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Removal of Cr, Ni and Co in the water of chromium mining areas by using Lemna gibba L. and Lemna minor L

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Keywords

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Abstract

This study investigated the use of *Lemna gibba* and *Lemna minor* plant species to absorb Cr, Ni and Co from Alacakaya mining area water. *Lemna gibba* and *L. minor* were separately placed to feed into two reactors. Water and plant samples were collected for eight consecutive days, and the pH, electric conductivity and temperature of the water were measured. The plants were washed, dried and burned at 300°C for 24 h in a drying oven. The samples were then analysed by ICP-MS (inductively coupled plasma mass spectroscopy) for concentrations of Cr, Ni and Co, which were 1.2, 0.9 and 0.5 μ g L⁻¹ respectively. On Day 8, the determined uptake of *L. gibba* and *L. minor* were: 196 and 398% for Cr; 307 and 1473% for Ni; and 166 and 223% for Co respectively. *Lemna gibba* and *L. minor* were thus effective in absorbing Cr, Ni and Co from mining water.

Introduction

Heavy metals (HM) have a high atomic weight and a density at least five times greater than that of water (Tchounwou et al. 2012). HM pollution in aquatic environments is one of the main problems affecting plant and animal lifes (Duffus 2002). HMs are classified into two categories by Gergen & Harmanescu (2012) and Rai et al. (2015) that these metals have no beneficial role and are positively toxic to lives, such as Ni, Cd, Hg, Pb, Cr and As. In contrast, metals such as Co, Fe, Cu, Cr (+3), Mn, Zn are essential for plant and animal life but may become toxic if the concentrations are too high. HM toxicities depend on several factors, including chemical species, route of exposure, dose, nutritional status, gender and genetics. Arsenic, mercury, chromium, lead and cadmium are prioritised in term of public health significance because of their high degree of toxicity (Tchounwou et al. 2012). Due to industrial and mining activities, toxic heavy metals such as As, Pb, Hg, Cd, Cr, Ni, Fe, Cu, Co and Zn have caused widespread water, air and soil contamination (Rai et al. 2015).

Chromium (Cr) enters into natural ecosystems from industrial activities such as iron and steel manufacturing, chromium plating, wood preservation, chrome leathering, smelting processes, mining, fuel production, industrial outflow and other anthropogenic sources (OECD 2003). Cr toxicity in plants is connected with its valence state: Cr (III) is less toxic, whereas Cr (VI) is highly toxic and also mobile (Shanker *et al.* 2005). There is no evidence to suggest that Cr and Ni play an essential role in plant metabolism, although high concentrations of Cr and Ni are known to have toxic effects on both plants and animals (Suné *et al.* 2007; Kabata-Pendias 2011; Drzewiecka *et al.* 2012). However, the antioxidative enzymatic system of plants can be stimulated under Ni stress, helping them to tolerate high Ni concentrations (Jócsák *et al.* 2008; Gonzalez *et al.* 2015). Cobalt (Co) is essential for blue-green algae and microorganisms, although there is some evidence that it has a beneficial effect on plant growth, whether it is in fact essential for plant life remains unclear. Co is a component of vitamin B₁₂, which is its only known function (Pais & Jones 2000). According to Environment Canada's 2013 report, 2.5 µg Co²⁺ L⁻¹ is considered as nontoxic.

Of the different techniques for removing of heavy metals, phytoremediation is among the cost-effective and ecologically friendly, in that it uses living green plants for *in situ* removal of contaminants from water and soil (Sood *et al.* 2012; Tatar & Obek 2014; Goswami *et al.* 2014; Sasmaz *et al.* 2015). Phytoremediation depends on the ion uptake mechanism, as well as the physiological, anatomical and morphological characteristics of each species (Rahman & Hasegawa 2011). Floating macrophytes usually uptake metal or contaminants through the process of rhizofiltration (Chaudhuri *et al.* 2014). *Lemna* sp. has been selected because of its faster growth rate and easer harvest, in phytoremediation

studies by many scientists (Zayed et al. 1998; Obek 2009; Sasmaz & Obek 2009, 2012). Among the aquatic macrophytes, Lemna sp. can float and grow quickly on water, and is one of the most advantageous plants in terms of pesticide or metal removal (Dirilgen 2011; Li et al. 2011). Moreover, its low cost, long storage capacity, minimal chemical and biological sludge volume, ease of transport, ability to grow under different climatic conditions and fast reproduction rates are additional advantages (Khataee et al. 2012; Materazzi et al. 2012). According to Khataee et al. (2012), the optimum pH and temperature range needed for a high growth rate of Lemna sp. are 4–9 and 5–25°C respectively. The present study determined Cr. Ni and Co concentrations in mining water and aquatic plants (L. gibba L. and L. minor L.) growing in Alacakaya chromite deposits. Changes in Cr, Ni and Co concentrations in both L. minor L. and L. gibba L. were measured daily, as were calculations of the phytoremediation potential of L. gibba L. and L. minor L. in the mining water for Cr, Ni and Co. The optimal harvesting time for Cr, Ni and Co. of L. gibba L. and L. minor L. was also determined, and the phytoremediation potential for Cr, Ni and Co of L. gibba L. and L. minor L. was compared.

Material and methods

Apparatus

A Perkin-Elmer Elan 9000 ICP-MS was used to determine Cr, Ni and Co concentrations in this study. The operation conditions of ICP-MS are given in Sasmaz & Yaman (2008).

The study area

This study was carried out in the Marmek sector of the Alacakaya mining area, Elazig, Turkey (E39°49'41.80" and 38°32'36.39") (Fig. 1). Mining operations have been ongoing in this area since 1936. The Alacakaya region is one of the most important chrome ore producing districts in Turkey, and was divided into different mining sectors according to the nature of the deposits, lithological characteristics, geo-graphical disposition and the structural position. This deposit is related to ultramafic rocks (dunites, peridotites, pyroxenites) that outcrop around Alacakaya (Engin *et al.* 1983). These rocks also contain high amounts of Cr, Ni and Co. Chrome ore is extracted through open pit operations or galleries in the study area. There is common water effluent coming from the mining area and this water is deposited in the lake, after that charged into the Dicle river.

Water and plant samples

The chemical composition of the mining water may vary depending on the geologic units and mineralisation type. These factors can also affect the pH, temperature ($T^{\circ}C$) and

electric conductivity (EC) of the water. The water and *L. minor* L. and *L. gibba* L. plant samples were collected for eight consecutive days with sterile plastic bottles from the Alacakaya mining area (Fig. 1). Determination of the pH was accomplished with either an Orion 4-Star pH meter with gelfilled pH electrodes, or an Oakton pH tester 30. It was used ICP-MS for cation analyses and test tubes for anion analyses (carbonates, nitrates, sulfates, fluoride) (Table 1). Temperature was recorded using a traceable digital thermometer. Electrical conductivity was measured with an Orion 4-Star conductivity meter and an Orion conductivity electrode. In this study, the plants are systematically identified as *L. gibba* L. and *L. minor* L., according to the typology given in *Flora of Turkey and the East Aegean Islands* (Davis 1984).

Preparation of samples

Lemna gibba L. and L. minor L. were delivered from the Botanical Gardens at Istanbul University in August 2013. The plants were grown for two in a natural pool laboratory, and were then adapted in reactors, separately. Four hundred grams of the each plant were placed into each reactor in size $60 \times 40 \times 35$ cm (Fig. 2), as described by Tatar & Obek (2014). One reactor contained L. gibba L. and the other L. minor L. The reactors operated under a sustained regime of flow volume (3.85 L s⁻¹) of mining water (Figs 1 and 3), but the flow volume of water through each reactor is lower than in 3.85 3.85 L s⁻¹. So, these plants were always fed with fresh water in each reactor during the experiment time. Samples of both L. gibba L. and L. minor L. were collected daily; about 50 g of plant samples were taken from each reactor during the eight-day duration of the experiment. The plant samples were thoroughly washed with tap water, rinsed with distilled water, and dried at 60°C for 24 h in the laboratory. A chelating EDTA wash was also applied, with no differences observed between EDTA washing and non EDTA washing. The dried plant samples (approximately 50 g) were then reduced to ash by heating at 300°C for 24 h. The ashed samples were subsequently digested in HNO₃ (Merck, Darmstadt, Germany) for one hour, followed by digestion in a mixture of HCI: HNO₃: H₂O (1:1:1, v/v; 6 mL per 1.0 g of the ashed sample) for 1 h at 95°C. The samples were then analysed with ICP-MS techniques (Group SO200 was used for water samples and Group VG104 was used for ashed plant samples) for Cr, Ni and Co.

Statistical analyses were carried out using Analysis of Variance (ANOVA) and Student Newman Keul's Procedure (SNK) (Sokal & Rohlf 1995) on SPSS 15.0 software (IBM Corp., Armonk, NY, USA). The metal results (Mn, Fe, Mg, Na, Al, K, P and S) belong to the *L. gibba* L. and the *L. minor* L. of the study area, and were correlated with Cr, Ni and Co using the Spearman Rank correlation.



Fig. 1. Location map of the study area.

Results and discussion

Cr, Ni and Co concentrations in mining water

Water samples were collected daily during the eight-day experiment in the field. The results of the chemical analysis of the eight daily water samples were too close to each other and no significant changes were observed for each metal. The mean Cr, Ni and Co concentrations were determined to be 1.2 ± 0.2 , 0.9 ± 0.1 and $0.05 \pm 0.01 \ \mu g \ L^{-1}$ in the mining water (P < 0.5), respectively, as shown in Table 1. Physicochemical characteristics such as pH, T (°C) and EC, together with analytical data of the major ions in the mining water samples, are also presented in Table 1. The pH values of the mining water ranged from 8.60 to 9.05 (mean: 8.85 ± 0.2); the temperature varied within a range of 20.02-22.4°C (mean: $21.4 \pm 1^{\circ}$ C); and the EC values ranged from 2.13 to 2.45 mS cm^{\circ 1} (mean: 1.21 ± 0.1 mS cm^{\circ 1}) (Table 1). These results indicate the close effects of numerous factors, including the distance to the mining water feeding area; the residence time to the flow system in the mineralized area of the mining water; the flow time of the mining water coming from the feeding area; and the relatively long-term water-rock interaction in the mineralised area. For these reasons, these parameters of the mining water (pH, T and EC) were very similar to each other over the eight-day duration of the experiment.

As shown in Table 1, mean Cr, Ni and Co concentrations in the mining water samples were lower than the limit values (50, 20 and 50 μ g L⁻¹ respectively), established for drinking water by the World Health Organization (WHO) (2008) and the Food and Agriculture Organization (FAO) (2011). This also causes heavy metal pollution in the water and surrounding soil along the Dicle River. Toxic contaminants are not easy to be removed after contamination of the surface soil and ground water, and can directly enter the human body through these media. Because mining runoff causes both soil and water contamination in the environment, it is very important to rehabilitate the soil and ground water around the mining areas polluted by HMs (Caussy et al. 2003; Dong et al. 2010). Ning et al. (2011) indicated that the HM concentrations of surface water in the gold mining area were higher than class III or class IV of the national surface water quality standards. Along the flow direction, the concentrations of HMs decreased the further away the water was from the sources of pollution. It was ascertained that the metal

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Parameter	т (°С)	рН	EC (mS cm ⁻¹)	HCO_3^- (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)	SO₄ (mg L ⁻¹)	F ⁻ (mg L ⁻¹)	Ca (mg L ⁻¹)	Mg (mg L ⁻¹)	Κ (mg L ⁻¹)
DL	-	-	-	-	-	-	-	0,05	0,05	0,05
Mining water	21.4 ± 1	8.85 ± 0.2	1.21 ± 0.1	220 ± 10	0.94 ± 0.8	620 ± 35	0.12 ± 0.1	21 ± 2	17 ± 2	0.8 ± 0.1
Parameter	<u>Na</u> (mg L ⁻¹)	Fe (μg L ⁻¹)	$\frac{Mn}{(\mu g L^{-1})}$	<u>s</u> (μg L ⁻¹)	<u>Ρ</u> (μg L ⁻¹)	<u>B</u> (μg L ⁻¹)	$\frac{\mathbf{Zn}}{(\mu g L^{-1})}$	<u>Cr</u> (μg L ⁻¹)	$\frac{Ni}{(\mu g L^{-1})}$	<u>Co</u> (μg L ⁻¹)
DL	0,05	10	0,05	1	10	5	0,5	0,5	0,2	0,02
Mining water	1.5 ± 0.2	196 ± 20	10.2 ± 1	2.6±0.3	17 ± 3	109 ± 5	9.7 ± 0.5	1.2±0.2	0.9 ± 0.1	0.05 ± 0.01

Table 1 Physicochemical characteristics of mining water in the study area and detection limits of ICP-MS for the anion and cations



Fig. 2. The plants were placed in each reactor, separately. One reactor contained *L. gibba* L. and the other *L. minor* L.

content of the soil and ground water varies depending on the possible sources of the metals.

Three hydrochemical facies have been identified based on the contents of major cations and anions (Ca–Mg–HCO₃; Ca– Mg–Fe–SO₄; Na–Cl–NO₃). Water types in the aquifer were specified by using Piper's (1944) trilinear plotting technique. Fe, Ca, Mg, Mn and Na were the dominant cations, and represented more than 90% of the cation in the study area. Sulfate and bicarbonate are the prevailing components for the mining water in the study area, representing 88–95% of the major anion. The mining water could be characterized as Fe– Ca–Mg–Mn–SO₄ bicarbonate water.

Cr, Ni and Co in *Lemna minor* L. and *Lemna* gibba L

Phytoremediation is an efficient and cost-effective method for decontaminating environments. However, in order to optimize the system, knowledge about how heavy metals affect plant physiology must be obtained prior to designing a system of decontamination (Pilon-Smits 2005). Certain aquatic plants are considered to be heavy metal pollution indicators and are successfully used as a method for monitoring environmental pollution (Cenci 2000). The heavy metals (As, Hg, Cd, Cu, Co, Zn, Ag, Cr, Tl and Pb) are toxic and dangerous because of their ability to accumulate in biological organisms over time (Baby et al. 2010). There are different factors that can affect the uptake mechanism of Cr. Ni and Co, such as plant species, bioavailability of the metal, root zone, environmental conditions, chemical properties of the contaminant, properties of medium (pH, organic matter, phosphorus content) and addition of chelating agent (Tangahu et al. 2011)

Cr concentrations of *L. gibba* L. (LG-0) and *L. minor* L. (LM-0) before the experimental study were 4.9 and 5.4 mg kg⁻¹ respectively (Fig. 4) (P < 0.05). These Cr values can thus be

accepted as control groups for both LG-0 and LM-0. From the first day of the experimental study, L. gibba L. and L. minor L. accumulated 4.8 and 5.8 mg Cr kg⁻¹ respectively, on a daily basis (P < 0.05). In the study, the amounts of Cr absorbed from low Cr concentrations in the mining water by L. gibba L. decreased from 2% on the first day, to 20% on the second day, to 4% on the third day and to 10% on the fourth day. However, the uptake of Cr increased in subsequent days, by 41% on the fifth day, 29% on the sixth day, 27% on the seventh day and 196% on the eighth day. The amounts of Cr absorbed by L. minor L. increased from 7.4% on the first day and to 35.2% on the second day. Cr accumulations linearly increased until the eighth day of experiment, and were observed to increase 133% on the fifth day and 398% on the eighth day. As presented in Fig. 4, maximum accumulations of Cr were observed on the fifth day and eighth day for L. gibba L., and the fifth day and the eighth day for L. minor L. Although very low concentrations (mean: 1.2 μ g L⁻¹) of Cr were contained in the mining water, L. gibba L. and L. minor L. accumulated 8000 and 17 916 times more chromium than in the mining water respectively. Lemna minor L. was observed to have the ability to accumulate Cr better than in L. gibba L., compared to chromium values of both species before the experimental study (Fig. 4). Chromium in L. gibba L. and L. minor L. (P < 0.05) showed a high linear Spearman's correlation with the Ni, Co, Mn and K, and negative correlations with Ca, Mg and Cu (Table 2). Chromium (Cr) is the second most common metal contaminant in ground water, soil and sediments due to its widespread industrial usage, hence posing a serious environmental concern. Among various valence states, Cr (III) and Cr (VI) are the most stable forms. Cr (VI) is the most persistent in the soil and is highly toxic for biota (Singh et al. 2013). Uysal (2013) determined the ability of Lemna minor to remove Cr (VI) ions from waste water in a continuous flow pond system and found in plants grown in



Fig. 3. These reactors were operated under a sustained regime of flow volume of the mining water.



Fig. 4. Cr accumulations by Lemna gibba L. and Lemna minor L.

the first chamber of pond operated at pH 4.0. Abdallah (2012) determined that L. gibba performed extremely well at removing the chromium from their solutions and was capable of removing up to 84% of chromium during the 12-day experiment. Elmaci et al. (2009) detected the best removal rate of Cr by L. minor at 20 mg L^{-1} : 62.5% at 20 mg L^{-1} . Ucuncu et al. (2013) concluded that L. minor L. was capable of relatively rapid and effective bioremediation for Pb and Cr and can feasibly be used in freshwater ecosystems contaminated primarily with those two metals. Goswami & Majumder (2015) indicated that L. minor has the potential to tolerate Ni and Cr in lower concentrations. L. minor met the basic characteristics of metal hyperaccumulation and was found to be a hyperaccumulator of both Ni and Cr in all experimental concentrations. Obek (2009) determined L. gibba L.'s heavy metal accumulating capability in secondary treatment effluence and found it to have high ability to remove Cr in secondary treatment effluence as well: 300% on the first day, 360% on the second day and 500% on the fifth day of experimental period.

Ni concentrations in *L. gibba* L. (LG-0) and *L. minor* L. (LM-0) before this experimental study were 9.2 mg kg⁻¹ and 3.7 mg kg⁻¹ respectively (Fig. 5) (*P* < 0.05). The values of LG-

0 and LM-0 for Ni were accepted as control groups for both plants (Fig. 5). Beginning on the first day of the experimental study, Ni accumulation by L. gibba L. decreased from 9.2 to 5.2 mg Ni kg⁻¹ with negative uptake (39%) and *L. minor* L. accumulated 5.2 mg Ni kg⁻¹ with 41% positive uptake (P < 0.05). During the eight-day study, the amount of Ni in the water, which had a low Ni concentration, decreased to 45% on the second day, and to 26, 21, 10% on subsequent days, followed by an increases 5% on the sixth day, 20% on the seventh day and 307% on the eighth day as L. gibba L. accumulated it. L. minor L. showed a regular increase in Ni accumulation from the first day until the last day of the experimental study (41% on the first day, 132% on the second day, 568% on the fifth day, 1095% on the seventh day and 1473% on the eighth day). Although very low concentrations (mean: 0.9 μ g L⁻¹) of Ni were observed in the mining water, on the eighth day. L. gibba L. and L. minor L. accumulated 31 333-times and 60 555-times more Ni than in the mining water respectively. Lemna minor L. also showed important linear increases during the experimental study, and was observed to have the ability to accumulate higher levels of Ni than L. minor L., compared to Ni values of L. minor L. before the experimental study (Fig. 5). Ni values in both L. gibba L. and *L. minor* L. (P < 0.05) showed a high linear with the HMs Cr, Ni and Mn, and a negative Spearman's correlation with Ca, Mg and Cu (Table 2). According to Goswami & Majumder (2015), the efficiency of *L. minor* in the removal of Ni and Cr from aqueous solutions was investigated at concentrations of 3.05, 3.98 and 4.9 mg L^{-1} for Ni. L. minor L. showed both higher bioaccumulation and percentage of Ni removal than Cr. Statistical analysis suggested that the growth of the plant was affected by the toxic effect of both Ni and Cr. It is suggested that *L. minor* L. can remove Ni and Cr from aqueous solution and can also accumulate the same in considerable concentrations, when the initial metal concentrations are low. Furthermore, Goswami & Majumder (2015) indicated

Table 2 Spearman's correlation coefficients between some metals with Cr, Ni and Co in Lemna gibba L. and Lemna minor L.

	Fe	Ca	Mg	Na	Al	К	Р	S	Mn	Cu	Cr	Ni	Со
Fe	1												
Ca	0,37	1,00											
Mg	0,37	0,99	1,00										
Na	-0,22	-0,73	-0,68	1,00									
Al	0,19	0,21	0,20	0,09	1,00								
Κ	0,26	-0,59	-0,61	0,49	0,06	1,00							
Р	-0,53	-0,95	-0,93	0,69	-0,29	0,51	1,00						
S	-0,06	-0,86	-0,86	0,69	-0,03	0,88	0,77	1,00					
Mn	-0,15	-0,86	-0,84	0,52	-0,19	0,66	0,77	0,79	1,00				
Cu	0,65	0,87	0,87	-0,69	0,19	-0,39	-0,86	-0,67	-0,71	1,00			
Cr	0,24	-0,49	-0,46	0,39	-0,12	0,52	0,29	0,49	0,76	-0,39	1,00		
Ni	0,31	-0,38	-0,35	0,33	-0,09	0,47	0,17	0,40	0,69	-0,30	0,98	1,00	
Со	0,25	-0,54	-0,50	0,46	-0,11	0,60	0,33	0,58	0,78	-0,42	0,97	0,97	1,00



that *L. minor*, if cultured in the vicinity of Ni and Cr contaminated effluents, could possibly treat and therefore remove the toxic metals from the water, rendering it less toxic or even nontoxic. Therefore, *L. minor* might be useful in the treatment of water contaminated with Ni and Cr, individually. Obek (2009) determined Ni accumulation using *L. gibba* L. in secondary treatment effluents, but observed no significant changes in Ni accumulation levels during the seven day experimental period. According to results by Appenroth *et al.* (2010), duckweeds are barely suitable for phytoremediation of Ni²⁺ contaminated waste water; they are, however, very useful for biomonitoring because they have a high phytotoxic sensitivity against Ni²⁺.

Before the experimental study, Co concentrations of L. gibba L. (LG-0) and L. minor L. (LM-0) were 0.87 and 0.94 mg kg^{-1} respectively (Fig. 6) (P < 0.05). These values were accepted as control groups for both L. gibba L. and L. minor L. From the first to the seventh day of the experimental study, L. gibba L. was observed low increase and decreases in levels of Co accumulation; on the eighth day, a significant increase (166% uptake) in the accumulation of Co by L. gibba L. was observed. L. minor L. showed a regular increase in Co accumulation from the first day until the last day of the experimental study (28% on the first day, 33% on the second day, 54, 68, 91, 137, 191 and 223% on the subsequent days). Although very low concentrations (mean: 0.05 μ g L⁻¹) of Co were observed in the mining water (Table 1), L. gibba L. and L. minor L. accumulated 29 000 times and 42 000 times more cobalt, respectively, than in the mining water on the eighth day. L. minor L. was observed to have the ability to accumulate higher levels of Co than L. gibba L., compared to Co values for both plants before the experimental study began (Fig. 6). Cobalt in *L. gibba* L. and *L. minor* L. (P < 0.05) showed a high linear Spearman's correlation with Cr, Ni, Mn, K, S and negative correlations with Ca, Mg and Cu (Table 2). Sree et al. (2015) concluded that after exposure to Co^{2+} duckweed growth is initially (four days in our experimental setup) inhibited to a greater extent than photosynthesis resulting in surplus carbohydrates and starch accumulation; thereafter, photosynthesis declines in the presence of Co²⁺ leading to restricted availability of carbohydrates while at the same time remobilising the initially stored starch. As a result, it was observed that the applicability of this technology can be applied 'in situ' to remediate mining, ground water and surface waters. Also, phytoremediation has been perceived to be a more environmentally friendly 'green' and lowtech alternative to more active and intrusive remedial methods (Jadia & Fulekar 2008).

Conclusion

In this study, among phytoremediation plants for Cr, Ni and Co, L. gibba L. and L. minor L. were shown to be a costeffective, ecologically safe and effective method for the treatment of contaminated mining water. The results of our study demonstrate that L. minor L. accumulated more Cr, Ni and Co than L. gibba L. when compared to their control group counterparts (LG-0 and LM-0). The sequence of heavy metals accumulated by L. gibba L. and L. minor L. was determined to be Ni > Cr > Co and optimal harvesting times of L. gibba L. and L. minor L. for Cr, Ni and Co. L. gibba L. and L. minor L. accumulated 31 333 times and 60 555 times more Cr, 31 333 times and 60 555 times more Ni and 29 000 times and 42 000 times more Co than in the mining water respectively. The removal of Cr. Ni and Co in contaminated waters by L. gibba L. and L. minor L. is environmentally and nondestructively cost-effective. Therefore, the harvesting of L. gibba L. and L. minor L. in mineralised waters should be avoided so that they can help control pollution in the aquatic environment and reduce the health risks to humans and animals caused by heavy metal contamination. In the same time, the metals could be recovered from plant mass by using the leaching method with cyanide or strong acids after the plants were harvested at the end of the experiment.



Fig. 6. Co accumulations by Lemna gibba L. and Lemna minor L.

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References

Abdallah, M.A. (2012) Phytoremediation of Heavy Metals from Aqueous Solutions by Two Aquatic Macrophytes, *Ceratophyllum demersum* and *Lemna gibba* L. *Environ. Technol.*, **33**, 1609–1614.

Appenroth, K.J., Krech, K., Keresztes, Á., Fischer, W. and Koloczek, H. (2010) Effects of Nickel on the Chloroplasts of the Duckweeds Spirodela polyrhiza and Lemna minor and Their Possible Use in Biomonitoring and Phytoremediation. Chemosphere, **78**, 216–223.

Baby, J., Raj, J., Biby, E.T., Sankarganesh, P., Jeevitha, M.V., Ajisha, S.U. and Rajan, S.S. (2010) Toxic Effect of Heavy Metals on Aquatic Environment. *Int. J. Biol. Chem. Sci.*, **4**, 939–952.

Caussy, D., Gochfeld, M. and Gurzau, E. (2003) Lessons from Case Studies of Metals: Investigating Exposure Bioavailability and Risk. *Ecotox. Environ. Safe*, **56**, 45–51.

Cenci, R.M. (2000) The Use of Aquatic Moss (Fontinalis antipyretica) as Monitor of Contamination in Standing and Running Waters: Limits and Advantages. J. Limnol., **60**, 53–61.

Chaudhuri, D., Majumder, A., Misra, A.M. and Bandyopadhyay, K. (2014) Cadmium Removal by *Lemna minör* and *Spirodela polyrhiza*. *Int. J. Phytorem.*, **16**, 1119–1132.

Davis, P.H. 1984. Flora of Turkey and the East Aegean Island. Edinburgh University Press, Edinburgh, Spain.

Dirilgen, N. (2011) Mercury and Lead: Assessing the Toxic Effects on Growth and Metal Accumulation by *Lemna minor*. *Ecotoxicol. Environ. Saf.*, **74**, 48–54.

Dong, D., Li, H., Zhang, J. and Sun, L. (2010) Removal of Heavy Metals from Mine Water by Cyanobacterial Calcification. *Min. Sci. Technol.*, **20**, 566–570.

Drzewiecka, K., Mleczek, M., Gasecka, M., Magdziak, Z. and Golinski, P. (2012) Changes in *Salix viminalis* L. 'Cannabina' Morphology and Physiology in Response to Nickel Ions—Hydroponic Investigations. J. Hazard. Mater., **217–218**, 429–438.

Duffus, J.H. (2002) "Heavy Metals" A Meaningless Term? IUPAC (International Union of Pure Applied Chemistry). *Pure Appl. Chem.*, **74**, 793–807.

Elmaci, A., Ozengin, N. and Yonar, T. (2009) Removal of Chromium (III) and Copper (II), Lead (II) and Zinc (II) using *Lemna minor L. Fres. Env. Bull.*, **18**, 538–542.

Engin, T., Balci, M., Sümer, Y. and Ozkan, Y.Z. (1983) General Geological Setting and the Structural Features of the Guleman Peridotite Unit and the Chromite Deposits. *Bull. Min. Res. Exp. Ins. Turkey*, **95**, 34–56.

Environment Canada. 2013. Federal Environment Quality Guideline Cobalt. Canadian Council of Ministers of the Environment, Winnipeg.

FAO. 2011. Food and Agriculture Organization of the United Nations. Joint FAO/WHO food standards programme codex committee on contaminants in foods, Codex Alimentarius Commission, pp. 64–89. Gergen, I. and Harmanescu, M. (2012) Application of Principal Component Analysis in the Pollution Assessment with Heavy Metals of Vegetable Food Chain in the Oldmining Areas. *Chem. Cent. J.*, **6**, 56.

Gonzalez, C.I., Maine, M.A., Cazenave, J., Hadad, H.R. and Benavides, M.P. (2015) Ni Accumulation and its Effects on Physiological and Biochemical Parameters of *Eichhornia crassipes*. *Environ*. *Exp*. *Bot.*, **117**, 20–27.

Goswami, C. and Majumder, A. (2015) Potential of *Lemna minor* in Ni and Cr Removal from Aqueous Solution. *Pollution*, **1**, 373–385.

Goswami, C., Majumder, A., Misra, A.K. and Bandyopadhyay, K. (2014) Arsenic Uptake by *Lemna minor* in Hydroponic System. *Int. J. Phyto.*, **16**, 1221–1227.

Jadia, C.D. and Fulekar, M.H. (2008) Phytoremediation: The Application of Vermicompost to Remove Zinc, Cadmium, Copper, Nickel and Lead by Sunflower Plant. *Environ. Eng. Manage*. J., **7**, 547–558.

Jócsák, I., Villányi, V., Rabnecz, G. and Droppa, M. (2008) Investigation of Nickel Stress Induction in Terms of Metal Accumulation and Antioxidative Enzyme Activity in Barley Seedlings. *Acta Biol. Szeged*, **52**, 167–171.

Li, S.X., Feng-Ying, F., Yang, H. and Jian-Cong, N. (2011) Thorough Removal of Inorganic and Organic Mercury from Aqueous Solutions by Adsorption on *Lemna minor* Powder. *J. Hazard. Mater.*, **186**, 423–429.

Kabata-Pendias, A. 2011. *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, FL.

Khataee, A., Movafeghi, A., Torbati, S., Salehi Lisar, S. and Zarei, M. (2012) Phytoremediation Potential of Duckweed (*Lemna minor* L.) in Degradation of CI Acid Blue 92: Artificial Neural Network Modeling. *Ecotoxicol. Environ. Saf.*, **80**, 291–298.

Materazzi, S., Canepari, S. and Aquili, S. (2012) Monitoring Heavy Metal Pollution by Aquatic Plants. *Environ. Sci. Poll. Res.*, **19**, 3292–3298.

Ning, N., Liyuan, Y., Jirui, D. and Xugui, P. (2011) Heavy Metal Pollution in Surface Water of Linglong Gold Mining Area, China. Proc. Environ. Sci., **10**, 914–917.

Obek, E. (2009) Bioaccumulation of Heavy Metals from the Secondary Treated Municipal Waste Water by *Lemna gibba*. *Fres. Environ. Bull.*, **18**, 2159–2164.

OECD. (2003) Technical guidance for the environmentally sound management of specific waste streams: Used and scrap personal computers. Organization for Economic Cooperation and Development Working Group on Waste Prevention and Recycling.

Pais, I. and Jones, J.B. (2000) *The Handbook of Trace Elements*. St Lucie Press, Florida, 222 p

Pilon-Smits, E.A. (2005) Phytoremediation. *Ann. Rev. Plant Biol.*, **56**, 15–39.

Piper, A.M. (1944) A Graphic Procedure in the Geochemical Interpretation of Water Analyses. *Trans. Am. Geophys. Union*, **25**, 914–923.

Rahman, M.A. and Hasegawa, H. (2011) Aquatic Arsenic: Phytoremediation Using Floating Macrophytes. *Chemosphere*, 83, 633–646.

Rai, S., Gupta, S. and Mittal, P.C. (2015) Dietary Intakes and Health Risk of Toxic and Essential Heavy Metals through the Food Chain in Agricultural, Industrial, and Coal Mining Areas of Northern India. *Hum. Ecol. Risk Assess.*, **21**, 913–933. Sasmaz, M., Topal, E.I.A., Obek, E. and Sasmaz, A. (2015) The Potential of *Lemna gibba* L. and *Lemna minor* L. to Remove Cu, Pb, Zn, and As in Gallery Water in a Mining Area in Keban, Turkey. *J. Environ. Man*, **163**, 246–253.

Sasmaz, A. and Obek, E. (2009) The Accumulation of Arsenic, Uranium, and Boron in *Lemna gibba* L. Exposed to Secondary Effluents. *Ecol. Eng.*, **35**, 1564–1567.

Sasmaz, A. and Obek, E. (2012) The Accumulation of Silver and Gold in *Lemna gibba* L. Exposed to Secondary Effluents. *Chem. Erde Geochem.*, **72**, 149–152.

Sasmaz, A. and Yaman, M. (2008) Determination of Uranium and Thorium in Soil and Plant Parts Around Abandoned Pb-Zn-Cu Mining Area. Commun. Soil Sci. Plant Anal., 39, 2568–2583.

Shanker, A.K., Cervantes, T.C., Loza-Tvera, H. and Avudainayagam, S. (2005) Chromium Toxicity in Plants. *Environ. Int.*, **31**, 739–753.

Singh, H.P., Mahajan, P., Kaur, S., Batish, D.R. and Kohli, R.K. (2013) Chromium Toxicity and Tolerance in Plants. *Environ. Chem. Lett.*, **11**, 229–254.

Sokal, R.R. and Rohlf, F.J. 1995. *Biometry: The Principles and Practice of Statistics in Biological Research* (3rd edn). W.H. Freeman and Co, New York, p 887.

Sood, A., Uniyal, P.L., Prasanna, R. and Ahluwalia, A.S. (2012) Phytoremediation Potential of Aquatic Macrophyte, *Azolla*. *Ambio*, **41**, 122–137.

Sree, K.S., Keresztes, A., Mueller-Roeber, B., Brandt, R., Eberius, M., Fischer, W. and Appenroth, K.J. (2015) Phytotoxicity of Cobalt lons on the Duckweed *Lemna minor* - Morphology, Ion Uptake, and Starch Accumulation. *Chemosphere*, **131**, 149–156.

- Suné, N., Sanchez, G., Caffaratti, S. and Maine, M.A. (2007) Cadmium and Chromium Removal Kinetics by Two Aquatic Macrophytes. *Environ. Pollut.*, **145**, 467–473.
- Tangahu, B.V., Abdullah, S.R.S., Basri, H., Idris, M., Anuar, N. and Mukhlisin, M. (2011) A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants Through Phytoremediation. *Int. J. Chem. Eng.*, **939161**, 1–31.

Tatar, S.Y. and Obek, E. (2014) Potential of *Lemna gibba* L. and *Lemna minor* L. for Accumulation of Boron from Secondary Effluents. *Ecol. Eng.*, **70**, 332–336.

Tchounwou, P.B., Yedjou, C.G., Patlolla, A.K. and Sutton, D.J.
(2012) Heavy Metals Toxicity and the Environment. Luch, A. In Molecular, Clinical and Environmental Toxicity, vol. 101, pp. 133–164. Basel: Springer.

Ucuncu, E., Tunca, E., Fikirdeşici, S., Özkan, A.D. and Altindag, A. (2013) Phytoremediation of Cu, Cr and Pb Mixtures by *Lemna minor*. *Bull. Environ. Contam. Toxicol.*, **91**, 600–604.

Uysal, Y. (2013) Removal of Chromium Ions from Wastewater by Duckweed, *Lemna minor* L. by Using a Pilot System with Continuous Flow. *J. Hazard. Mater.*, **263**, 486–492.

WHO. (2008) *Guidelines for Drinking Water Quality*. Geneva: World Health Organization.

Zayed, A., Gowthaman, S. and Terry, N. (1998) Phytoaccumulation of Trace Elements by Wetland Plants: L. Duckweed. *J. Environ. Qual.*, **27**, 715–721.