Li uptake, accumulation and effect on *Salvinia natans* macrophytes metabolism

Anamaria Iulia Török[1], Ana Moldovan[1,2], Erika Levei[1], Oana Cadar[1], Anca Becze[1] and Emilia Neag[1]

[1]INCDO-INOE2000, Research Institute for Analytical Instrumentation, ICIA Cluj-Napoca Subsidiary, 400293 Cluj-Napoca, Romania

[2] Technical University, Faculty of Materials and Environmental Engineering, 400641, Cluj-Napoca, Romania

E-mail: iulia.torok@icia.ro

Abstract

Lithium (Li) is a highly used element in electromobility and in other energy-storage manufacturing processes due to its excellent physical and chemical properties such as excellent conductor of heat and electricity. The use of aquatic plants for the uptake of Li from contaminated aqueous solutions and the production of Li-enriched biomass presents benefits for the circular economy. The aim of this study was to investigate the capacity of *Salvinia natans* macrophytes to uptake and accumulate Li from mono- and multielement aqueous solutions. The plants were exposed to various Li concentrations (10-50 mg/L Li as mono-, and 20 mg/L Cu, Zn, Cd and Li as multielement solution) for 7 days. The Li uptake and accumulation by the aquatic macrophytes metabolism was assessed by photosynthetic pigments, total protein contents, and antioxidant activity. The Fourier-transform infrared (FTIR) spectroscopy was performed to provide information on the plant's functional groups, after the Li treatments. The Li content in plants was determined to assess the synergistic or antagonistic interaction with the macro-and micronutrients from the growing medium

Aims:

The primary aim of our study was to develop an alternative method for the uptake of Li from aqueous solutions using *Salvinia natans* as live biofilter, and to study the accumulation of Li from mono- as well from multielement aqueous solutions (containing Li, Cu, Zn, and Cd) and to determine the induced stress effect in the *Salvinia natans* macrophyte metabolism.

Fig. 1. Aquatic plant *Salvinia natans*

Fig. 2. Batch experiments for Li uptake with mono- and multielement solutions using *Salvinia natans* aquatic plants

Materials and methods:

Aquatic plant: *Salvinia natans*

Acclimatization period: 3 days in modified Hoagland nutrient solution exposed to 10/14 h light/dark photoperiod, at room temperature, before the Li treatment

Li treatment: 7 days, plants kept in mono- (10-50 mg/L) Li, and in multielement solutions (20 mg/L Cu, Zn and Cd) along with the nutrients.

The experiments parameters: 2 g of plant material was added in 250 ml solutions at room temperature with 10/14 h light/dark photoperiod using LED lamps.

Sampling: For the macro- and microelements determination, the plant samples were washed with distilled water, oven dried at 65 °C, and grounded and digested with 5 mL 65% HNO_3 and 2 mL 30% H_2O_2

Macro and microelement determination: 5300 Optima DV (Perkin–Elmer, Waltham, MA, USA) Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) for macro and ELAN DRC II (Perkin–Elmer, Waltham, MA, USA) Inductively Coupled Plasma Quadrupole Mass Spectrometer (ICP-MS) for microelements.

Plant characterization:

-The photosynthetic pigments (chlorophyll a, -Chla and carotenoid- Car) were determined quantitatively using Thermoscientific NanaDrop One Spectrophotometer

-FTIR spectra, using Perkin Elmer BX II Fourier Transform Infrared Spectrophotometer

-Antioxidative capacity of the lipid soluble compounds (ACL) was determined using Analytik Jena PHOTOCHEM with photochemiluminescence

Experimental data analysis:

-Heatmap with hierarchical clustering dendrograms, in case of the plant's metal content

-Principal component analysis (PCA), to explain the variance of interrelated variables and to evaluate the correlation among the multiple characteristics of plants and the stress factors using stress markers, such as the photosynthetic pigments (chlorophyll a – Chla, carotenoid – Car), antioxidant capacity of the lipid soluble compounds and the plant N, C, H contents.

Results and Discussion:

- ***Salvinia natans* metal content after the Li treatments**

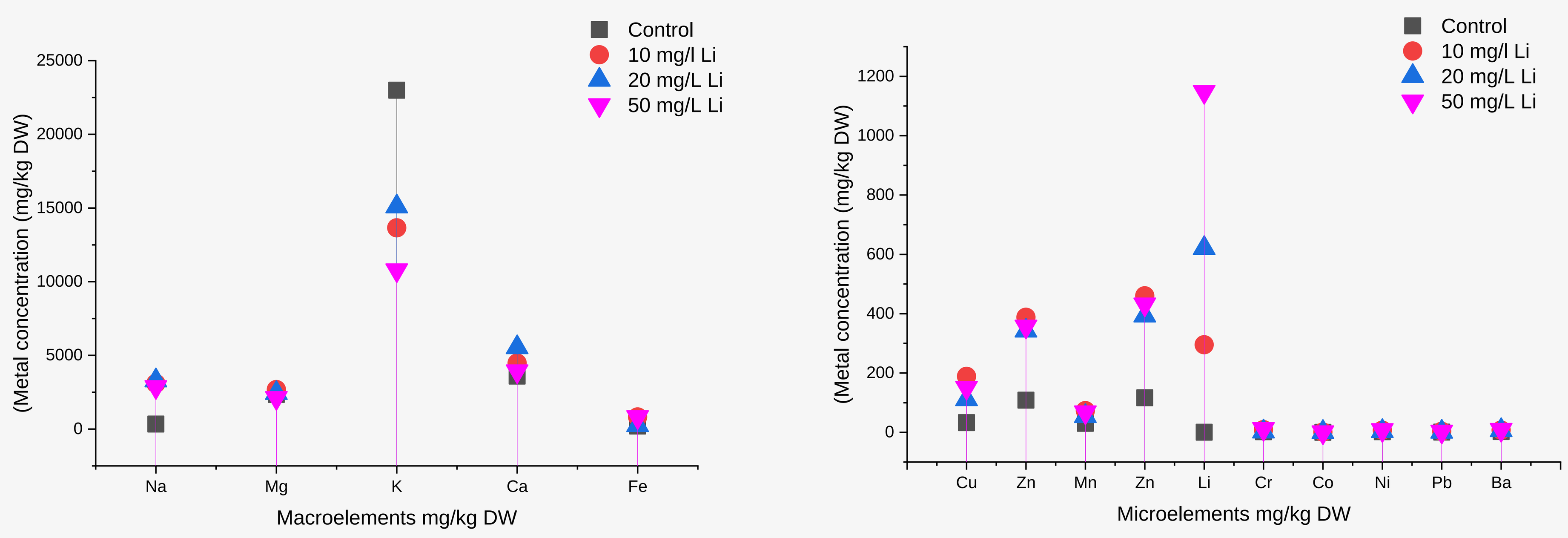

Fig. 3. *Salvinia natans* control and treated plants macro and microelement content after Li treatment using 10, 20, 50 mg/L initial concentrations

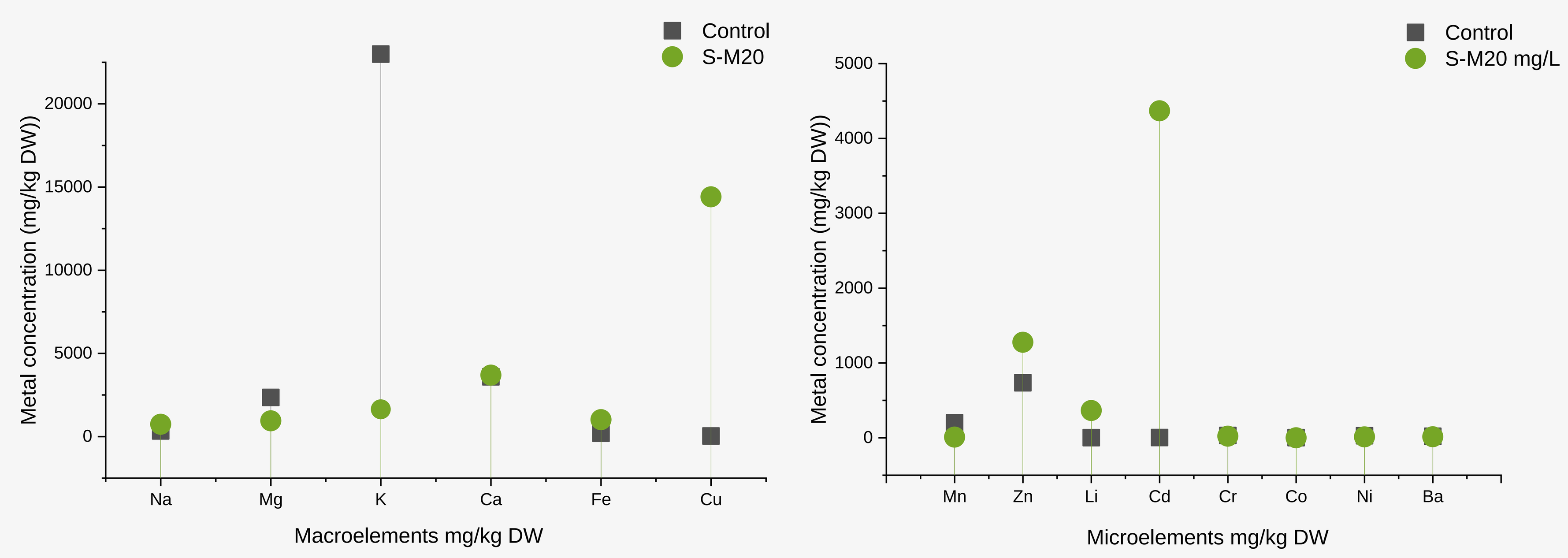

Fig. 4. *Salvinia natans* control and treated plants macro and microelement after the multielement treatment using a 20 mg/L Li, Cu, Zn, Cd) initial concentrations

- **Assessment of the Li treatments on the *Salvinia natans* metabolism through:**
  - photosynthetic pigments content
  - lipid-soluble antioxidant activity

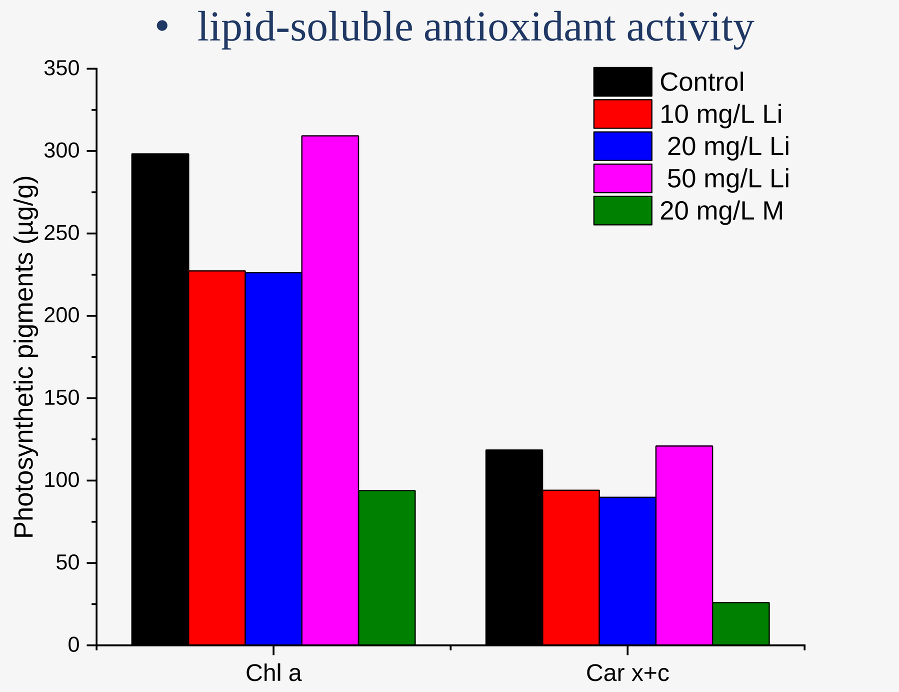

Fig. 5. *Salvinia natans* photosynthetic pigments content (Chla, Car) after the Li mono- (10, 20, 50 mg/L) and multielement treatment (20 mg/L Li, Cu, Zn, Cd)

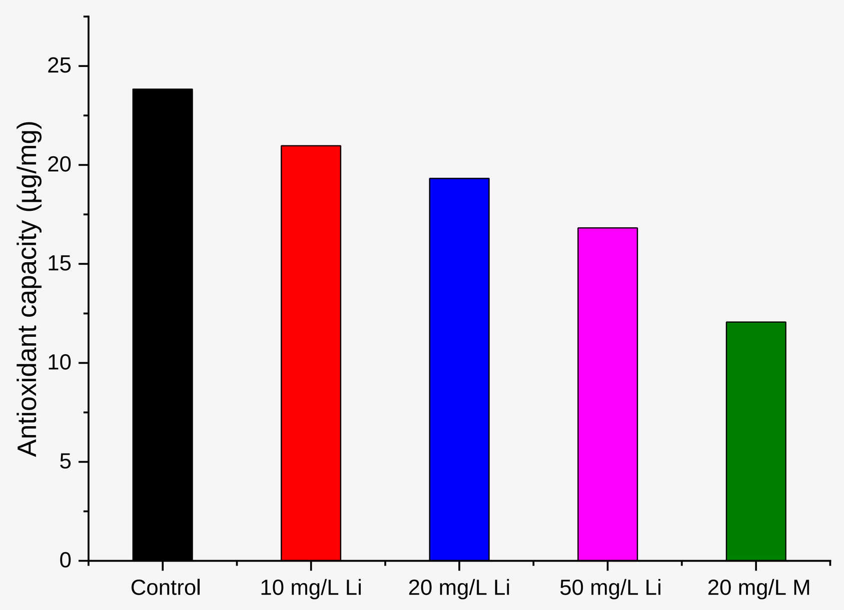

Fig. 6. Antioxidative capacity of the *Salvinia natans* lipid soluble compounds after the Li treatments.

- ***Salvinia natans* characterization after the Li treatment using FTIR analysis**

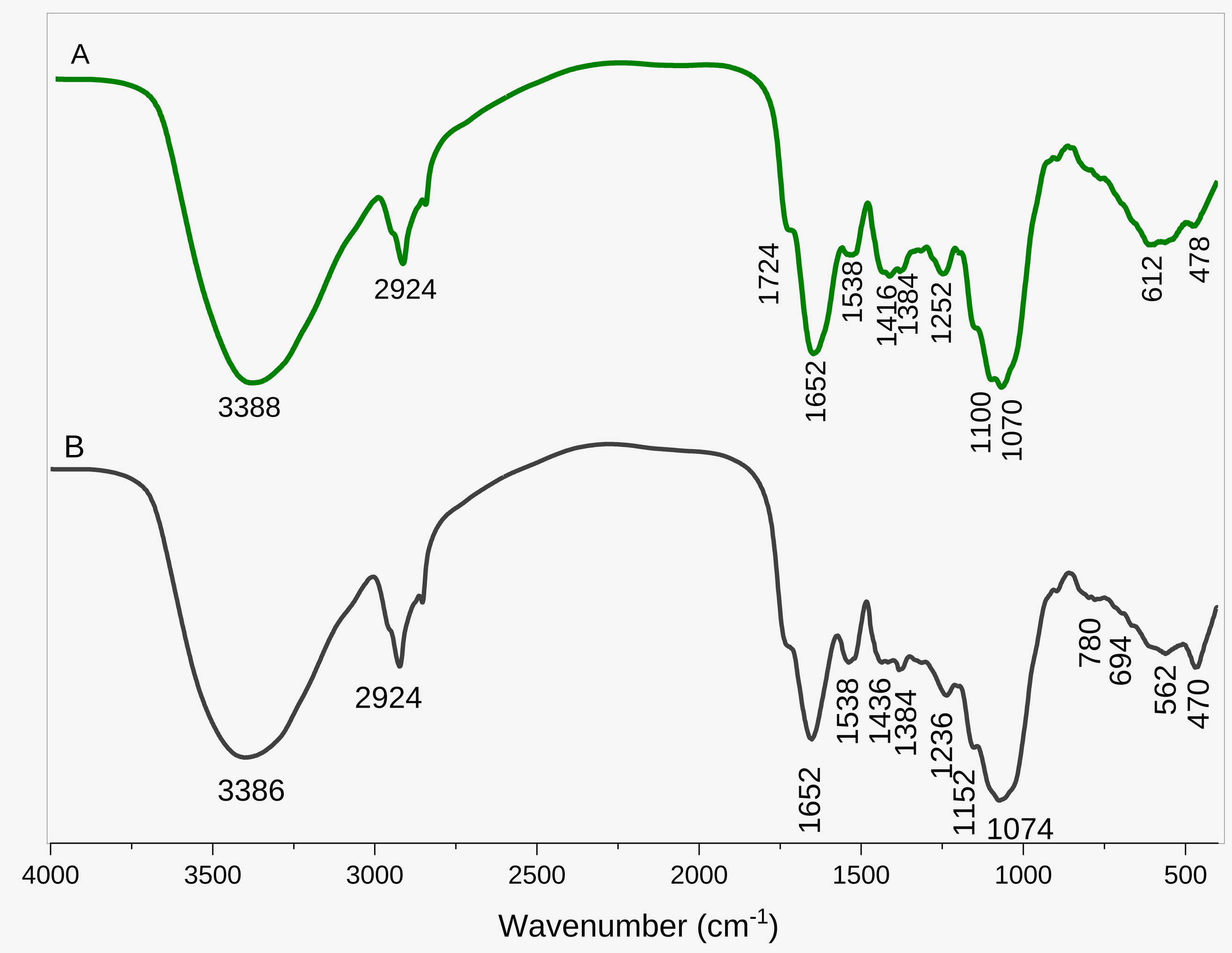

Figure 7. FTIR spectral features of *Salvinia natans* control plant (**A**), in comparison with the treated plant spectra (50 mg/L Li) (**B**)

- **Experimental data analysis using OriginPro (2019b):**
  - Heatmap with hierarchical clustering dendrograms
  - Principal component analysis

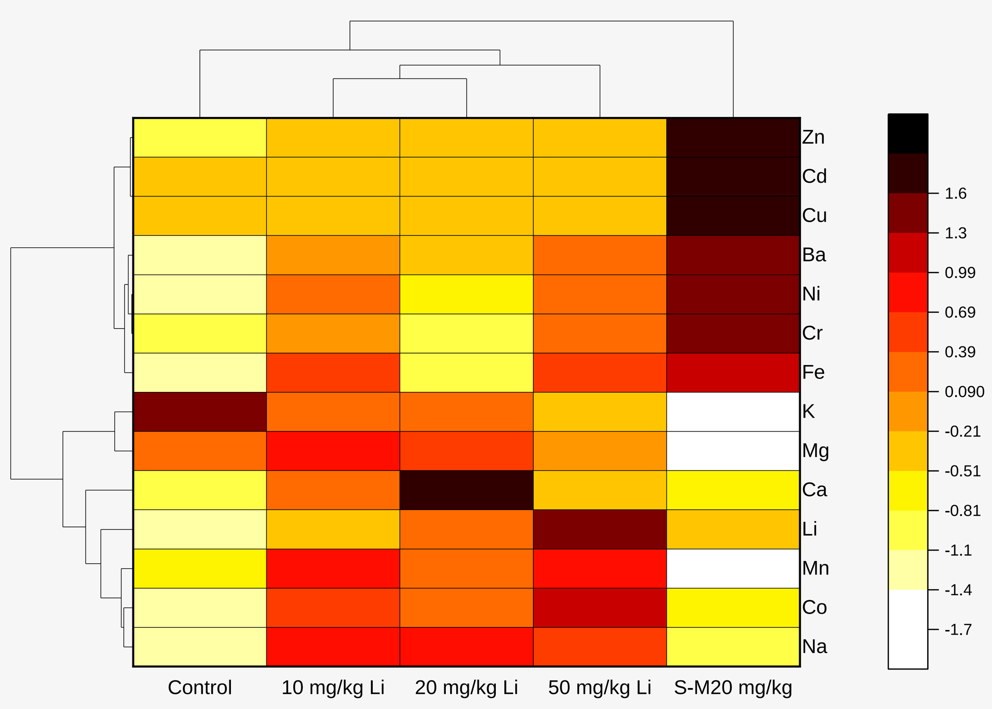

Fig 8. Logarithmic (Log10) values of the macrophytes's macro- and microelements presented in heatmap with hierarchical clustering dendrogram after the Li treatment in comparison with the control plant

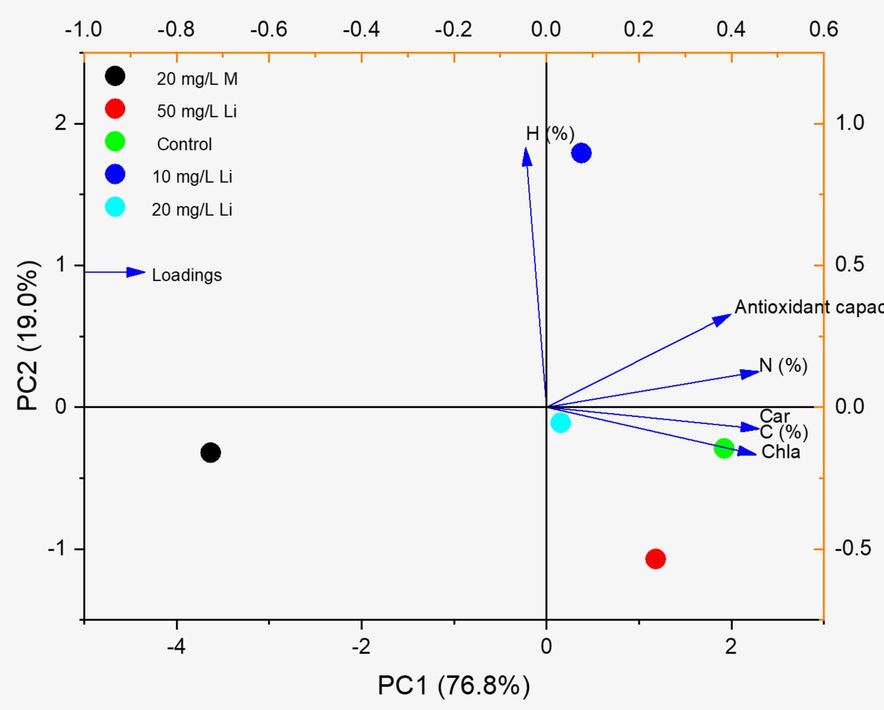

Fig.9. Principal component analysis of chlorophyll a (Chla) , carotenoid (Car), antioxidant capacity of lipid soluble compounds, N, C, and H contents after the Li treatment, in comparison with the control plant content.

Conclusions:

- The highest Li uptake was observed in case of the plants treated with 50 mg/L Li monolement solutions, which was 3 times greater than the 20 mg/L multielement treatment and 4 times higher than the 10 mg/L Li monoelement treatment.
- The multielement treatment (20 mg/L Li, Cu, Zn and Cd) induced a high K, Mg, and Mn loss in the treated *Salvinia natans* biomass, due to the competition between metals during the Li, Cu, Zn and Cd adsorption processes.
- The treated *Salvinia natans* generally showed a decreased photosynthetic pigment content, with the exception of 50 mg/L Li monolement treatments, where the chlorophyll a (Chl a) content was similar to the control plants value.
- The antioxidant capacity of the lipid soluble compound was quantified to determine the induced stress effect on the plant metabolism.
- The treated plants antioxidant capacity decreased with the increase of Li monoelement concentrations.
- FTIR analysis was performed to determine the functional groups involved in the Li adsorption process.
- The FTIR analysis showed shifted peak changes in the 1400 and 1200 cm^{-1} as well in the 1000-600 cm^{-1} domain

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