biological processes, such as (i) sedimentation of particulate phosphorous (organic and inorganic absorbed PO_4^{3-}), (ii) precipitation associated with mineral particles within the water column, (iii) sorption (adsorption/absorption) in wetland soils (fixation of phosphate by iron and aluminum in the soil), and (iv) biological uptake by plants and micro-organisms (Díaz *et al.,* 2013).

4.2.4. Sulfate

Figure 4d shows the variation of sulfate concentration in water samples from the wetland inflow and outflow during the sampling period. Unlike nitrite, nitrate and phosphate, an increase in the sulfate concentration has been reported at the two sampling sites from 35.8 mg L^{-1} at the inlet to 57.9 mg L^{-1} at the outlet, thus showing a removal efficiency of -61.67%, with no significant difference ($P>0.05$) (Table 3). Minimum and maximum concentrations of sulfate at the upstream of the wetland were 20.8 and 46.2 mg L^{-1}, while at the downstream they were 15.1 and 181.1 mg L^{-1}. Similar results have been detected by Gruyer *et al*. (2013) and Bezbaruah *et al*. (2003), where instead of decreasing, sulfate concentration have increased in the constructed wetland outflow. This phenomena might be due to the denitrifying bacteria activity, chemolytho-autotrophic, that use reduced sulfur compounds in the form of sulfide as an electron donor (Sierra-Alvarez *et al.*, 2007). This nitrate reduction and S-oxidizer bacteria will oxidize sulfide back to SO_4^{2-} during denitrification (Nelson *et al.,* 1986). The activity of these bacteria may explain the high removal of NO_3^- and the release of SO_4^{2-} in the wetlands (Sturman *et al.*, 2008). However, values obtained in the wetland inflow and outflow, are within the acceptable range of 1000 mg L^{-1} for surface water set by MoE Decision 8/1 (MoE, 2001) (Tables 1 and 2), while the proposed maximum allowable limit for sulfate of the National Standard for treated domestic wastewater reuse for irrigation is 500 mg L^{-1} (Margane and Steinel, 2011).

4.3. Time course evolution of the biological parameters

Figure 5 displays time course evolution of BOD_5, COD, the ratio of BOD_5/COD and DO in water samples from the wetland inflow and outflow. Results shows, that the wetland increased DO (average 34%) and reduced BOD_5 (average 54.3%) and COD (average 41%). Student's t-test analysis revealed that these changes were significant at $p<0.05$ (Table 3). The increasing of oxygen concentration in the wetland outflow was presumably due to the cascade input tubing and wind mixing in deep open-water areas as a result of passive aeration. Also, growth of oxygen provided by algae and submerged plants may also have contributed to these results (Todd *et al.,* 2009). COD and BOD_5 average values in the outflow samples were 154.7 mg L^{-1} and 31.7 mg L^{-1}, respectively, and were slightly above the range of the environmental limit values for surface water set by MoE Decision 8/1 (MoE, 2001). As such, the Lebanese surface water discharge limits refer COD<125 mg L^{-1} and BOD_5<25 mg L^{-1}. On the other hand, previous studies have proved that complete elimination of COD and BOD cannot be accomplished in constructed wetlands. In fact, the decomposition of plant residues and other naturally occurring organic materials in the wetland will produce BOD and COD (Lu *et al.,* 2016; Brix, 1997; Karathanasis *et al.,* 2003). Moreover, the comparison of the BOD and COD removal efficiency obtained with previous studies undertaken by Abi Saab et al. (2018) and Amacha *et al.* (2017) on the same wetland reveals that the removal rate of these parameters has decreased over the years. Therefore, it is worth to be noted that the implementation of an artificial aerated system is highly recommended in this case, as it contributes to increase DO concentration and therefore improve treatment performance, especially for BOD_5 and COD removal rate (Nivala *et al.,* 2020).

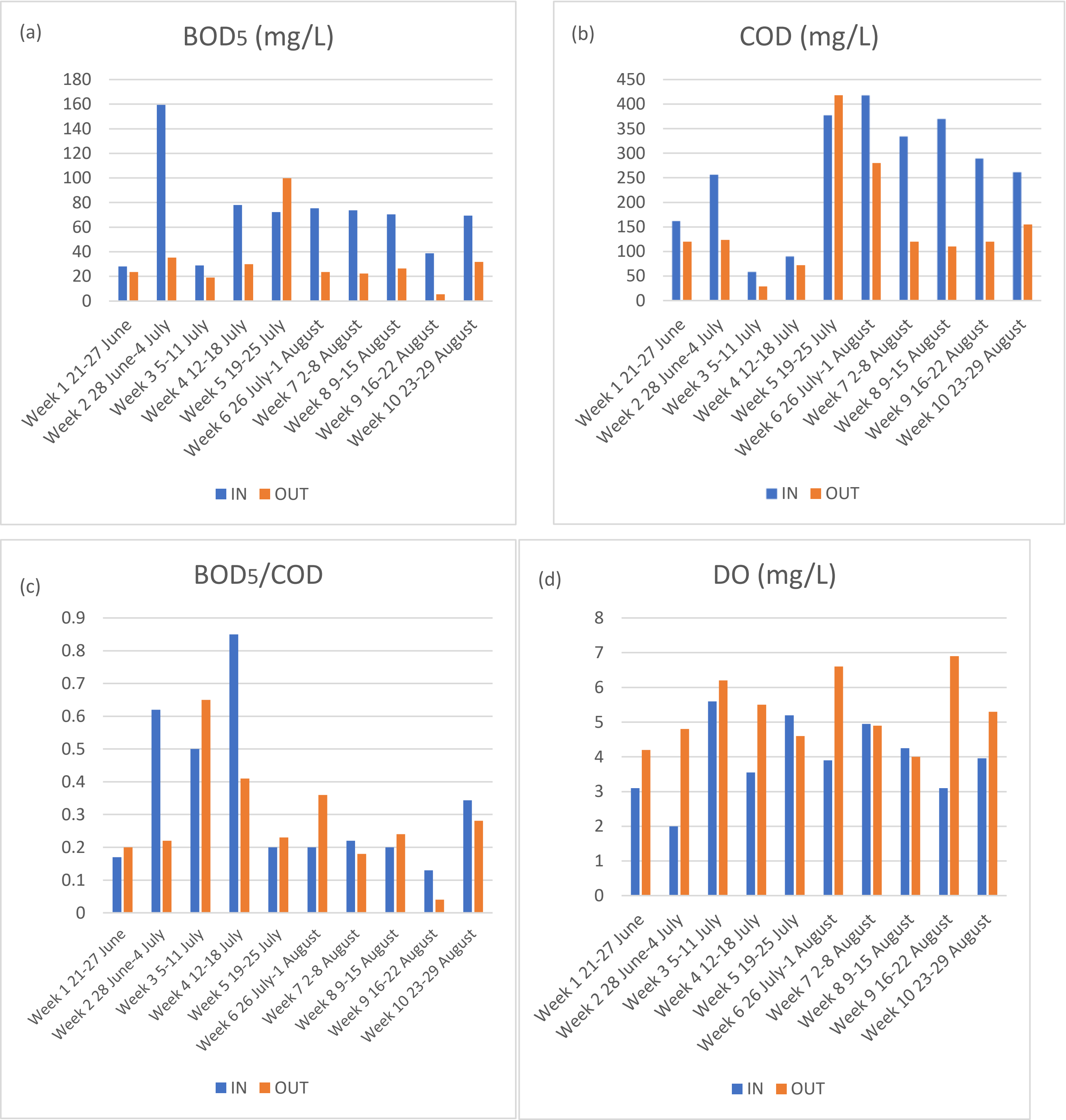


Figure 5. Time course evolution of biological oxugen demand (5a), chemical oxygen demand (5b), ratio of BOD5/COD (5c) and dissolved oxygen (5d).

Moreover, the calculated BOD$_5$/COD ratio (Figure 5c), from both the wetland inlet and outlet, ranged between 0.1 and 1.0 during the sampling period, indicating a presence of biodegradable material, meaning that the limit of organic matter can be decayed by microbes in natural and artificial treatment conditions (Samudro and Mangkoedihardjo, 2010).

The high levels of BOD$_5$ and COD observed in the effluent might be due to high amount of organic matter from domestic wastewater and agricultural inputs, and the processing of hides and skins of the poultry industry, as well as various chemicals sources, mainly paper and plastic industries, largely spread in the Litani River basin, which discharge their loads directly into the environment, thereby increasing the levels of BOD_5 and COD in the river waters. In the downstream site of the wetland, the levels of BOD_5 and COD were significantly lower than the upstream site, thus indicating the capability of the aquatic plants in de-polluting the river waters through the wetland biological process. Dong *et al*., (2016) showed the role of vegetation should not be ignored in the process of wastewater purification in constructed wetlands, as root oxygen released contributes to pollutant removal, alongside with other environmental and hydraulic factors within a constructed wetland.

Figure 5d illustrates the time course evolution of dissolved oxygen (DO) concentration of water samples from the wetland inflow and outflow. In the influent samples, average DO concentration was 3.96 mg L^{-1}, while in the effluent samples the average concentration raised to 5.30 mg L^{-1}. This increase in the concentration of the dissolved oxygen may be due to the oxygen released by the root systems of the wetland plants, as described by Wang *et al.* (2015) who demonstrated that plant roots improve oxygen conditions, thereby supporting the aerobic processes in constructed wetlands in flooded conditions. On the other hand, to investigate the effect of vegetation on microbial processes by increasing oxygen concentrations in the rhizosphere, BOD_5 and COD levels in the effluent returning to the rivers haven decreased, compared to the level obtained at the inflow gate of the wetland.

5. Conclusions

Results of this study showed the constructed wetland has successfully achieved high removal rate of nitrate (NO_3^-), nitrite (NO_2^-) and phosphate (PO_4^{3-}), but nut of sulfate (SO_4^{2-}), the one concentration was found to increase at the wetland downstream. Moreover, biological oxygen demand (BOD_5) and chemical oxygen demand (COD) reduction, along with the enrichment of the wetland waters at the downstream in dissolved oxygen (DO), resulted in improved water quality of effluents returning to the river. The rest of the parameters mean values, namely, electrical conductivity (EC), total dissolved solid (TDS), were within the recommended levels for natural surface water. Therefore, the constructed wetland has clearly contributed to reducing the level of pollution in the river, and improving its deteriorated water quality and ecologic viability.

The presence of *Phragmites australis* and *Sparganium erectum* has been shown a great impact on the removal of pollutants, due to which both organic and inorganic pollutants have been effectively treated by these two aquatic plants, making them suited for the treatment of mixed types of pollutants by multiple removal mechanisms, such phytoaccumulation, phytodegradation, phyto-transformation, phytovolatilization, and Phytoextraction, to clean up or detoxify pollutants (Karam et al., 2021; Ali et al., 2022).

A deeper comprehensive performance assessment of the constructed wetland system for de-polluting the waters of the Litani River, over a longer time period, is needed. . The current research shows the potential of wastewater treatment by means of a constructed wetland, as sustainable and cost effective technology, and the gained experience may be scalable to other sites and environments across the country.

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