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Original Research

Response of Algae to Heavy Metal Removing with Particular Reference to pH

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Abstract

The accumulation capacity of heavy metals by algae as affected by the pH of fresh water is the main objective of this work, which is the first unitary study in Akre-Dhouk Province of Iraq's Kurdistan region. The water samples of 10 selected sites in the months of August and November 2016 were analyzed using atomic absorption spectrometry in order to determine the bioaccumulation factor for taxa *Scytonema subcynatum, Nostoc muscarum, Batracospermum boryanum, Batracospermum atrum, Batracospermum moniliform, Spirogyra subsalsa, Oedogonium tumidulum,* and *Chara bruunii*. In water, we recorded the values of heavy metals content at permissible levels. For Chlorophyta and Cyanophytathe accumulation value positively correlated with pH, while in Rhodophyta it was negative. Consequently, the highest concentrations were registered by *Oedogonium tumidulum* for Ti (1019.361 µg. l^{-1}), Cr (65.678 µg. l^{-1}), Fe (2.380 µg. l^{-1}), Co (7.846 µg. l^{-1}), Ni (205.527 µg. l^{-1}), As (12.591 µg. l^{-1}), *Batracospermum boryanum* for Cu (196.257 µg. l^{-1}), *Batracosoermu atrum* for Hg (0.069 µg. l^{-1}), Pb (134.510 µg. l^{-1}), *Batracospermum moniliform* for Zn (334.508 µg. l^{-1}), Se (0.773 µg. l^{-1}), *Spirogyra subsalsa*, for Mn (425.292 µg. l^{-1}) and *Scytonema subcynatum* for Cd (0.075 µg. l^{-1}).

Keywords: bioaccumulation, heavy metals, freshwater, algae

Introduction

The role of heavy metals in environmental issues has become increasingly prominent in recent years as ecological awareness has achieved global proportions. An important development is the use of algae and other biomass to scavenge toxic and precious metals [1].

The bioaccumulation of heavy metals in aquatic food webs not only threatens directly biodiversity, but sometimes may impact humans as well [2]. Heavy metal accumulation along food webs is related to the fact that living organisms absorb toxic substances at a rate higher than that at which these compounds are excluded due to metabolic activities [3]. Algae have high metal removal efficiency at a low level of metal ions in aqueous solution, as shown by different algae observed: from Chlorophyta, Phaeophyta, Rhodophyta continuously uptake Cd, Cu, Co, Pb, Ni, Cr, Fe and Mn from wastewater [4]. The nature of the adsorption of heavy metals depending on the unique structures of the cell wall in algal biomass that contains many functional groups such as carboxyl, amino, hydroxyl and sulfate that can bind to heavy metals at a particular pH value [5].

Ion exchange is one of the main biosorption mechanisms for heavy metals attracted by algae.

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However, other binding mechanisms like micro-precipitation and complexation are also involved in the process of heavy metal uptake [6]. The algal cells react using different defense systems to cop heavy metal stress, which includes compartmentalization, making complexes and the synthesis of binding proteins such as metallothioneins and phytochelatins, and translocates them into vacuoles, phototaxy, phytochelatin production, and large surface area/volume ratios [7].

The ionic strength of the media also shows a vital role on metal ion uptake, and a decrease in ionic strength helps increase the removal efficiency of metal ions, which may be due to the competition for the functional groups between the metal ions and other ions that played an important role [5].

The pH dependence of metal uptake is closely related to the metal chemistry in solution as well as the acid-based properties of various functional groups on the microalgal cell surface. At low pH, cell wall ligands could be closely associated with the hydronium ions $H3O^+$, thereby restricting the method of metal cations as a result of the repulsive force [8]. Nonetheless, as the pH increases, more ligands such as carboxyl, phosphate, imidazole and amino groups would be exposed (these carry negative charges), and subsequently an attraction of positive-charged metallic ions via a process of biosorption onto the cell surface ensues also opine that at low pH, functional groups are associated with H^+ ions, thus hampering the positively charged metal ions from binding (because of repulsive forces). They state that as the pH increases, those functional sites become deprotonated; therefore, their negative charges increase, and this facilitates binding to metal cations [9].

In Iraq and the Kurdistan region (Akre), the most common sources of water pollution for springs, streams, and rivers originate from chemical weathering, sewage effluent, municipal waste, and agricultural and industrial development in parallel with the increasing population and social activity, including tourism [10, 11]. Until the present time, no research has been carried out addressing Akre algal macrophytes and their ecology.

Therefore, the aim of this study is to compare the accumulation capacity of heavy metals by freshwater species from different sites representative of surface waters of the Akre district. These ecosystems are directly threatened by a diverse array of pollutants generated by human activity wastewater and touristic development of effluents and diffuse sources. The heavy metals (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Hg, and Pb) concentrations were used to calculate the bioconcentration factors for a different algal species. Thus, this study contributes to a better characterization of Akre freshwater from an integrated point of view, referring to the pollution with heavy metals at different compartment levels (water, algae).

Materials and Methodology

Sampling Sites

Kurdistan is a region located in northern Iraq, with Syria and Turkey neighboring countries. Ten representative sampling sites, marked with S1-S10 for the purpose of survey, were selected in both

Fig. 1. Map showing sampling stations Bjel (S1), Kunamar (S2), Galy-zanta river (S3), Galy-zanta spring(S4), Geske down(S5), Hashtgah down (S6), Hashtgah upper (S7), Grybitch (S8), Qasrey (S9), and Gesk upper (S10) in northern Iraq, Kurdistan region.

August and November, 2016 (Fig. 1). These sites were selected according to their pollution sources: Bjel (S1) (360°43'47"N-440°05'16"E), Kunamar (S2) (360°43'56"N-440°01'04"E) Galy-zanta River (S3) (360°44'36"N-430°58'25"E), Galy-zanta Spring (S4) (360°45'26"N-430°58'40"E), Geske down (S5) (360°46'32"N-430°58'21"E), Hashtgah down (S6) (360°46'34"N-430°58'23"E) Hashtgah upper (S7) (360°46'48"N-430°57'22"E), Grybitch (S8) (360°26'09"N-440°22'30"E), Qasrey (S9) (360°43'25"N-440°01'36"E), and Gesk upper (S10) (360°46'33"N-430° 58'19"E).

Sampling Procedure

Determining Heavy Metals Concentrations in Freshwater

Special consideration was given to sampling procedures, storage and analysis in order to avoid contamination. The water and algal samples were preserved and prepared before the preliminary analysis by using recommended standard methods [12]. For determining the total recoverable metal (representing the metal concentration in an unfiltered sample, which has been treated with a mineral acid), freshwater samples were taken from the surface of the monitoring locations by using Nansen bottles type or surface sampling devices. Immediately after the sampling, without prior filtration, the samples were transferred to storage in plastic bottles (polyethylene, polypropylene), acidified with ultrapure nitric acid (1-5 ml HNO_3. l-11 H_2O) to pH 2 and stored at 4°C prior to analysis [13, 3].

Determining Heavy Metals Concentrations in Algae

Algal species were collected and identified by direct microscopic examination (using an Olympus high-resolution binocular microscope) with the help of keys given by [14, 15]. Immediately after the sampling, algae samples were placed in plastic bags and transported to a laboratory to be frozen prior to analysis. A sample consisted of at least 10 individuals, and the entire algae is usually analyzed. Any possible contamination was avoided during the preparation of the algal samples. The samples were initially oven-dried at 105ºC and gently homogenized. Algae sample (0.3-0.5 g) mineralization was performed using Teflon digestion vessels in a microwave digestion system (MWS-2, Berghof Products Instruments). A three-step digestion program for algae and the addition of 10 ml of nitric acid were used and digested with nitric acid 65% ultrapure (Merck) and hydrogen peroxide (Merck) in sealed Teflon dishes. 1st step: 1408, 80% for 50, 2nd step: 1608, 85% for 50, and the 3rd step: 1758C, 90%, for 20 minutes, so every step is characterized by a specific temperature, power and time, for pseudo total dissolution. Once the digestion process was completed, after cooling the samples were diluted with 50 ml deionized water.

Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Hg, and Pb concentrations were analyzed by using a GBC AVANTA 3000 atomic absorption spectrometer with graphite furnace. Blank and standard solutions for analysis were prepared, respecting the same matrix as that of the samples. In order to preserve the accuracy of results (since there were not available reference materials), three replicates were analyzed for each sample. Also, QC tests (quality control) were realized after each set of 10 samples, with the mean recovery percentages being determined for each of the analyzed heavy metals.

The pH of the samples was determined using a HANNA water test portable meter. The observed range for these variables at the study sites was over the two seasons.

Data Analysis

The bioaccumulation factor (BCF) can be calculated as the ratio of the chemical concentration in the organism and the chemical concentration in the water at steady state [16]. For statistics we used the mean values and the correlation coefficient by SPSS 25 software for mac and ANOVA. Spearman's rank correlation and scatterplot matrix was used to examine the relationship between the data and the levels, and P 0.05 was used for all tests as significance level, according to the pair sample correlation coefficient that was used to observe the significant differences in heavy metals concentrations for both monitored periods, for $p<0.05$

Results and Discussion

Heavy Metals in Fresh Water

In point of heavy metal accumulation view in fresh water. the result (Table 1) is revealed that in November, the higher value was attributed to Se and Fe (0.1541, 0.1065 µg) in sites 1 and 3 respectively, while site 4 recorded maximum value for Pb (35.1750 µg) in addition to site 6 recorded maximum values for Co (1.2180 µg), As (2.0809 µg) and Hg 0.0293 µg); finally site 9 recorded the maximum value for Cd (0.1206 µg).

In August (Table 2), site 1 recorded maximum value for Fe, Se, and Cd, and Pb was (0.1046, 0.1980, 0.1211 and 27.1462 µg) respectively, while site 10 recorded maximum value for As and Hg (2.1996, 0.0223 µg). The higher concentrations of heavy metals recorded for site 6 in November and site 1 in August were explained by both daily routine of the village's labor-intensive activity every day regardless of the season, and tourist port activities, and for the rest of the sampling sites by their position that is less attended by tourists. According to the Guidelines for Drinking Water Quality (GDWQ)

Table 1. Heavy metal (µg. l^{-1}) in fresh water during November.

Site name / Metals	Fe	Co	As	Se	Cd	Hg	Pb	pH
Bjel	0.1017	1.0415	1.8243	0.1541	0.0731	0.0150	23.4775	7.4
Kunamar	0.0980	1.1026	1.8481	0.1200	0.0551	0.0150	21.0912	7.5
Galy-zanta river	0.1065	0.9695	1.8211	0.1200	0.1145	0.0150	28.4962	8
Galy-zanta spring	0.1047	0.9385	1.8784	0.1323	0.0891	0.0150	35.1750	8.2
Geske down	0.1024	1.0174	1.7996	0.1200	0.0853	0.0150	25.9476	7.91
Hashtgah down	0.0947	1.2180	2.0809	0.1200	0.0467	0.0293	20.3533	7.4
Hashtgah upper	0.0950	1.1568	1.8481	0.1266	0.0040	0.0150	21.0912	7.8
Grybitch	0.0980	1.0644	1.8007	0.1200	0.0872	0.0236	25.8322	7.6
Qasrey	0.1019	1.0190	1.8401	0.1200	0.1206	0.0150	24.7938	8.1
Gesk upper	0.1031	1.0239	1.7949	0.1200	0.0800	0.0271	26.4115	8.25
Mean	0.1006	1.05516	1.85362	0.1253	0.07556	0.0185	25.26695	7.816
Min-max WHO standard	200-2000	0.1-4	7-500	7-50	1-50	0.5-7	5-100	6.5-8.5

Notice: that Ti, Cr, Mn, Cu, Ni and Zn not detected.

(World Health Organization, 2018) the data obtained in this study for water quality are within permissible values [12].

Heavy Metals Concentrations in Algae

The calculated mean of the bioaccumulation factor (Table 3) from the three algal groups Cyanophyta, Chlorophyta and Rhodophyta were: for Ti 322.630 µg, Cr 188.043, Mn 109.941µg, Fe 0.816 µg, Co 3.242 µg, Ni 101.692 µg, Cu 74.857 µg, Zn 96.262 µg, As 4.605 µg, Se 0.295 µg, Cd 0.011µg, Hg 0.037 µg, and Pb 67.458 µg.

The Cyanophyte recorded Ti 183.120 µg, Cr 0.00, Mn 0.00 µg, Fe 0.460 µg, Co 2.307 µg, Ni 72.762 µg, Cu 1.862 µg, Zn 11.464 µg, As 3.226 µg, Se 0.173µg, Cd 0.0379 µg, Hg 0.034 µg, and Pb 16.748 µg, but Mn was not detected.

On the other hand, for Rhodophyta we found Ti 112.768 µg, Cr 17.271, Mn 77.9424 µg, Fe 0.579 µg, Co

Table 2. Heavy metal (µg. l^{-1}) in fresh water during August.

Site name / Metals	Fe	Co	As	Se	Cd	Hg	Pb	pH
Bjel	0.1046	0.9548	1.7876	0.1980	0.1211	0.0150	27.1462	7.7
Kunamar	0.0990	1.0566	2.1729	0.1200	0.0382	0.0150	22.4653	7.2
Galy-zanta river	0.1008	1.0438	2.0422	0.1200	0.0454	0.0150	25.0403	7.8
Galy-zanta spring	0.1013	1.0711	1.8238	0.1200	0.0254	0.0212	25.1557	7.7
Geske down	0.0947	0.4970	2.0590	0.1200	0.0000	0.0150	0.0000	7.5
Hashtgah down	0.0975	1.1243	1.8003	0.1200	0.0347	0.0150	25.8741	7.5
Hashtgah upper	0.0974	1.0970	1.8298	0.1200	0.0567	0.0150	22.9216	7.3
Grybitch	0.1004	1.0316	1.8268	0.1200	0.0471	0.0150	23.2205	7.6
Qasrey	0.0997	1.0633	1.8376	0.1610	0.0865	0.0150	22.1402	7.3
Gesk upper	0.0996	1.0728	2.1996	0.1200	0.0355	0.0223	21.3413	7.6
Mean	0.0995	1.00123	1.93796	0.1319	0.04906	0.01635	21.53052	7.52
Min-max WHO standard	200-2000	0.1-4	7-500	7-50	1-50	0.5-7	5-100	6.5-8.5

Notice: Ti, Cr, Mn, Cu, Ni and Zn not detected

Table 3. Mean of bioaccumulation metal concentrations (μg. l^{-1}) in algal species of Cyanophyta, Rhodophyta and Chlorophyta.

Species Name / Metals	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Cd	Hg	Pb
Scytonyma subcynatum	331.026	0.000	0.000	0.660	2.894	76.732	1.363	22.928	3.486	0.212	0.075	0.046	16.222
Nostoc muscarum	35.213	0.000	0.000	0.261	1.719	68.792	2.361	0.000	2.966	0.134	0.000	0.022	17.274
Batracospermum boryanum	0.000	0.000	45.782	0.197	1.423	98.504	196.257	0.000	1.238	0.196	0.000	0.047	124.661
Batracospermum atrum	4.318	0.000	0.000	0.151	1.369	46.514	177.678	20.380	2.922	0.440	0.000	0.069	134.510
Batracospermum moniliform	333.985	51.812	188.043	1.389	4.439	157.575	74.629	334.508	3.418	0.773	0.000	0.046	96.396
Spirogyra subsalsa	534.508	0.000	425.292	0.676	3.003	58.201	45.698	58.615	5.614	0.120	0.000	0.015	52.955
Oedogonium tumidulum	1019.361	65.678	110.471	2.380	7.846	205.527	26.013	237.407	12.591	0.188	0.000	0.015	30.189
Chara bruuni	97.122	0.000	0.000	0.329	1.922	46.640	7.323	61.251	3.593	0.264	0.000	0.033	20.556
Mean	322.630	188.043	109.941	0.816	3.242	101.692	74.857	96.262	4.605	0.295	0.011	0.037	67.458
Cyanophyta Mean	183.120	0.000	0.000	0.460	2.307	72.762	1.862	11.464	3.226	0.173	0.037	0.034	16.748
Rhodophyta Mean	112.768	17.271	77.942	0.579	2.410	100.864	149.521	118.296	2.526	0.469	0.000	0.054	118.522
Chlorophyta Mean	550.330	21.893	178.588	1.128	4.257	103.456	26.344	119.091	7.266	0.191	0.000	0.021	34.567

2.410 μg, Ni 100.864 μg, Cu149.521 μg, Zn 118.296 μg, As 2.526, Se 0.469 μg, Hg 0.054 μg, and Pb 118.522 μg, but Cd was not detected.

Finally, Chlorophyta were Ti 550.330 μg, Cr 21.893 μg, Mn 178.588 μg, Fe 1.128 μg, Co 4.257 μg, Ni 103.456 μg, Cu 26.344 μg, Zn 119.091μg, As 7.266 μg, Se 0.191 μg, Hg 0.021 μg, and Pb 34.567 μg, while Cd was not detected.

Additionally, the results indicate that Chlorophyta recorded a high accumulation factor value for eight heavy metals, Rhodophyta recorded a high accumulate factor value for four heavy metals, and Cyanophyta recorded for one heavy metal to accumulate metals within their tissue. The similar previous research demonstrated that the ability of algae to remove heavy metals and bioaccumulation capacity [4] varies with the different strains of algae, and it is generally in the following green algae descending order of Chlorophyta, Phaeophyta and Rhodophyta [17].

Due to the cell wall metal-binding capacity of bio sorbents which depends on a number of mechanisms such as blocking of functional groups, the displacement and/or substitution of essential metal ions and functional cellular units also possess intracellular mechanisms that enable them to cope with the toxic effects of metals. Metal-removing capability was both metal and alga-specific; certain algae performed better overall than the remaining strains [16].

Relationship between Heavy Metal Accumulation and pH

pH is one of the most important determining factors of the capacity of metal ion uptake by algal biomass, thus the nature of the bio sorbent would determine differences in selectivity and affinity to metal ions

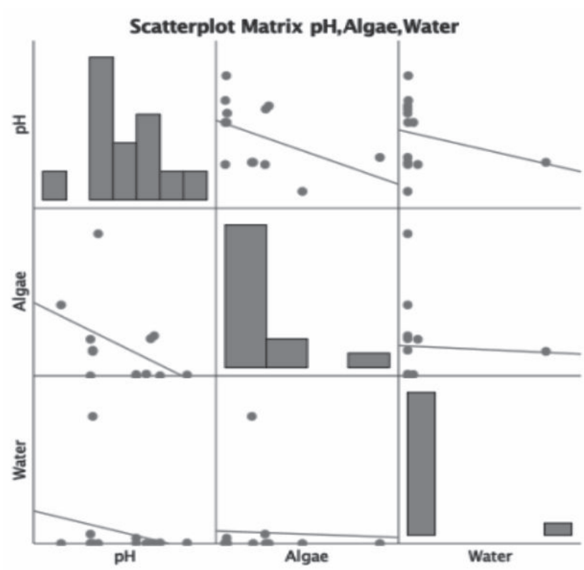

Fig. 2. Scatterplot matrix showing the correlation between pH, metal concentration in water and their bioaccumulation in algae.

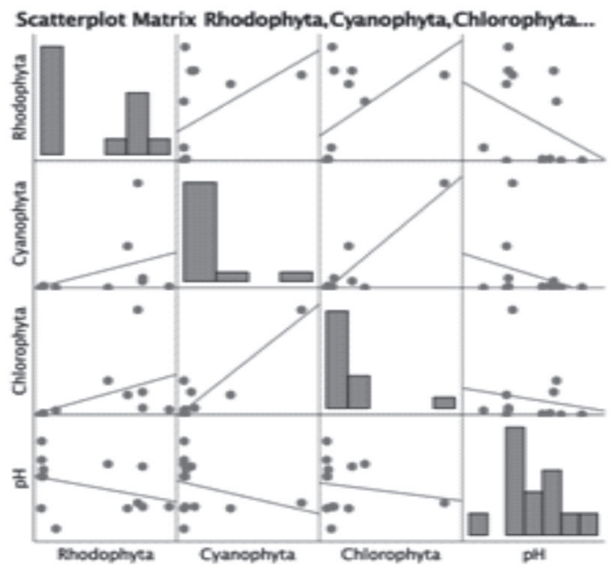

Fig. 3. Scatterplot matrix showing the correlation between pH and bioaccumulation in Rhodophyta, Cyanophyta, and Chlorophyta.

[9]. The scatterplot Matrix (Figs 2, 3) demonstrate the negative correlation between the metal concentration in water and their accumulation in algae in general, and as a group with water pH. As reported in similar studies, water heavy metal adsorption capacity is affected by the most important factor, which is pH. It generally affects the chemical metal states and availability of active groups on algal surface. The adsorption efficiency of different heavy metal ions was markedly increased with pH from 2.0-4.0, and then gradually decreased as pH increased from 6-8 due to a large quantity of $H3O^+$ ions that compete with tested heavy metals at binding sites [18].

Besides, metal ion uptake depends on pH and and is related to the metal ion complexation chemistry in water, and the behavior of many different functional groups present in the surface of algal cells as well as to complex formation constants. The tendency for selective metal ion uptake at an optimized pH is useful in targeted biosorption [19]. Bioaccumulation of heavy metals varies from species to species, depending on

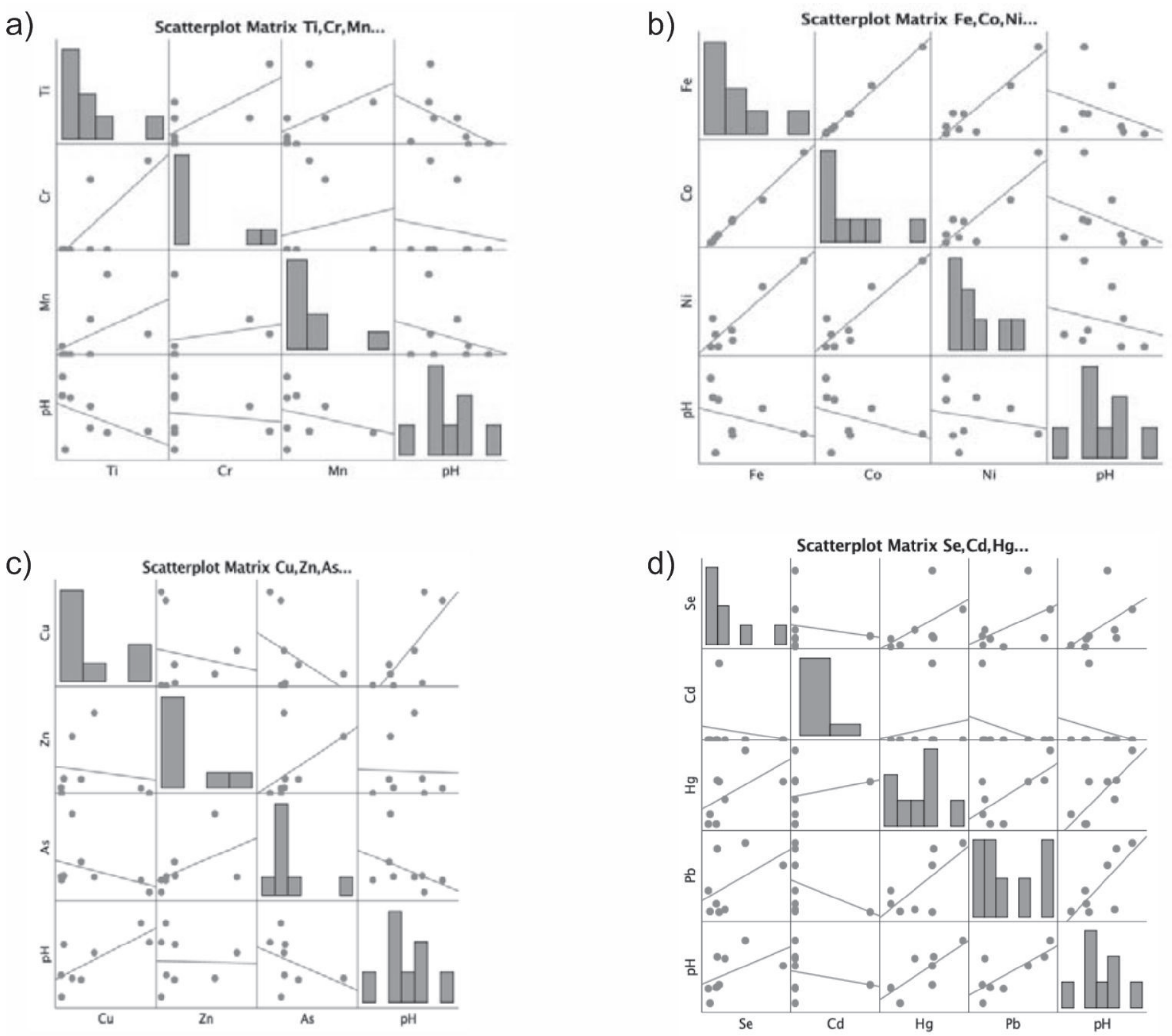

Fig. 4. Scatterplot matrix shows the correlation between: a) pH and Ti, Cr, and Mn accumulation in algae, b) pH and Fe, Co, and Ni accumulation in algae, c) pH and Cu, Zn, and As accumulation in algae, d) pH and Se, Cd, Hg, and Pb accumulation in algae.

Table 4. Correlation between metal concentrations (μg. l^{-1}) in fresh water and *Scytonema subcynatum*.

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	-0.363	0.371	-0.024	-0.002	-0.038	0.304	-0.567	1							
	Co	0.182	-0.144	-0.033	-0.169	.669*	0.119	-0.113	0.501	1						
	As	-0.339	0.224	-0.364	0.046	-0.571	-0.387	-0.274	-0.023	-0.481	1					
	Se	-0.263	0.389	0.38	0.287	-0.661	0.14	-0.213	-0.193	-.750*	0.051	1				
	Cd	-0.263	0.114	-0.439	0.25	-0.411	-0.064	-0.118	-0.103	-0.541	0.464	0.277	1			
	Hg	-0.541	0.453	0.123	-0.151	-0.118	0.359	-0.466	0.234	0.379	0.275	-0.51	0.139	1		
	Pb	-0.541	0.453	0.123	-0.151	-0.118	0.359	-0.466	0.234	0.379	0.275	-0.51	0.139	1.000**	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.343	0.115	-0.203	-0.487	-0.189	-0.169	-0.169	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

the pH level [20]. Thus, the presence of some other metals effects accumulation, such as Na+ decreases adsorption of positive metallic ion complexes and enhances negative complexes because of the protein and polysaccharide composition of the algal cell wall [21]. This is displayed in Fig. 3, which Chlorophyta, Cyanophyta, and Rhodophyta negatively correlated with pH, since these groups are hyper-absorbents and hyper-accumulators, absorbing and accumulating these elements from their environment into their bodies. These algae can be hyper-phytoremediators, and their presence in water reduces water pollution [7].

Its well-defined correlation coefficient between metals and pH in the scatterplot matrix figure (4a-d). The significant correlation found between Mn, Cr and Ti is shown in Fig. 4a), while Fig. 4b) shows positive correlation between Fe, Co and Ni, besides Fe correlated with Co. However, Fig. 4c) displays only As correlated with Zn, and finally Fig. 4d) shows significant correlation between Se, Hg and Pb. On the other hand, Cu, Se, Hg and Pb correlated with pH. The types, combinations, and concentrations of heavy metal ions vary greatly among waters. In multi-metal ion systems metal ions compete for binding to algal ligands, and the presence of some cations significantly influences the uptake of other metal ions by algal cells. Additionally, the role of light metal ions on the toxicity of heavier metal ion biosorption is very small. However, high concentrations of monovalent cations of Na^+, K^+ and Nitrate could increase the ionic strength of water [22].

Individually, *Scytonema subcynatum* shows a positive correlation between Co and Cd in water (Table 4), although Table 5 expresses the positive correlation between Co and Cd in *Nostoc muscarum* with As with Co and Hg in water. Many Cyanophyta have copious amounts of mucilaginous materials of various types – often primarily polysaccharide – that can be classified as a sheath, capsule or slime. These materials frequently have a substantial ability to bind various metal ions; additionally, the cell wall carries a negative charge due to the presence of carboxyl, phosphatic and other groups which are believed to be involved in binding of metals through ion exchange and other mechanisms [23].

Table 6 illustrates the positive correlation between Fe in *Batracospermum boryanum* with Se in water, whereas Table 7 shows the positive correlation between Se, Hg in *Batracospermum atrum* with Fe in water. Also, Table 8 shows the positive correlation between Fe and Pb in *Batracospermum moniliform* with Co and Cd, respectively. The physicochemical form of metal (speciation) is a critical factor controlling metal bioavailability, and competition with H+ at the cell membrane surface [24].

Moreover, Table 9 shows the positive correlation between Hg in *Spirogyra subsalsa* with Cd in water, but Table 10 shows the positive correlation between Se and Hg in *Oedogonium tumidulum* with Cd and

Table 5. Correlation between metal concentrations (µg. l^{-1}) in fresh water and *Nostoc muscarum.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	-0.363	0.371	-0.024	-0.002	-0.038	0.304	-0.567	1							
	Co	0.182	-0.144	-0.033	-0.169	.669*	0.119	-0.113	0.501	1						
	As	-0.339	0.224	-0.364	0.046	-0.571	-0.387	-0.274	-0.023	-0.481	1					
	Se	-0.263	0.389	0.38	0.287	-0.661	0.14	-0.213	-0.193	-.750*	0.051	1				
	Cd	-0.263	0.114	-0.439	0.25	-0.411	-0.064	-0.118	-0.103	-0.541	0.464	0.277	1			
	Hg	-0.541	0.453	0.123	-0.151	-0.118	0.359	-0.466	0.234	0.379	0.275	-0.51	0.139	1		
	Pb	-0.541	0.453	0.123	-0.151	-0.118	0.359	-0.466	0.234	0.379	0.275	-0.51	0.139	1.000**	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.343	0.115	-0.203	-0.487	-0.189	-0.169	-0.169	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 6. Correlation between metal concentrations (µg. l^{-1}) in fresh water and *Batracospermum boryanum.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	0.052	-0.13	-0.246	.781*	-0.238	-0.382	0.109	1							
	Co	-0.23	0.12	0.348	0.373	-0.023	0.269	0.052	0.359	1						
	As	-0.586	0.637	0.275	0.358	-0.546	0.268	-0.635	0.537	0.334	1					
	Se	0.231	-0.256	-0.062	0.523	0.363	0.038	0.148	0.245	0.287	-0.122	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c			
	Hg	0.495	-0.467	-0.511	-0.013	0.511	-0.107	0.258	-0.242	-0.612	-0.481	0.419	.c	1		
	Pb	-0.081	0.133	0.017	0.53	-0.587	-0.401	-0.131	0.58	-0.211	0.259	0.056	.c	-0.145	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	0.092	0.06	-0.478	0.152	.c	0.301	-0.345	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 7. Correlation between metal concentrations (µg. l[-1]) in fresh water and *Batracospermum atrum.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	-0.477	0.381	0.285	0.463	-0.384	0.249	-0.315	1							
	Co	0.481	-0.41	-0.366	0.455	0.179	-0.511	0.2	-0.186	1						
	As	0.028	0.073	0.074	0.545	0.107	0.275	-0.133	0.023	0.045	1					
	Se	.666*	-.788*	-.749*	0.257	0.663	-0.662	0.488	-0.034	0.149	0.004	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c		
	Hg	.702*	-.743*	-0.455	0.577	0.621	-0.598	0.497	0.139	0.469	0.147	.825**	.c	1		
	Pb	0.505	-0.308	0.058	0.268	0.442	-0.074	0.161	-0.084	-0.051	0.464	0.299	.c	0.338	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.463	-0.063	0.066	0.508	.c	0.38	0.207	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 8. Correlation between metal concentrations (µg. l[-1]) in fresh water and *Batracospermum moniliform.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	-.721*	.685*	0.018	0.194	-0.569	0.373	-.751*	1							
	Co	0.147	-0.131	-0.461	0.398	-0.17	-0.345	-0.017	0.214	1						
	As	0.534	-0.396	-0.026	0.224	0.23	-0.432	0.275	-0.615	0.3	1					
	Se	-0.102	0.055	-0.371	0.386	-0.153	-0.215	-0.273	0.324	.787*	0.272	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c			
	Hg	0.18	-0.416	-.667*	0.433	0.123	-0.328	0.365	0.213	0.317	-0.404	0.281	.c	1		
	Pb	0.511	-0.472	0.052	0.116	.769*	0.175	0.418	-0.404	-0.314	0.321	-0.101	.c	-0.063	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.582	-0.163	-0.085	-0.417	.c	0.439	0.401	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 9. Correlation between metal concentrations (µg. l^{-1}) in fresh water and *Spirogyra subsalsa.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.63	1												
	Se	0.17	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.63	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321									
Heavy metals in algae	Fe	-0.168	-0.054	-0.263	0.31	-0.425	-0.084	0.253	1							
	Co	-0.186	0.281	-0.223	0.042	-0.332	-0.407	-0.6	-0.29	1						
	As	-0.458	0.627	0.352	0.255	-0.586	0.073	-.712*	-0.251	0.456	1					
	Se	0.204	-0.428	-0.503	-0.14	0.267	-0.054	0.525	0.48	-0.286	-.840**	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c			
	Hg	0.432	-0.594	-0.591	0.143	.698*	-0.146	0.427	0.065	-0.395	-0.589	0.579	.c	1		
	Pb	-0.092	0.048	-0.446	0.274	-0.324	-0.163	-0.158	0.528	0.064	0.325	-0.004	.c	0.028	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	0.045	-0.538	-.800**	.689*	.c	0.578	-0.313	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 10. Correlation between metal concentrations (µg. l^{-1}) in fresh water and *Oedogonium tumidulu.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	0.508	-0.363	-0.368	0.222	0.209	-0.354	0.139	1							
	Co	0.308	-0.379	-0.17	0.487	0.299	-0.069	0.423	-0.33	1						
	As	-0.176	0.09	0.362	0.153	-0.078	0.604	0.262	-0.054	0.021	1					
	Se	0.56	-0.572	-0.258	.685*	0.53	-0.144	0.459	0.263	0.587	0.296	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c			
	Hg	0.4	-0.507	0.075	0.228	0.132	-0.21	.806**	-0.14	0.288	0.422	0.275	.c	1		
	Pb	-0.07	0.176	-0.363	-0.082	0.095	-0.151	-0.622	0.389	-0.29	-0.562	-0.081	.c	-.908**	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.069	0.595	0.15	0.378	.c	0.576	-0.481	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Table 11. Correlation between metal concentrations (μg. l^{-1}) in fresh water and *Chara bruunii.*

		Heavy metals in water							Heavy metals in algae							
		Fe	Co	As	Se	Cd	Hg	Pb	Fe	Co	As	Se	Cd	Hg	Pb	pH
Heavy metals in water	Fe	1														
	Co	-.948**	1													
	As	-0.482	0.625	1												
	Se	0.174	-0.174	-0.136	1											
	Cd	.800**	-.772*	-0.347	-0.111	1										
	Hg	-0.578	0.625	.729*	-0.281	-0.2	1									
	Pb	.782*	-.861**	-0.29	0.094	0.587	-0.321	1								
Heavy metals in algae	Fe	-0.177	0.147	-0.13	0.45	-0.572	-0.56	-0.253	1							
	Co	0.023	-0.109	-0.031	0.547	0.137	0.149	0.099	-0.145	1						
	As	0.639	-0.493	-0.278	0.009	.805**	-0.236	0.139	-0.284	-0.058	1					
	Se	0.392	-0.241	0.216	0.195	0.56	-0.025	0.069	-0.048	0.093	.768*	1				
	Cd	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c	.c			
	Hg	0.425	-0.317	0.037	0.366	0.127	-0.618	0.179	0.523	-0.04	0.244	0.484	.c	1		
	Pb	-0.066	0.037	-0.081	0.234	-0.07	-0.04	-0.026	0.132	-0.39	0.068	0.064	.c	-0.054	1	
	pH	.696*	-.778*	-0.293	-0.085	.693*	-0.15	.898**	-0.477	-0.068	0.277	0.112	.c	-0.05	0.259	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).
c Cannot be computed because at least one of the variables is constant

Pb respectively in water. Finally, Table 11 shows the positive correlation between As in *Chara bruunii* with Cd in water.

The ability of *Oedogonium tumidulum* is noticed by maximum bioaccumulation of the four metals Ti, Cr, Co and As. This means that wall composition varies with pH and in the presence of these metals, the sites acidified, anionic and become protonated [1]. However, the publications considered mainly in *Oedogonium* that accumulate Cd and Cr [4] and about their sensitivity and evolutionary strategies appear to coexist among algae from the polluting metal [25]. Rhodophyta division show selectivity toward the accumulation of heavy metals, except for Fe and Cu [26]. In all cases, the contents of heavy metals in the algae were a magnitude higher than in the water, which indicated good sorption properties of these organisms [27] because the mechanism of bonding to the biomass was also different [2, 21, 28] in their particularly efficient accumulators of metals due to high levels of sulfated polysaccharides and alginates within their cell walls [29], besides detoxification mechanisms of heavy metals – especially for Hg and Pb [16, 29] (although *Batracospermum atrum* and *Batracospermum monilifirm* show an ability of maximum bioaccumulation for two metals Hg, Pb and Fe, Se in order).

Although there have been studies on the biosorption of heavy metals using green algae as biosorbents, when biosorption studies are examined, it is seen that green algae effectively bio absorbs heavy metals [30]. *Spirogyra* sp. displays that have good sorption properties make algae a suitable tool in phytoremediation for metal Cr [31]. It is important that algae can increase the content of heavy metal ions by several orders of magnitude [32]. *Spirogyra aequinoctialis* reported that it has the ability to absorb Mn, Cd and Pb from polluted water [33]. *Spirogyra halliensis* has the capacity for bio sorption of heavy metals like Ni, Cr, Fe and Mn [28]. *Spirogyra* sp. Cd, Hg, As, Pb, Co, Ni, Cr, Fe, Mn, Cr, Cu, Fe, Mn, Zn [34] while *Spirogyra subsalsa* in our study recorded maximum bioaccumulation of metal Mn among other algae. A comparative overall analysis of the results obtained the tolerance of *Nostoc* sp. For As, Cu, Hg and Pb [3], while in our study *Nostoc muscarum* shows that maximum bioaccumulation for Co as comparative to other taxa (due to alterations in membrane permeability and strong surface negativity) could result in greater binding of the positively charged Al species to the membrane, rendering membrane structure and functions more sensitive to it [23]. This study showed *Scytonema subcynatum* to have maximum accumulation for only one metal as Cd relatively the Cyanobacteria have been tested for heavy metal removal, and *Scytonema hofmanii* showed the highest metal uptake for Pb [35].

Conclusions

This research studied heavy metals profiles and accumulation in water and algae for the period August and November 2016 within a representative area of the Akre District of the Kurdistan region. The bioconcentration factors for: *Scytonema subcynatum, Nostoc muscarum, Batracospermum boryanum, Batracospermum atrum, Batracospermum moniliform, Spirogyra subsalsa, Oedogonium tumidulum,* and *Chara bruunii* were calculated with their correlation coefficient with concentrations of metals Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Hg and Pb in water body complying with their bioaccumulation in algal species individually. The results show a close correlation between heavy metals concentrations in water and algae with their related to pH. The highest concentrations of heavy metals were recorded for (S6) sampling site in November and (S1) in August. Overall, the concentrations of metals in water were at permissible levels. The pattern of accumulation differed in algae. In the group Cyanophyte algae Ti> Ni> Pb> Zn> As>Co> Cu> Fe> Se> Cd> Hg, Cr, but Mn was not detected while Rhodophyta algae Pb> Cu> Zn> Ti> Ni> Mn> Cr> Co> As> Fe > Se> Hg, but Cd was not detected. Whereas Chlorophyta algae Ti> Mn> Zn>Ni> Pb> Cu> Cr> As> Co> Fe> Se> Hg, while Cd was not detected, which resulted in a positive correlation between Chlorophyta and Cyanophyta, while it was negative with Rhodophyta. There was positive correlation between metals in Cu, Se, Hg and Pb in algae and pH during accumulation and between metals Cr, Mn with Ti, Co, Ni with Fe, Zn with As, and finally Pb with Se and Hg within the algae. In addition, the highest value was recorded by *Oedogonium tumidulum* for metal Ti, Cr, Fe, Co, Ni, As, *Batracospermum boryanum* for metal Cu, *Batracospermum atrum* for Hg, Pb, *Batracospermum moniliform* for Zn, Se *Spirogyra subsalsa,* for Cr, and Mn *Scytonema subcynatum* for Cd. These algal species are used in many specialized studies as bioindicators, bioaccumulates and bioremediates of heavy metals pollution due to their specific biochemical processes.

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Conflict of Interest

The authors declare no conflict of interest.

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