

## Trophic status of water and level of pollutants as measures of efficiency of water treatment regime at Kafr El-Shinawy drinking-water treatment plant, Damietta

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### Abstract

This work aims to study the seasonal fluctuation in physicochemical characteristics, trophic status, and some chemical and biological pollutants influencing phytoplankton diversity, and water quality in raw and treated water at Kafr El-Shinawy drinking-water treatment plant, Damietta - Egypt seasonally during 2018. Phytoplankton distribution was affected by the trophic status of water, level of pollutants, and physicochemical treatment processes (coagulation, flocculation and sedimentation) of water. The predominance of phytoplankton species, especially *Aphanizomenon flos aquae* (Cyanophyta), *Gomphosphaeria lacustris* (Cyanophyta), *Microcystis aeruginosa* (Cyanophyta), *Nostoc punctiforme* (Cyanophyta), *Oscillatoria limnetica* (Cyanophyta), *Pediastrum simplex* (Chlorophyta), and *Melosira granulata* (Bacillariophyta) in treated water was much less than in raw water. Trihalomethanes (THMs) levels in treated waters were higher than in raw water. On the contrary, lower concentrations of heavy metals were recorded in treated water. Phytoplankton cells exhibited a bioaccumulation capacity for heavy metals especially Mn, Zn, and Fe in both raw and treated water. Intracellular levels of microcystins were lower (0.003 - 0.011  $\mu\text{g L}^{-1}$ ) whereas the extracellular levels were higher (1.00 - 2.01  $\mu\text{g L}^{-1}$ ) in treated water than raw water, and the former recorded the highest level in raw water during summer (1.3  $\mu\text{g L}^{-1}$ ). Hence, the levels of dissolved microcystins and THMs in treated water were higher than the allowable limit, especially during summer, the season of luxurious growth of *Microcystis* species.

**Keywords:** Drinking water; Microcystins; Phytoplankton; Physicochemical analyses; Trophic state; Water quality.

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### Introduction

Water pollution has become one of the most important environmental problems worldwide. Water treatment plants, mainly aims to improve the quality of water to make it appropriate for

drinking and human consumption. Water treatment involves some physical processes such as settling and filtration, chemical processes such as disinfection and coagulation, in addition to biological processes such as slow sand filtration. The nutrient state and physicochemical characteristics of water have an important role in the fluctuations of the phytoplankton community

(Kumar and Sahu 2012). One of the natural bio-indicators of water quality is phytoplankton occurrence and abundance due to their sensitivity, nutrient availability, and environmental conditions (e.g. water temperature and level of salinity (Manickam et al. 2012). Water quality can be assessed through both qualitative and quantitative monitoring of phytoplankton as they are the primary producers representing the first trophic level in the food chain. The occurrence of harmful cyanobacterial blooms in drinking water represents a serious threat to human and animal health worldwide. Cyanobacterial growth adversely affects odor, taste, and color of water as some of these cyanobacteria produce potent toxins called cyanotoxins. There are more than 100 identified variants of cyanotoxins that are commonly produced by the genera, *Microcystis*, *Anabaena*, *Aphanizomenon*, *Fischerella*, *Planktothrix*, *Anabaenopsis*, *Aphanocapsa*, *Cylindrospermopsis*, *Gleotrichia*, *Gomphosphaeria*, *Hapalosiphon*, *Nodularia*, *Nostoc*, *Oscillatoria*, *Phormidium*, *Pseudanabaena*, and *Synechococcus* (Chorus et al. 2000; Mohamed and Carmichael 2000; Vesterkvist et al. 2012; Paerl and Otten 2013). Although cyanobacterial cells can survive in water for long periods due to their ability to form thick-walled resting cells, the production of cyanotoxins is affected by several environmental conditions such as temperature, salinity, irradiance, and nutrients (Visser et al. 2016).

As a result of chlorine addition during treatment of drinking water, Trihalomethanes (THMs) including chloroform, dichlorobromomethane, and dibromochloromethane are produced as byproducts. THMs have short-term and long-term hazardous effects on human health. Essential serious problem arises from the increase in THMs during water transport by the water pipe network. The present work aims to study the effect of seasonal changes in physicochemical characteristics and the trophic status of water as well as the levels of pollutants, and microbial toxins on water quality and phytoplankton diversity at the input and output sites of a drinking-water treatment plant at Damietta.

## Material and methods

### *Sampling sites*

The study site was Kafr El-Shinawy drinking

water treatment plant that is situated at 31° 41.816' N and 31° 17.325' E. Water samples were collected seasonally (at three month intervals) in glass bottles from both the intake and output sites of Kafr El-Shinawy water treatment plant during 2018 to determine the phytoplankton composition in relation to physicochemical properties, trophic status and levels of pollutants of the native and treated water.

### *Physicochemical properties of water*

Temperature, turbidity, pH, and electrical conductivity (EC) were measured in the field. Temperature and pH of water samples were measured using the laboratory glass thermometer and a pH meter (model HI 8314, Hanna Instruments Ltd), respectively. Water turbidity was measured directly using Hanna instrument microprocessor turbidity meter. Water EC was measured using Jenway conductivity meter model 470. Total alkalinity, dissolved oxygen (DO), biochemical oxygen demand (BOD), silica, ammonia, nitrite, nitrate, total nitrogen, and orthophosphate were estimated in the laboratory according to APHA (1996). The total phosphorus in water samples was determined according to Grasshoff (1975).

The heavy metals, iron, manganese, zinc, copper, chromium, cobalt, cadmium, nickel, and lead in water samples was assayed in water by using a Perkin-Elmer – 2380 atomic absorption spectrophotometer as described by Sudharsan et al. (2012). All physicochemical analyses of water samples were triplicated.

Trihalomethane compounds in native and treated water were estimated according to U.S. EPA Method 551.1 (1995).

### *Phytoplankton composition*

Raw and treated water samples were collected seasonally for microscopic examination using a conical bolting nylon net of 0.069 mm mesh and a mouth diameter of 35 cm with the help of an outrigger canoe. The samples were filtered through fine mesh nylon and fixed in Lugol's solution and 4% formalin and algal cells were enumerated using an inverted light microscope (Sharma 2002). Phytoplankton identification was performed with reference to Botes (2003), Krammer and Lange-Bertalot (1986), and Tikkanen (1986) using an EXACTA+OPTECH GmbH light microscope (Model B3) - Code

K7161, Germany

#### *Extraction and estimation of intracellular and extracellular microcystins*

To determine the intracellular (particulate) and extracellular microcystins in raw and treated water, subsamples (250 ml) were filtered through a 0.45 µm cellulose filter (Whatman, UK). The filtrate was kept frozen to be used for extracellular (dissolved) microcystins. The residue with trapped cells was frozen, extracted twice in 80 % methanol and centrifuged at  $10,000 \times g$  for 10 min. The supernatants were pooled together, and the organic solvent was blown with sterilized air. The aqueous fraction remaining after removing the organic solvent was filtered through GF/C filter paper and stored frozen until analysis. Concentrations of extracellular and intracellular microcystins were determined by High-performance liquid chromatography (HPLC) (Column, Nucleosil 5 C 1 ~ (150 × 4.6 mm). Solvent system was: methanol - 0.05 M phosphate buffer (pH 3) (58:42). The flow rate was 1 ml/min. Detection was at 238 nm (**Harada et al. 1990**).

#### *Biochemical composition of the predominant phytoplankton in raw and treated waters.*

Proteins and lipids (% DW) of predominant species were estimated during winter and summer according to **AOAC (2000)** and carbohydrates were estimated spectrophotometry according to **Dubois et al. (1956)**.

Chlorophyll-a - as a measure of phytoplankton biomass - was determined spectrophotometrically in 90% acetone extract of raw and treated waters according to **Metzener et al. (1965)** using the following equations:

$$\text{Chlorophyll-a} = 11.78 (A_{663}) - 2.29 (A_{647})$$

Concentrations of the heavy metals (Fe, Mn, Zn, Cu, Cr, Co, Cd, Ni, and Pb) in phytoplankton cells from raw and treated water were estimated seasonally by using a Perkin-Elmer – 2380 atomic absorption spectrophotometer as described by **Sudharsan et al. (2012)**.

#### *Statistical analyses*

Data were analyzed using two-way ANOVA, followed by mean separation according to the

Duncan's multiple range test at  $P < 0.05$ . Two-tailed Pearson product-moment correlation was performed to examine the relationship between all physicochemical parameters, phytoplankton diversity, and microcystin concentrations. Statistical analysis was done using SPSS version 22.

## Results

### *Physicochemical properties of water*

The effect of the main factors (water treatment and season) and their interaction was significant ( $P < 0.05$ ) on most physicochemical parameters of water at Kafr El-Shinawy treatment plant as shown in Table 1.

Table 2 summarizes the physico-chemical characteristics of the raw and treated water at Kafr El-Shinawy treatment plant during 2018. The results showed significant variations in temperatures of both raw and treated water ranging from  $17.95 \pm 2.48$  °C during winter to  $31.0 \pm 2.44$  °C during summer, with optimum for phytoplankton growth during autumn and spring (25.0 - 26.0 °C). Turbidity recorded higher values in raw water than that in treated water with lower values in both raw and treated water during winter. Water pH value was generally in the alkaline side and ranged between 7.76 and 8.51 with lower values in treated than raw water. In both raw and treated water, EC was highest in summer (Table 2). Throughout the four seasons, raw water recorded higher alkalinity compared with treated water. Dissolved Oxygen (DO) showed higher concentrations in treated than raw water 6.67 and 7.57 mg L<sup>-1</sup>, respectively (Table 2). It is also observed that DO in raw water increased by decreasing water temperature. On the contrary, BOD of both raw and treated water increased with increasing water temperature. Silica concentrations were higher in treated than raw water and approached their maxima during winter. Concentrations of both ortho-P and total-P were higher in raw water than that in treated water, with limited seasonal variability.

The effect of the main factors (water treatment and season) and their interaction on heavy metals concentrations of water was significant (Table 3).

**Table 1.** Two- way ANOVA showing the effect of the main factors (water treatment and season) and their interaction on physicochemical parameters of water at Kafr El-Shinawy drinking-water treatment plant – Damietta.

Variable and treatment of variation	df	F	P	Variable and treatment of variation	df	F	P
<b>Temperature</b>				<b>Silica</b>			
Water treatment	1	1216.89	0.000	Water treatment	1	381.045	0.000
Season	3	23956.6	0.000	Season	3	576.301	0.000
Water treatment × season	3	75.704	0.000	Water treatment × season	3	208.962	0.000
<b>Turbidity</b>				<b>Ammonia</b>			
Water treatment	1	16419.6	0.000	Water treatment	1	13268.6	0.000
Season	3	306.935	0.000	Season	3	79.881	0.000
Water treatment × season	3	113.231	0.000	Water treatment × season	3	79.881	0.000
<b>pH</b>				<b>Nitrite</b>			
Water treatment	1	108.926	0.000	Water treatment	1	1216.00	0.000
Season	3	30.894	0.000	Season	3	59.368	0.000
Water treatment × season	3	1.6570	0.216	Water treatment × season	3	59.368	0.000
<b>Conductivity</b>				<b>Nitrate</b>			
Water treatment	1	0.1560	0.698	Water treatment	1	9130.08	0.000
Season	3	365.173	0.000	Season	3	20.306	0.000
Water treatment × season	3	0.7250	0.552	Water treatment × season	3	20.306	0.000
<b>Total alkalinity</b>				<b>Total-N</b>			
Water treatment	1	940.612	0.000	Water treatment	1	92852.0	0.000
Season	3	1681.57	0.000	Season	3	22.522	0.000
Water treatment × season	3	9.2190	0.001	Water treatment × season	3	22.522	0.000
<b>DO</b>				<b>Ortho-P</b>			
Water treatment	1	1315.09	0.000	Water treatment	1	13572.3	0.000
Season	3	181.031	0.000	Season	3	4.250	0.022
Water treatment × season	3	134.635	0.000	Water treatment × season	3	2.250	0.122
<b>BOD</b>				<b>Total-P</b>			
Water treatment	1	13489.7	0.000	Water treatment	1	3864.39	0.000
Season	3	988.937	0.000	Season	3	6.556	0.004
Water treatment × season	3	224.678	0.000	Water treatment × season	3	9.912	0.001

The effect of water treatment was stronger (with higher F ratio) than that of season for all determined heavy metals that decreased in treated water than that in raw water. Levels of all the measured heavy metals especially Mn, Zn, and Fe were higher in phytoplankton cells than that in raw water and treated water (Table 4). Correlation between heavy metals and other physicochemical parameters of both raw and treated water is presented in Table 5.

The effect of the main factors (water treatment and season) and their interaction on THMs in raw and treated water was significant ( $P < 0.05$ ) as shown in Table 6. The effect of water treatment was stronger (with higher F ratio) than that of a season for all tested THMs. The present results showed that high values of THMs in water were during summer, whereas low concentrations were during

winter, with an increase in treated water. The water treatment exhibited its maximum efficiency in winter. THMs specification shows that their presence in both raw and treated water was in the order: chloroform > dichlorobromomethane > dibromochloromethane.

As shown in Fig. 1, chloroform concentrations in raw and treated water was in the range of 2.79 – 17.43 mg L<sup>-1</sup> and 18.42 – 69.75 mg L<sup>-1</sup>, respectively. The results showed significant variations in dichlorobromomethane in raw and treated water ( $P < 0.05$ ) ranging from 1.52 mg L<sup>-1</sup> (in raw water during winter) to 48.36 mg L<sup>-1</sup> (in treated water during summer). The maximum concentration of dibromochloromethane was 25.98 mg L<sup>-1</sup> in treated water during summer. Moreover, THMs correlated negatively with nutrients in both the native and treated water.

**Table 2.** Seasonally variations in physicochemical characteristics (Mean  $\pm$  SE, n = 3) of raw and treated waters of Kafr El-Shinawy drinking-water treatment plant – Damietta.

Water characteristic	Water treatment	Season			
		Winter	Spring	Summer	Autumn
Temperature ( $^{\circ}$ C)	Raw water	17.95 $\pm$ 2.48 <sup>b</sup>	25.5 $\pm$ 2.54 <sup>cd</sup>	31.0 $\pm$ 2.44 <sup>g</sup>	26.0 $\pm$ 2.69 <sup>e</sup>
	Treated water	16.1 $\pm$ 1.59 <sup>a</sup>	25.0 $\pm$ 2.58 <sup>c</sup>	29.4 $\pm$ 1.79 <sup>f</sup>	25.1 $\pm$ 2.51 <sup>c</sup>
Turbidity (NTU)	Raw water	4.30 $\pm$ 0.38 <sup>d</sup>	6.01 $\pm$ 0.57 <sup>f</sup>	6.00 $\pm$ 0.57 <sup>f</sup>	5.04 $\pm$ 0.50 <sup>e</sup>
	Treated water	1.27 $\pm$ 0.12 <sup>a</sup>	1.50 $\pm$ 0.15 <sup>b</sup>	1.86 $\pm$ 0.18 <sup>c</sup>	1.34 $\pm$ 0.13 <sup>a</sup>
pH	Raw water	7.76 $\pm$ 0.91 <sup>d</sup>	8.12 $\pm$ 0.81 <sup>g</sup>	8.51 $\pm$ 0.75 <sup>h</sup>	7.90 $\pm$ 0.79 <sup>ef</sup>
	Treated water	7.34 $\pm$ 0.72 <sup>a</sup>	7.58 $\pm$ 0.75 <sup>bc</sup>	7.86 $\pm$ 0.78 <sup>e</sup>	7.53 $\pm$ 0.74 <sup>b</sup>
Conductivity (dS m <sup>-1</sup> )	Raw water	540.0 $\pm$ 35.0 <sup>a</sup>	600.7 $\pm$ 60.1 <sup>e</sup>	750.0 $\pm$ 73.3 <sup>f</sup>	550.3 $\pm$ 34.7 <sup>b</sup>
	Treated water	550.0 $\pm$ 51.1 <sup>b</sup>	590.3 $\pm$ 58.1 <sup>d</sup>	755.0 $\pm$ 73.9 <sup>g</sup>	554.0 $\pm$ 54.5 <sup>bc</sup>
Total Alk. (mg L <sup>-1</sup> )	Raw water	147.0 $\pm$ 13.8 <sup>c</sup>	162.0 $\pm$ 16.0 <sup>e</sup>	174.0 $\pm$ 17.3 <sup>g</sup>	147.3 $\pm$ 14.4 <sup>bc</sup>
	Treated water	136.1 $\pm$ 13.1 <sup>a</sup>	151.3 $\pm$ 14.8 <sup>d</sup>	164.7 $\pm$ 16.3 <sup>ef</sup>	140.3 $\pm$ 14.0 <sup>b</sup>
DO (mg L <sup>-1</sup> )	Raw water	6.83 $\pm$ 0.61 <sup>e</sup>	6.09 $\pm$ 0.58 <sup>b</sup>	5.10 $\pm$ 0.50 <sup>a</sup>	6.20 $\pm$ 0.59 <sup>c</sup>
	Treated water	7.10 $\pm$ 0.71 <sup>g</sup>	7.57 $\pm$ 0.74 <sup>h</sup>	6.67 $\pm$ 0.67 <sup>d</sup>	7.00 $\pm$ 0.64 <sup>f</sup>
BOD (mg L <sup>-1</sup> )	Raw water	2.71 $\pm$ 0.27 <sup>e</sup>	2.99 $\pm$ 0.29 <sup>f</sup>	3.81 $\pm$ 0.32 <sup>h</sup>	3.50 $\pm$ 0.35 <sup>g</sup>
	Treated water	1.51 $\pm$ 0.15 <sup>a</sup>	2.00 $\pm$ 0.18 <sup>c</sup>	2.23 $\pm$ 0.22 <sup>d</sup>	1.71 $\pm$ 0.17 <sup>b</sup>
Silica (mg L <sup>-1</sup> )	Raw water	2.51 $\pm$ 0.52 <sup>c</sup>	3.10 $\pm$ 0.30 <sup>d</sup>	3.60 $\pm$ 0.31 <sup>f</sup>	2.23 $\pm$ 0.22 <sup>a</sup>
	Treated water	4.00 $\pm$ 0.34 <sup>h</sup>	3.30 $\pm$ 0.32 <sup>e</sup>	3.67 $\pm$ 0.35 <sup>fg</sup>	2.33 $\pm$ 0.22 <sup>b</sup>
Ammonia (mg L <sup>-1</sup> )	Raw water	0.42 $\pm$ 0.038 <sup>f</sup>	0.35 $\pm$ 0.034 <sup>d</sup>	0.28 $\pm$ 0.021 <sup>c</sup>	0.39 $\pm$ 0.038 <sup>e</sup>
	Treated water	0.02 $\pm$ 0.001 <sup>ab</sup>	0.01 $\pm$ 0.001 <sup>a</sup>	0.01 $\pm$ 0.001 <sup>a</sup>	0.01 $\pm$ 0.001 <sup>a</sup>
Nitrite (mg L <sup>-1</sup> )	Raw water	0.20 $\pm$ 0.015 <sup>g</sup>	0.09 $\pm$ 0.008 <sup>de</sup>	0.08 $\pm$ 0.007 <sup>d</sup>	0.12 $\pm$ 0.011 <sup>f</sup>
	Treated water	0.05 $\pm$ 0.003 <sup>c</sup>	0.01 $\pm$ 0.002 <sup>a</sup>	0.01 $\pm$ 0.002 <sup>a</sup>	0.03 $\pm$ 0.004 <sup>b</sup>
Nitrate (mg L <sup>-1</sup> )	Raw water	0.31 $\pm$ 0.031 <sup>h</sup>	0.27 $\pm$ 0.026 <sup>g</sup>	0.24 $\pm$ 0.023 <sup>e</sup>	0.28 $\pm$ 0.028 <sup>f</sup>
	Treated water	0.20 $\pm$ 0.003 <sup>d</sup>	0.15 $\pm$ 0.002 <sup>c</sup>	0.09 $\pm$ 0.002 <sup>ab</sup>	0.08 $\pm$ 0.002 <sup>a</sup>
Total -N (mg L <sup>-1</sup> )	Raw water	2.72 $\pm$ 0.270 <sup>d</sup>	2.74 $\pm$ 0.272 <sup>de</sup>	2.91 $\pm$ 0.223 <sup>g</sup>	2.76 $\pm$ 0.275 <sup>def</sup>
	Treated water	0.19 $\pm$ 0.009 <sup>c</sup>	0.11 $\pm$ 0.003 <sup>a</sup>	0.20 $\pm$ 0.004 <sup>c</sup>	0.15 $\pm$ 0.004 <sup>b</sup>
Ortho - P (mg L <sup>-1</sup> )	Raw water	0.021 $\pm$ 0.005 <sup>cd</sup>	0.020 $\pm$ 0.002 <sup>c</sup>	0.020 $\pm$ 0.002 <sup>c</sup>	0.020 $\pm$ 0.002 <sup>c</sup>
	Treated water	0.006 $\pm$ 0.0001 <sup>ab</sup>	0.005 $\pm$ 0.0001 <sup>a</sup>	0.006 $\pm$ 0.0001 <sup>ab</sup>	0.006 $\pm$ 0.0001 <sup>ab</sup>
Total - P (mg L <sup>-1</sup> )	Raw water	1.70 $\pm$ 0.13 <sup>d</sup>	1.82 $\pm$ 0.178 <sup>ef</sup>	1.99 $\pm$ 0.21 <sup>g</sup>	1.80 $\pm$ 0.22 <sup>e</sup>
	Treated water	0.50 $\pm$ 0.056 <sup>b</sup>	0.50 $\pm$ 0.055 <sup>b</sup>	0.52 $\pm$ 0.057 <sup>bc</sup>	0.45 $\pm$ 0.050 <sup>a</sup>

**Table 3.** Two- way ANOVA showing the effect of the main factors (water treatment and season) and their interaction on heavy metals concentrations of raw and treated waters at Kafr El-Shinawy drinking-water treatment plant – Damietta.

Variable and treatment of variation	df	F	P	Variable and treatment of variation	df	F	P
<b>Fe</b>				<b>Co</b>			
Water treatment	1	94848.0	0.000	Water treatment	1	1366561	0.000
Season	3	118.327	0.000	Season	3	84521.0	0.000
Water treatment $\times$ season	3	130.171	0.000	Water treatment $\times$ season	3	70721.0	0.000
<b>Mn</b>				<b>Cd</b>			
Water treatment	1	3910.10	0.000	Water treatment	1	2726112	0.000
Season	3	51.391	0.000	Season	3	12703.2	0.000
Water treatment $\times$ season	3	9.1420	0.001	Water treatment $\times$ season	3	12503.2	0.000
<b>Zn</b>				<b>Ni</b>			
Water treatment	1	41538.8	0.000	Water treatment	1	84807.7	0.000
Season	3	97.835	0.000	Season	3	2718.66	0.000
Water treatment $\times$ season	3	365.482	0.000	Water treatment $\times$ season	3	2009.74	0.000
<b>Cu</b>				<b>Pb</b>			
Water treatment	1	3087049	0.000	Water treatment	1	2910436	0.000
Season	3	135273	0.000	Season	3	5660.00	0.000
Water treatment $\times$ season	3	75513.0	0.000	Water treatment $\times$ season	3	6620.00	0.000
<b>Cr</b>							
Water treatment	1	15987.0	0.000				
Season	3	677.667	0.000				
Water treatment $\times$ season	3	197.667	0.000				

**Table 4.** Seasonally variations in concentrations of some heavy metals (Mean  $\pm$  SE, n = 3) in raw and treated waters, and phytoplankton cells Kafr El-Shinawy drinking-water treatment plant – Damietta.

Heavy metal	Treatment	Season			
		Winter	Spring	Summer	Autumn
<b>Water</b>					
Fe (mg L <sup>-1</sup> )	Raw	0.097 $\pm$ 0.0048 <sup>de</sup>	0.120 $\pm$ 0.0060 <sup>g</sup>	0.100 $\pm$ 0.0050 <sup>def</sup>	0.094 $\pm$ 0.0047 <sup>d</sup>
	Treated	0.060 $\pm$ 0.0030 <sup>c</sup>	0.051 $\pm$ 0.0026 <sup>b</sup>	0.040 $\pm$ 0.0020 <sup>a</sup>	0.060 $\pm$ 0.0030 <sup>c</sup>
Mn (mg L <sup>-1</sup> )	Raw	0.067 $\pm$ 0.0034 <sup>g</sup>	0.057 $\pm$ 0.0029 <sup>e</sup>	0.070 $\pm$ 0.0035 <sup>h</sup>	0.061 $\pm$ 0.0031 <sup>f</sup>
	Treated	0.014 $\pm$ 0.0007 <sup>ab</sup>	0.020 $\pm$ 0.0010 <sup>c</sup>	0.030 $\pm$ 0.0015 <sup>d</sup>	0.010 $\pm$ 0.0005 <sup>a</sup>
Zn (mg L <sup>-1</sup> )	Raw	0.037 $\pm$ 0.0019 <sup>g</sup>	0.032 $\pm$ 0.0016 <sup>def</sup>	0.030 $\pm$ 0.0015 <sup>de</sup>	0.029 $\pm$ 0.0015 <sup>d</sup>
	Treated	0.020 $\pm$ 0.0010 <sup>c</sup>	0.016 $\pm$ 0.0008 <sup>ab</sup>	0.020 $\pm$ 0.0010 <sup>c</sup>	0.015 $\pm$ 0.0008 <sup>a</sup>
Cu (mg L <sup>-1</sup> )	Raw	0.021 $\pm$ 0.0011 <sup>d</sup>	0.025 $\pm$ 0.0025 <sup>ef</sup>	0.024 $\pm$ 0.0012 <sup>e</sup>	0.027 $\pm$ 0.0014 <sup>g</sup>
	Treated	0.004 $\pm$ 0.0002 <sup>a</sup>	0.004 $\pm$ 0.0002 <sup>a</sup>	0.010 $\pm$ 0.0005 <sup>c</sup>	0.005 $\pm$ 0.0003 <sup>ab</sup>
Cr (mg L <sup>-1</sup> )	Raw	0.005 $\pm$ 0.0003 <sup>c</sup>	0.005 $\pm$ 0.0005 <sup>c</sup>	0.005 $\pm$ 0.0003 <sup>c</sup>	0.006 $\pm$ 0.0003 <sup>d</sup>
	Treated	0.002 $\pm$ 0.0001 <sup>a</sup>	0.002 $\pm$ 0.0001 <sup>a</sup>	0.002 $\pm$ 0.0001 <sup>a</sup>	0.003 $\pm$ 0.0002 <sup>b</sup>
Co (mg L <sup>-1</sup> )	Raw	0.020 $\pm$ 0.0010 <sup>d</sup>	0.020 $\pm$ 0.0020 <sup>d</sup>	0.024 $\pm$ 0.0012 <sup>e</sup>	0.020 $\pm$ 0.0010 <sup>d</sup>
	Treated	0.009 $\pm$ 0.0005 <sup>ab</sup>	0.010 $\pm$ 0.0005 <sup>c</sup>	0.010 $\pm$ 0.0005 <sup>c</sup>	0.008 $\pm$ 0.0004 <sup>a</sup>
Cd (mg L <sup>-1</sup> )	Raw	0.040 $\pm$ 0.0020 <sup>f</sup>	0.030 $\pm$ 0.0030 <sup>e</sup>	0.026 $\pm$ 0.0013 <sup>d</sup>	0.022 $\pm$ 0.0011 <sup>c</sup>
	Treated	0.003 $\pm$ 0.0002 <sup>a</sup>	0.004 $\pm$ 0.0002 <sup>ab</sup>	0.004 $\pm$ 0.0002 <sup>ab</sup>	0.003 $\pm$ 0.0002 <sup>a</sup>
Ni (mg L <sup>-1</sup> )	Raw	0.018 $\pm$ 0.0009 <sup>e</sup>	0.021 $\pm$ 0.0011 <sup>fg</sup>	0.022 $\pm$ 0.0022 <sup>h</sup>	0.020 $\pm$ 0.0020 <sup>f</sup>
	Treated	0.008 $\pm$ 0.0004 <sup>c</sup>	0.007 $\pm$ 0.0004 <sup>ab</sup>	0.006 $\pm$ 0.0003 <sup>a</sup>	0.013 $\pm$ 0.0007 <sup>d</sup>
Pb (mg L <sup>-1</sup> )	Raw	0.021 $\pm$ 0.0011 <sup>d</sup>	0.022 $\pm$ 0.0011 <sup>de</sup>	0.022 $\pm$ 0.0022 <sup>de</sup>	0.019 $\pm$ 0.0019 <sup>c</sup>
	Treated	0.005 $\pm$ 0.0003 <sup>ab</sup>	0.004 $\pm$ 0.0002 <sup>a</sup>	0.004 $\pm$ 0.0002 <sup>a</sup>	0.004 $\pm$ 0.0002 <sup>a</sup>
<b>Phytoplankton</b>					
Fe (mg L <sup>-1</sup> )	Raw	0.910 $\pm$ 0.0455 <sup>d</sup>	1.020 $\pm$ 0.0510 <sup>g</sup>	0.980 $\pm$ 0.0490 <sup>f</sup>	0.950 $\pm$ 0.0475 <sup>e</sup>
	Treated	0.320 $\pm$ 0.0160 <sup>c</sup>	0.320 $\pm$ 0.0160 <sup>c</sup>	0.250 $\pm$ 0.0125 <sup>a</sup>	0.270 $\pm$ 0.0135 <sup>ab</sup>
Mn (mg L <sup>-1</sup> )	Raw	0.550 $\pm$ 0.0275 <sup>e</sup>	0.450 $\pm$ 0.0225 <sup>d</sup>	0.600 $\pm$ 0.0180 <sup>g</sup>	0.560 $\pm$ 0.0280 <sup>ef</sup>
	Treated	0.090 $\pm$ 0.0500 <sup>b</sup>	0.090 $\pm$ 0.0045 <sup>b</sup>	0.160 $\pm$ 0.0080 <sup>c</sup>	0.076 $\pm$ 0.0038 <sup>a</sup>
Zn (mg L <sup>-1</sup> )	Raw	0.350 $\pm$ 0.0175 <sup>g</sup>	0.300 $\pm$ 0.0150 <sup>f</sup>	0.280 $\pm$ 0.0140 <sup>e</sup>	0.280 $\pm$ 0.0140 <sup>e</sup>
	Treated	0.050 $\pm$ 0.0045 <sup>ab</sup>	0.045 $\pm$ 0.0023 <sup>a</sup>	0.080 $\pm$ 0.0040 <sup>d</sup>	0.070 $\pm$ 0.0035 <sup>c</sup>
Cu (mg L <sup>-1</sup> )	Raw	0.110 $\pm$ 0.0055 <sup>e</sup>	0.160 $\pm$ 0.0160 <sup>f</sup>	0.200 $\pm$ 0.0100 <sup>g</sup>	0.230 $\pm$ 0.0115 <sup>h</sup>
	Treated	0.020 $\pm$ 0.0025 <sup>b</sup>	0.016 $\pm$ 0.0008 <sup>a</sup>	0.050 $\pm$ 0.0025 <sup>d</sup>	0.028 $\pm$ 0.0014 <sup>c</sup>
Cr (mg L <sup>-1</sup> )	Raw	0.025 $\pm$ 0.0013 <sup>d</sup>	0.030 $\pm$ 0.0030 <sup>e</sup>	0.033 $\pm$ 0.0017 <sup>f</sup>	0.036 $\pm$ 0.0018 <sup>g</sup>
	Treated	0.012 $\pm$ 0.0010 <sup>ab</sup>	0.010 $\pm$ 0.0005 <sup>a</sup>	0.010 $\pm$ 0.0005 <sup>a</sup>	0.018 $\pm$ 0.0009 <sup>c</sup>
Co (mg L <sup>-1</sup> )	Raw	0.120 $\pm$ 0.0060 <sup>c</sup>	0.120 $\pm$ 0.0120 <sup>c</sup>	0.210 $\pm$ 0.0105 <sup>c</sup>	0.180 $\pm$ 0.0090 <sup>d</sup>
	Treated	0.050 $\pm$ 0.0006 <sup>a</sup>	0.070 $\pm$ 0.0035 <sup>b</sup>	0.070 $\pm$ 0.0035 <sup>b</sup>	0.050 $\pm$ 0.0025 <sup>a</sup>
Cd (mg L <sup>-1</sup> )	Raw	0.250 $\pm$ 0.0125 <sup>f</sup>	0.200 $\pm$ 0.0200 <sup>d</sup>	0.220 $\pm$ 0.0110 <sup>e</sup>	0.190 $\pm$ 0.0095 <sup>c</sup>
	Treated	0.020 $\pm$ 0.0025 <sup>a</sup>	0.020 $\pm$ 0.0010 <sup>a</sup>	0.021 $\pm$ 0.0011 <sup>ab</sup>	0.020 $\pm$ 0.0010 <sup>a</sup>
Ni (mg L <sup>-1</sup> )	Raw	0.090 $\pm$ 0.0045 <sup>e</sup>	0.120 $\pm$ 0.0060 <sup>f</sup>	0.150 $\pm$ 0.0150 <sup>h</sup>	0.140 $\pm$ 0.0140 <sup>g</sup>
	Treated	0.040 $\pm$ 0.0010 <sup>bc</sup>	0.022 $\pm$ 0.0011 <sup>a</sup>	0.039 $\pm$ 0.0020 <sup>b</sup>	0.050 $\pm$ 0.0025 <sup>d</sup>
Pb (mg L <sup>-1</sup> )	Raw	0.180 $\pm$ 0.0090 <sup>g</sup>	0.170 $\pm$ 0.0085 <sup>f</sup>	0.160 $\pm$ 0.0320 <sup>e</sup>	0.150 $\pm$ 0.0300 <sup>d</sup>
	Treated	0.024 $\pm$ 0.0020 <sup>bc</sup>	0.020 $\pm$ 0.0010 <sup>a</sup>	0.023 $\pm$ 0.0012 <sup>b</sup>	0.024 $\pm$ 0.0012 <sup>bc</sup>

The effect of the main factors (water treatment and season) and their interaction on THMs in raw and treated water was significant ( $P < 0.05$ ) as shown in Table 6. The effect of water treatment was stronger (with higher F ratio) than that of a season for all tested THMs. The present results showed that high values of THMs in water were during summer, whereas low concentrations were during winter, with an increase in treated water. The water treatment exhibited its maximum efficiency in winter. THMs specification shows that their presence in both raw and treated water was in the order: chloroform > dichlorobromomethane >

dibromochloromethane.

As shown in Fig. 1, chloroform concentrations in raw and treated water was in the range of 2.79 – 17.43 mg L<sup>-1</sup> and 18.42 – 69.75 mg L<sup>-1</sup>, respectively. The results showed significant variations in dichlorobromomethane in raw and treated water ( $P < 0.05$ ) ranging from 1.52 mg L<sup>-1</sup> (in raw water during winter) to 48.36 mg L<sup>-1</sup> (in treated water during summer). The maximum concentration of dibromochloromethane was 25.98 mg L<sup>-1</sup> in treated water during summer. Moreover, THMs correlated negatively with nutrients in both the native and treated water.

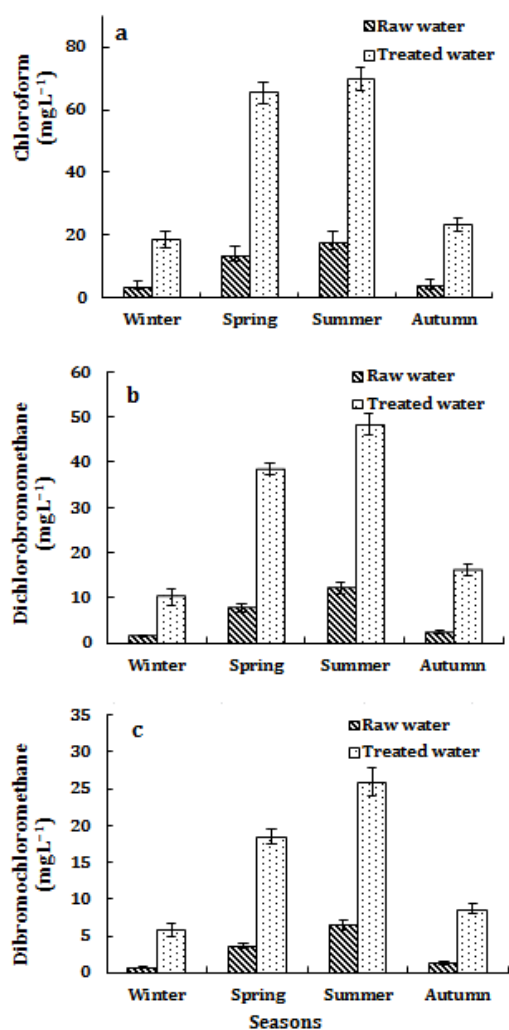
**Table 5.** Pearson's Correlation between physicochemical parameters and season at intake and output of Kafr El-Shinawy drinking-water treatment plant – Damietta.

	Turb.	pH	EC	Alkalinity	DO	BOD	Si	Ammonia	Nitrite	Nitrate	Total N	Ortho - P	Total - P	Fe	Mn	Zn	Cu	Cr	Co	Cd	Ni	Pb	
<b>Turb.</b>	1																						
<b>pH</b>	-.818**	1																					
<b>EC</b>	.175	.600**	1																				
<b>Alkalinity</b>	-.574**	.859**	.858**	1																			
<b>DO</b>	-.860**	-.871**	-.437*	-.650**	1																		
<b>BOD</b>	-.929**	-.866**	.337	.655**	-.870**	1																	
<b>Si</b>	-.224	.037	.545**	.323	.004	-.222	1																
<b>Ammonia</b>	.906**	.584**	-.141	.269	-.638**	.818**	-.469*	1															
<b>Nitrite</b>	.728**	.397	-.238	.114	-.424*	.643**	-.511*	.928**	1														
<b>Nitrate</b>	.930**	.633**	-.085	.325	-.686**	.842**	-.423*	.996**	.916**	1													
<b>Total N</b>	.968**	.718**	.014	.415*	-.780**	.899**	-.354	.974**	.864**	.988**	1												
<b>Ortho - P</b>	.959**	.689**	-.010	.394	-.747**	.882**	.356	.983**	.883**	.993**	.998**	1											
<b>Total - P</b>	.969**	.717**	.029	.417*	-.794**	.919**	-.353	.965**	.832**	.976**	.993**	.989**	1										
<b>Fe</b>	.477*	.020	-.644**	-.230	-.115	.202	-.349	.585**	.499*	.566**	.517**	.534**	.499*	1									
<b>Mn</b>	.744**	.906**	.701**	.818**	-.915**	.851**	-.119	.511*	.361	.564**	.661**	.631**	.671**	-.205	1								
<b>Zn</b>	.597**	.540**	.313	.395	-.696**	.649**	.158	.561**	.555**	.596**	.635**	.631**	.635**	.054	.721**	1							
<b>Cu</b>	.372	.656**	.667**	.640**	-.637**	.604**	-.108	.138	-.040	.169	.264	.221	.306	-.483*	.76**	.293	1						
<b>Cr</b>	.088	.113	-.369	-.149	.128	.055	-.459*	.087	-.050	.061	.050	.044	.089	.494*	-.292	-.553**	.0	1					
<b>Co</b>	.121	.194	.326	.213	-.203	.125	.381	.172	.368	.202	.202	.214	.153	0	.381	.683*	-.087	-.857**	1				
<b>Cd</b>	.930**	.632**	-.018	.398	-.701**	.808**	-.311	.920**	.796**	.936**	.938**	.938**	.926**	.112	.565**	.503*	.183	.195	.103	1			
<b>Ni</b>	.672**	.319	-.268	.154	-.350	.409*	-.114	.676**	.579**	.685**	.666**	.678**	.639**	.851**	.134	.18	-.295	.312	-.029	.777**	1		
<b>Pb</b>	.464*	.137	-.320	-.035	-.075	.391	-.524**	.670**	.721**	.632**	.562**	.586**	.569**	.521**	.026	.087	-.140	.360	-.023	.557**	.504*	1	

\*\* statistically significant correlation at  $p < 0.01$ , \* Statistically significant correlation at  $p < 0.05$ .

**Table 6.** Two- way ANOVA showing the effect of the main factors (water treatment and seasons) and their interaction on Chlorophyll-a of phytoplankton, THMs levels, phytoplankton diversity, and microcystin concentrations in water at Kafr El-Shinawy drinking-water treatment plant – Damietta.

Variable and treatment of variation	df	F	P	Variable and treatment of variation	df	F	P
<b>Chloroform</b>				<b>Bacillariophyta (cell number)</b>			
Water treatment	1	17443729	0.000	Water treatment	1	116079.7	0.0000
Season	3	4172580	0.000	Season	3	881887.5	0.000
Water treatment × season	3	1427454	0.000	Water treatment × season	3	280940.1	0.000
<b>Dichlorobromomethane</b>				<b>Intramicrocystin concentrations</b>			
Water treatment	1	719773777	0.000	Water treatment	1	2910.82	0.0000
Season	3	190202800	0.000	Season	3	137.260	0.000
Water treatment × season	3	63348845	0.000	Water treatment × season	3	134.908	0.000
<b>Dibromochloromethane</b>				<b>Extramicrocystin concentrations</b>			
Water treatment	1	195832036	0.000	Water treatment	1	11184.8	0.0000
Season	3	50480612	0.000	Season	3	2138.21	0.000
Water treatment × season	3	16022276	0.000	Water treatment × season	3	194.464	0.000
<b>Cyanophyta (cell number)</b>				<b>Phytoplankton chlorophyll-a</b>			
Water treatment	1	10630415	0.000	Water treatment	1	22814.1	0.000
Season	3	1693782	0.000	Season	3	5920.19	0.000
Water treatment × season	3	1461754	0.000	Water treatment × season	3	4592.06	0.000
<b>Chlorophyta (cell number)</b>							
Water treatment	1	2898449	0.000				
Season	3	4172580	0.000				
Water treatment × season	3	6563210	0.000				



**Fig. 1** Concentrations of chloroform (a), dichlorobromomethane (b), and dibromochloromethane (c) in raw and treated water of Kafr El-Shinawy drinking-water treatment plant – Damietta. Values are means of three replicates  $\pm$  SE.

### 3.2. Phytoplankton composition

Three phytoplankton groups were found in raw and treated waters, viz. Cyanophyta, Chlorophyta and Bacillariophyta. The phytoplankton density in treated water was much less than those in raw water. The effect of the main factors (water treatment and season) and their interaction on the phytoplankton community at the study area was significant ( $P < 0.05$ ) as shown in Table 6. The effect of water treatment was stronger (with higher F ratio) than that of a season for only cell number of Chlorophyta, meanwhile, the effect of season was stronger on Cyanophyta and Bacillariophyta.

The phytoplankton community of raw water

was composed mainly from Cyanophyta which contributed up to 67.8% of the total cell number during spring, summer (91.74%), autumn (69.75%), winter (14.04%); and followed by Bacillariophyta, which represents 16.48% during spring, summer (4.96%), autumn (25.70%), and winter (77.93%). Meanwhile, Chlorophyta in raw water represents 15.75% of the total cell number during spring, summer (3.31%), autumn (4.55%), winter (8.03%). In treated water, Chlorophyta was the predominant phytoplankton group which contributed 61.95% during winter, spring (82.35%) and autumn (22.58%) of the total cell number, with no detection during summer (Fig. 2). Cyanophyta ranked the second position of dominance with cell number of 13.53% during spring, (77.78%) during summer, and (48.39%) during autumn of the total cell number with no detection during winter. While Bacillariophyta in treated water represents 4.12% during spring, summer (22.22%), autumn (29.03%), and winter (38.05%).

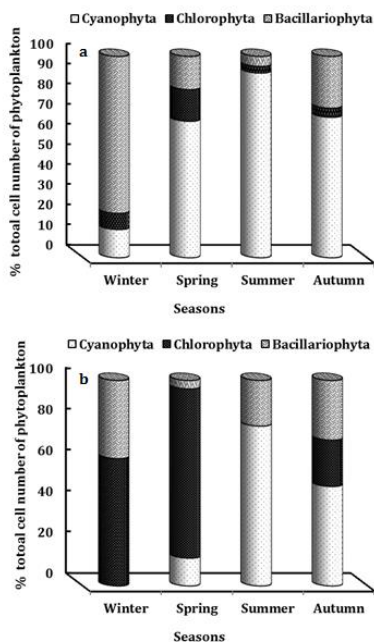
The maximum cell numbers of phytoplankton was found in raw water during summer ( $55.5 \times 10^7$  cell L<sup>-1</sup>). The species composition of raw water (47 taxa) was richer than that of treated water (only 15 taxa). During winter, *Oscillatoria limnetica* was predominated in raw water (98.5% total phytoplankton). Meanwhile, *Microcystis aeruginosa* predominated during summer (57.5%). Other Cyanophyta species also coexisted but in low numbers (Table 7). *Pediastrum simplex* was the predominant Chlorophyta in raw water throughout the year. In raw water, *Melosira granulate* predominated Bacillariophyta during winter and autumn while, *Cyclotella meneghiniana* and *Diatoma elongatum* were the predominant Bacillariophyta during spring and summer, respectively. In treated water, some Chlorophyta and Bacillariophyta coexisted in low numbers.

Pearson's correlation coefficient revealed that the composition of phytoplankton community depends on the physicochemical parameters of water, which in turn depends on water treatment and seasons. As shown in Table 8, a significant positive correlation was reported between Cyanophyta cell numbers and concentration of total nitrogen ( $r = 0.419$ ,  $P < 0.05$ ), and total phosphorus ( $r = 0.456$ ,  $P < 0.05$ ), and between Bacillariophyta cell numbers and both silica ( $r = 0.356$ ,  $P < 0.01$ ) and nitrite ( $r = .580$ ,  $P < 0.01$ ).



**Table 7.** Seasonally variation in the cell number (cell  $\times 10^5 L^{-1}$ ) of the different phytoplankton groups at the intake and output of Kafr El-Shinawy drinking-water treatment plant – Damietta.

Phytoplankton group	Winter		Spring		Summer		Autumn	
	Intake	Output	Intake	Output	Intake	Output	Intake	Output
<b>Cyanophyta</b>								
<i>Anabaena circinalis</i>	-	-	116	-	188	-	32	-
<i>A. variabilis</i>	-	-	112	-	178	-	28	-
<i>A. constricta</i>	-	-	97	-	168	-	23	-
<i>Aphanizomenon flos aquae</i>	5	-	1485	-	3919	-	860	-
<i>Chroococcus limneticus</i>	-	-	1182	-	1867	-	885	-
<i>Coelosphaerium kuetzinglanum</i>	-	-	30	-	80	-	10	-
<i>Gloeocapsa aeruginosa</i>	-	-	1185	0.06	2441	0.2	466	0.05
<i>Gomphosphaeria lacustris</i>	6	-	1566	-	3958	-	809	-
<i>Merismopedia glauca</i>	4	-	606	-	971	-	30	-
<i>M. elegans</i>	-	-	499	-	602	-	25	-
<i>M. incerta</i>	-	-	456	-	872	-	28	-
<i>Microcystis aeruginosa</i>	10	-	5828	0.17	29314	0.5	10416	0.1
<i>Nostoc linckia</i>	-	-	222	-	973	-	63	-
<i>N. spongiaeforme</i>	-	-	205	-	932	-	65	-
<i>N. punctiforme</i>	3	-	1800	-	1600	-	660	-
<i>Oscillatoria agardhii</i>	-	-	800	-	2000	-	1200	-
<i>O. limnetica</i>	1900	-	700	-	200	-	300	-
<i>Phormidium corium</i>	-	-	419	-	693	-	250	-
<b>Chlorophyta</b>								
<i>Actinastrum hantzschii</i>	44	-	200	-	133	-	88	-
<i>Ankistrodesmus angustus</i>	50	-	140	-	40	-	31	-
<i>Botryococcus braunii</i>	31	-	180	-	77	-	37	-
<i>Chlamydomonas</i> spp.	52	-	171	-	93	-	83	-
<i>Chlorella vulgaris</i>	31	-	154	0.1	96	-	53	0.07
<i>Coelastrum microporum</i>	36	-	161	-	81	-	45	-
<i>Dictyosphaerium pulchellum</i> H. C. Wood	109	-	592	-	157	-	33	-
<i>Oocystis marssonii</i>	45	-	393	-	236	-	67	-
<i>Pandorina morum</i>	17	-	180	-	100	-	80	-
<i>Pediastrum clathratum</i>	10	-	164	-	90	-	56	-
<i>P. duplex</i>	65	-	186	-	133	-	129	-
<i>P. simplex</i>	510	0.3	1078	0.6	393	-	273	-
<i>Scenedesmus dimorphus</i>	37	0.4	187	0.7	80	-	10	-
<i>Staurastrum rotula</i> Nordstedt	45	-	106	-	83	-	59	-
<i>Ulothrix subitillissima</i>	20	-	130	-	44	-	10	-
<b>Bacillariophyta</b>								
<i>Amphora coffeaeformis</i>	157	-	69	-	72	-	115	-
<i>Cyclotella meneghiniana</i>	1827	-	783	-	347	-	907	-
<i>Cyclotella</i> spp.	600	0.2	504	-	302	-	405	-
<i>Diatoma elongatum</i>	830	-	207	-	377	-	420	-
<i>Fragilaria capucina</i>	183	-	37	-	38	-	127	-
<i>F. cortonensis</i>	242	-	72	-	10	-	128	-
<i>Melosira granulata</i>	1931	-	688	-	370	-	923	-
<i>Navicula radiosa</i>	923	-	243	-	253	0.2	300	-
<i>Nitzschia palea</i>	200	-	104	0.07	0	-	191	0.09
<i>N. vermicularis</i>	631	0.03	301	-	246	-	522	-
<i>Stephanodiscus dubius</i>	1502	-	404	-	250	-	805	-
<i>Synedra acus</i>	706	0.2	480	-	340	-	544	-
<i>S. ulna</i>	800	-	250	-	120	-	480	-
<i>S. gracillies</i>	166	-	67	-	29	-	83	-



**Fig. 2** Seasonal variations in percentage of cell numbers of different phytoplankton groups in raw water (a) and treated (b) water of Kafr El-Shinawy treatment plant – Damietta.

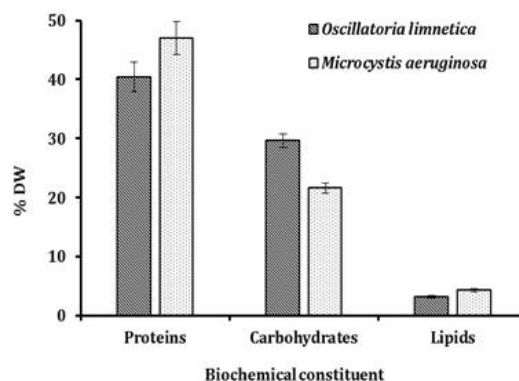
*Intracellular and extracellular microcystins*

The effect of the main factors (water treatment and season) and their interaction on the levels of intracellular and extracellular microcystin was significant ( $P < 0.05$ ) with a higher effect of water treatment (higher F ratio) than that of season (Table 6). Both intracellular and extracellular (dissolved) microcystins recorded their higher concentrations during summer. Throughout the study period, the intracellular microcystin levels were lower in treated water than in raw water. In raw water, the lowest intracellular microcystin was obtained during winter ( $0.71 \mu\text{g L}^{-1}$ ) while the highest concentration was  $1.7 \mu\text{g L}^{-1}$  during summer (Table 9). The maximum concentrations of dissolved microcystins in raw water ( $1.30 \mu\text{g L}^{-1}$ ) was lower than that in treated water ( $2.01 \mu\text{g L}^{-1}$ ) during summer. Also, the minimum concentrations of dissolved microcystins in raw water ( $0.56 \mu\text{g L}^{-1}$ ) during winter was lower than that in treated water ( $1.00 \mu\text{g L}^{-1}$ ) during autumn.

*Biochemical composition of the predominant phytoplankton species in raw and treated water*

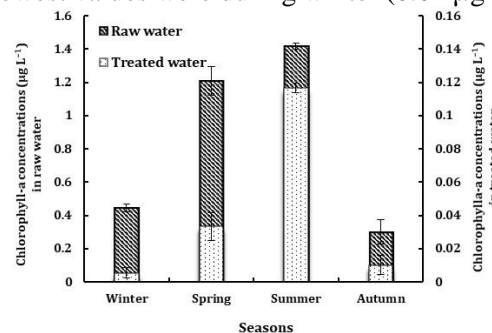
Biochemical constituents of the predominant species in raw water; *Oscillatoria limnetica* and

*Microcystis aeruginosa* were estimated during winter and summer, respectively (Fig. 3). Protein, lipid and carbohydrates were significantly different between the two species. *M. aeruginosa* was richer in protein (47 % DW) and lipid (4.28 % DW) than *O. limnetica* (40.4 and 3.2 % DW, respectively). By contrast, total carbohydrate were higher in *O. limnetica* (29.6 % DW) than *M. aeruginosa* (21.6 % DW).



**Fig. 3** Variations in concentrations of some biochemical constituents (% DW) of *Oscillatoria limnetica* in winter and *Microcystis aeruginosa* in summer, respectively in raw water at Kafr El-Shinawy drinking-water treatment plant – Damietta. Values are means of three replicates  $\pm$  SE.

The effect of the main factors (water treatment and season) and their interaction on chlorophyll-a content of phytoplankton of raw and treated water was very highly significant ( $P < 0.05$ ) with a higher effect of water treatment than that of a season (Table 6). The chlorophyll-a content in phytoplankton was significantly higher in raw water than in treated water during the study period ( $P < 0.01$ ), particularly during spring (Fig. 4). Chlorophyll-a content was generally highest during summer ( $1.42 \mu\text{g L}^{-1}$ ), followed by spring ( $1.21 \mu\text{g L}^{-1}$ ), while the lowest values were during winter ( $0.04 \mu\text{g L}^{-1}$ ).



**Fig. 4** Phytoplankton chlorophyll-a contents ( $\mu\text{g L}^{-1}$ ) in raw and treated water of Kafr El-Shinawy drinking-water treatment plant – Damietta. Values are means of three replicates  $\pm$  SE.

**Table 8.** Pearson's correlation coefficients between trophic status of water, THMs levels, phytoplankton diversity, and microcystin concentration at the intake and output of Kafr El-Shinawy drinking-water treatment plant – Damietta.

	Silica	Ammonia	Nitrite	Nitrate	Total N	Ortho P	Total P	Chloroform	Dichlorobromomethane	Dibromochloromethane	Cyanophyta number	Chlorophyta number	Bacillariophyta number	Intramicrocystin	Extramicrocystin
<b>Silica</b>	1														
<b>Ammonia</b>	-.469*	1													
<b>Nitrite</b>	-.511*	.928**	1												
<b>Nitrate</b>	-.423*	.996**	.916**	1											
<b>Total N</b>	-.354	.974**	.864**	.988**	1										
<b>Ortho P</b>	-.356	.983**	.883**	.993**	.998**	1									
<b>Total P</b>	-.353	.965**	.832**	.976**	.993**	.989**	1								
<b>Chloroform</b>	.466*	-.733**	-.694**	-.727**	-.708**	-.704**	-.692**	1							
<b>Dichlorobromomethane</b>	.450*	-.719**	-.682**	-.712**	-.691**	-.689**	-.675**	.993**	1						
<b>Dibromochloromethane</b>	.465*	-.727**	-.688**	-.719**	-.697**	-.696**	-.680**	.981**	.997**	1					
<b>Cyanophyta number</b>	-.062	.299	.065	.331	.419*	.384	.456*	-.003	.080	.107	1				
<b>Chlorophyta number</b>	.344	-.575**	-.520**	-.583**	-.593**	-.582**	-.592**	.365	.260	.212	-.745**	1			
<b>Bacillariophyta number</b>	-.356**	.309	.580**	.273	.158	.194	.102	-.470*	-.454*	-.431*	-.496*	-.209	1		
<b>Intramicrocystin</b>	.838**	.090	.301	.209	.334	.393	.376	.111	-.097	-.097	.382	-.259	-.222	1	
<b>Extramicrocystin</b>	-.176	.535**	-.841**	-.816**	-.821**	-.768**	-.781**	.924**	.935**	.942**	.087	.303	.521**	-.504*	1

\*\* . statistically significant correlation at p< 0.01, \* . Statistically, significant correlation at p< 0.05.

**Table 9.** Seasonally variations in concentrations ( $\mu\text{g L}^{-1}$ ) of intracellular and extracellular microcystins (Mean  $\pm$  SE, n = 3) in raw and treated waters at Kafr El-Shinawy drinking-water treatment plant – Damietta.

Microcystin	Treatment	Season			
		Winter	Spring	Summer	Autumn
Intracellular microcystin	Raw	0.710 $\pm$ 0.0284 <sup>d</sup>	0.980 $\pm$ 0.0392 <sup>f</sup>	1.700 $\pm$ 0.0680 <sup>e</sup>	0.880 $\pm$ 0.0352 <sup>c</sup>
	Treated	0.009 $\pm$ 0.0003 <sup>b</sup>	0.009 $\pm$ 0.0003 <sup>b</sup>	0.011 $\pm$ 0.0003 <sup>bc</sup>	0.003 $\pm$ 0.0001 <sup>a</sup>
Extracellular microcystin	Raw	0.560 $\pm$ 0.0168 <sup>a</sup>	0.680 $\pm$ 0.0340 <sup>b</sup>	1.300 $\pm$ 0.0520 <sup>f</sup>	0.740 $\pm$ 0.0518 <sup>c</sup>
	Treated	1.210 $\pm$ 0.0242 <sup>e</sup>	1.780 $\pm$ 0.0890 <sup>e</sup>	2.010 $\pm$ 0.1005 <sup>h</sup>	1.000 $\pm$ 0.0400 <sup>d</sup>

## Discussion

Evaluation of the efficiency of water treatment regimes, in terms of the alteration in the physicochemical characteristics of water before and after treatment is essential for recommendation of water usage in drinking and othe domestic purposes (Sarkar et al. 2020). The present work revealed that raw water at Kafr El-Shinawy drinking-water treatment plant is highly trophic with high load of nutrients and silica, along with a slightly alkaline pH and low DO levels. Water temperature was correlated positively with pH ( $r = 0.667$ ,  $p < 0.01$ ), EC ( $r = 0.755$ ,  $p < 0.01$ ), alkalinity ( $r = 0.788$ ,  $p < 0.01$ ), and BOD ( $r =$

0.517,  $p < 0.01$ ). These correlations agreed with that obtained by Sharma et al. (2008) and Shehata and Badr (2010). The intimate correlation between water temperature and pH is in agreement with Larsen (2013) who reported that temperature changes affect ion concentrations and hence the water pH. Variations in water temperature have been reported to strongly affect the composition, bioactivity, and growth of phytoplankton community (Rasconi et al. 2017). Water turbidity was significantly correlated with nutrient concentrations (ammonia, nitrite, nitrate, total nitrogen, ortho-P, and total-P) in water. The high turbidity of raw water compared with treated water might be related to high organic pollution of raw water and the efficiency of treatment in water purification.

Water pH is an important factor in the aquatic system, that directly affect phytoplankton community. Slight changes in water pH might be due to biological activity such as photosynthesis and respiration (Nassar et al. 2014). The slight decrease in pH of treated water below that of raw water was due to the addition of chlorine and alum during treatment processes of raw water (Larsen, 2013).

Dissolved Oxygen (DO) level is an indicator of the water's ability to support a well-balanced aquatic life and acts as an indicator of the trophic status of the water body (George et al. 2012, Salah and El-Moselhy 2015) The increase in DO of treated water above that of raw water might be due to the physico-chemical treatment processes of water such as aeration, coagulation, sedimentation, filtration, and addition of oxidative agents. These treatments increased DO and decreased the turbidity of treated water. A significant negative correlation between DO and water temperatures ( $r = -0.502$ ,  $p < 0.05$ ) was also reported by Shehata and Badr (2010). Low values of DO in raw water during the summer might be attributed to high sewage and agricultural pollution, that enhance microbial growth in raw water.

Low silica concentrations in raw water might be related to the high growth of diatoms, especially during winter. But, the increased silica in treated water can be related to water recycling of reactive silica as a result of disruption and hydrolysis of some diatoms through water treatment in the flocculation basin and during other treatment processes (Shehata and Badr 2010). The extremely low levels of ammonia and nitrite in treated water may be attributed to the oxidation of ammonia and nitrite in the flocculation basin by chlorine. The overall low levels of inorganic nitrogen (ammonia, nitrite, and nitrate) in treated water might be related to their reaction with the chemical reagents during water treatment in the flocculation basin. The pattern of low nutrient level in treated water below raw water, with marked seasonal interaction points to an efficient water treatment regime at the experimental water treatment station.

Some heavy metals are xenobiotics, such as Pb, and Cd; whereas some other heavy metals including Cu, Zn, and Cr are essential elements for human body in small quantities, but turn toxic in high doses. In the present study, the low concentrations of heavy metals (Fe, Mn, Zn, Cu,

Cr, Co, Cd, Ni, Pb) in treated water than in raw water may be related to coagulation and sedimentation processes in treatment basins, in addition to the efficiency of physico-chemical water treatment processes including ion exchange and precipitation. The levels of all the measured heavy metals, especially Mn, Zn, and Fe were higher in phytoplankton cells than in raw water and treated water. Phytoplankton is widely used as bio-indicator of heavy metal pollution in water bodies. Bioaccumulation capacity of phytoplankton for heavy metals depends on metal type and phytoplankton species. Phytoplankton cells contain different functional groups, including amino, thio, carboxylic, and hydroxo that can interact with heavy metals (Pourkhabbaz et al. 2018). One of the serious problems for human health is high levels of THMs in drinking water that can lead to considerable burden of bladder cancer (Evlampidou et al. 2020). High concentrations of THMs in treated waters were related to the production of THMs as by-products during the chlorination of water (Ivahnenko and Zogorski 2006).

Phytoplankton community can be considered as a bio-indicator for water quality. In the present study, Cyanophyte species predominated phytoplankton in raw water during summer and spring as a result of their optimal growth at high temperatures (Reynolds 1984). The predominance of Bacillariophyta in raw water during winter was in agreement with Ganjian et al. (2010) who concluded that Bacillariophyta growth was favored by the low temperature. High numbers of Chlorophyta in water during the winter might be attributed to dominance of various species of *Pediastrum* that flourishes in winter months (Cho et al. 2017). In contrast to the present result, Rajagopal et al. (2010) pointed out that the productivity of Chlorophyta increased at high water temperature. High turbidity of water during summer is responsible for the decrease in Chlorophyta growth as it prevents sufficient light required for Chlorophyta growth (Boyd 1990). A negative correlation between Bacillariophyta numbers and silica concentration of water was also reported by Cetin and Sen (1998).

Estimating phytoplankton chlorophyll-a content in water is a direct way of tracking phytoplankton growth and algal blooms (Driver and Justus, 2016). High phytoplankton chlorophyll-a levels indicate the

high nutrient content of water especially nitrogen and phosphorus. Differences in chlorophyll-a concentration during the study period and according to water treatment reflect changes in phytoplankton numbers in raw and treated water. Similar to cell numbers of Cyanophyta, phytoplankton chlorophyll-a concentrations was not completely depleted after various treatment processes.

The present results are in agreement with **Mohamed et al. (2015)** that microcystin production increases in accordance with the increase in water temperature and level of nutrients. The existence of higher concentrations of extracellular microcystin in treated water than raw water can be related to the release of the intracellular microcystin in water as a consequence of membrane leakage of cyanobacterial cells through the effect of pre-oxidant compounds such as chlorine dioxide, ozone, copper sulfate, and chlorine on membrane integrity (**Pantelic et al. 2013**). Meanwhile, the high levels of extracellular microcystin in treated water occurred at the expense of intracellular microcystin. There were various microcystins variants produced by *M. aeruginosa*, isolated from the Nile River such as microcystin-LR, microcystin-RR, and microcystin-YR. Moreover, environmental conditions can also indirectly affect microcystin production (**Mohamed 2011**).

## Conclusions

Phytoplankton composition depends on the changes in physicochemical properties of water as well as the trophic status and pollutant content in water. The optimized physicochemical properties of water and high trophic status increase the phytoplankton growth especially, cyanobacteria to a level of bloom formation. The high growth of cyanobacteria led to production of cyanotoxins with high content of intracellular microcystin and low content of extracellular microcystin in raw water. On the contrary, most of the intracellular microcystins were released in treated water during water treatment processes. Phytoplankton cells control the levels of heavy metals in raw and treated water through their bioaccumulation capacity. Consequently, Heavy metal levels in raw and treated water are less than those in phytoplankton cells. THMs were higher in treated water than in raw water,

with marked efficiency of the physical-chemical treatment of water in the flocculation basin. The dissolved microcystin and THMs contents in treated water are higher than the allowable limit.

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

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## الملخص العربي

### عنوان البحث: الحالة الغذائية للمياه ومستوى الملوثات كمقاييس لكفاءة نظام معالجة المياه بمحطة معالجة مياه الشرب بكفر الشناوي بدمياط

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يهدف هذا البحث إلى دراسة التغيرات الموسمية في الخصائص الفيزيائية والكيميائية، والحالة الغذائية، وبعض الملوثات الكيميائية والبيولوجية التي تؤثر على تنوع العوالق النباتية، ونوعية المياه في المصدر وبعد المعالجة بمحطة معالجة مياه الشرب بكفر الشناوي بدمياط - مصر خلال عام ٢٠١٨. تشير الدراسة الحالية إلى أن توزيع العوالق الطحلبية تأثر بكل من الحالة الغذائية للمياه، ومستوى الملوثات وكذلك عمليات معالجة المياه الفيزيائية والكيميائية (التخثر، والتلبد، والترسيب). كانت سيادة العوالق الطحلبية وخاصة أجناس *Aphanizomenon flos aquae*, *Gomphosphaeria lacustris*, *Microcystis aeruginosa*, في المياه المعالجة أقل بكثير من تلك الموجودة في مياه المصدر. كانت تركيزات مركبات ثلاثي الهالوميثان في المياه المعالجة أعلى من تلك الموجودة في مياه المصدر وعلى النقيض كانت تركيزات المعادن الثقيلة وخاصة المنجنيز والزنك والحديد في كل من مياه المصدر و أظهرت خلايا العوالق الطحلبية قدرتها على تراكم المعادن الثقيلة وخاصة المنجنيز والزنك والحديد في كل من مياه المصدر و المياه المعالجة. كانت تركيزات الميكروسيسيتين داخل الخلايا أقل (٠,٠٠٣ - ٠,٠١١ ميكروجرام/لتر) بينما كانت تركيزاته خارج الخلايا أعلى (١,٠٠ - ٢,٠١ ميكروجرام/لتر) في المياه المعالجة عن المياه الخام، وقد كان أعلى تركيز للميكروسيسيتين داخل الخلايا في المياه الخام خلال فصل الصيف (١,٣ ميكروجرام/لتر). ومن هنا نستنتج أن تركيز كل من الميكروسيسيتين و مركبات ثلاثي الهالوميثان أعلى نسبيًا في المياه المعالجة عن الحد المسموح به خاصة خلال النمو المرتفع لأجناس طحلب *Microcystis* في موسم الصيف.