University of Pannonia
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Monitoring of the mobilization of heavy metal content of sediments, and the reduction of its heavy metal content with chemical and biological methods

THESES OF DOCTORAL (PH.D.) DISSERTATION

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Veszprém
2022

Content

INTRODUCTION

The Danube, as the largest river in Hungary, has significant industrial, logistical and tourist roles. Floodplains and backwaters along the coast also have a role as ecological corridors. It is well known that there are several industrial facilities from the source of the Danube to its estuary, the pollution of them has also had an impact on water quality in recent decades. The most dangerous components of the emitted pollutants are heavy metals, which can be present in both water and sludge. These elements mean a significant health risk as they are able to accumulate in the organisms within the food chain where they can exert their toxic, mutagenic, teratogenic or carcinogenic effects. Among these contaminants, some chemical elements (e.g. Cu, Zn) have essential physiological effects, but if they are predominant, they can become toxic.

In addition to the environmental risk in river sediments, it is important to mention the wide range of by-products, sludges, and slags from industrial processes, which also contain metal oxides or heavy metals. Within these metals, while some (e.g. Cd, Hg) are highly toxic, others (e.g. rare earths, Ni) could be reusable as a raw material for industrial processes in the future.

Wetlands, especially their sediments, can be storages of toxic elements and are therefore a potential source of environmental hazard. There are many chemical-physical and biological methods for their remediation. Among the biological methods, there are several phytoremediation procedures, such as phytovolatilization, rhizofiltration, phytostabilization, phytodegradation, and phytoextraction. In these processes, the metal accumulation capacity of plant species is used to remove contaminants from soils or water and sludge. The advantage of phytoremediation methods is that they are lower costs, natural, and therefore do not harm the environment. Several metal-accumulator plant species (e.g. *Brassicacee, Alyssum, and Thlaspi*) are now known.

Apart from bioremediation, a new area is bio (phyto) mining, during which continuous or induced phytoextraction were made by hyperaccumulative plant species (e.g. *Alyssum*, *Berkheya*) on mining dumps or soils with high toxic element concentration. Good results for nickel recovery have been achieved in Australia and France. From the roots of *A. bertolonii* up to 1.9-

7.7% Ni and from the shoots *B. coddii* 0.49% Ni can be detected. When its shoots were burned in a biomass furnace, the ash can contain up to 82% Ni crystalline metal, which can be efficiently recovered and sold as a raw material.

RESEARCH GOALS

One of my doctoral research aims was to determine the metal content of large and small watercourses and to assess the phytoextraction potential of the endemic plant species, which will promote more cost-effective biological treatment of contaminated areas in the future. When extracting metals by plants, it was also important to determine in which part of the plant (roots or shoots) the elements accumulate.

Other focus point of my research was the reduction of the high lead and zinc content of converter sludge, also using phytoextraction method and promoting the possibility of recycling the converter sludge into technology. Accordingly, I set the following goals:

1. Investigation of toxic elements of river sediments
2. Investigation of toxic elements of aquatic plants (and their parts) which are growing on river sediment
3. Reduction of lead and zinc content of converter sludge by phytoextraction
4. Performing synergy examination on river environment
5. Reducing the lead and zinc content of converter sludge by synergy.

EXPERIMENTAL METHODS

1. Sampling sites along the river Danube

Four sampling places were chosen along the river Danube: (H1) Rácalmás, (H2) Dunaújváros, (H3) Kisapostag and (H4) Dunaföldvár (Fig. 1.) The sampling sites were located from Rácalmás to Dunaföldvár. The sampling river section was between 1586,2-1560,6 river km. In the town, several types of industrial factories are working e.g. the steel company of ISD-Dunaferr Ltd., the Hankook Tire Hungary Ltd., and also the paper industries as Hamburger Hungaria Ltd., Vajda Papír Ltd. Many types of contaminants might be produced by these companies, although the sewage waters are cleaned, and the permissible limits of any contaminants are assessed and considered before reaching the effluents of the receiving water body. The final reservoir of the emitted sewage water is the river Danube.

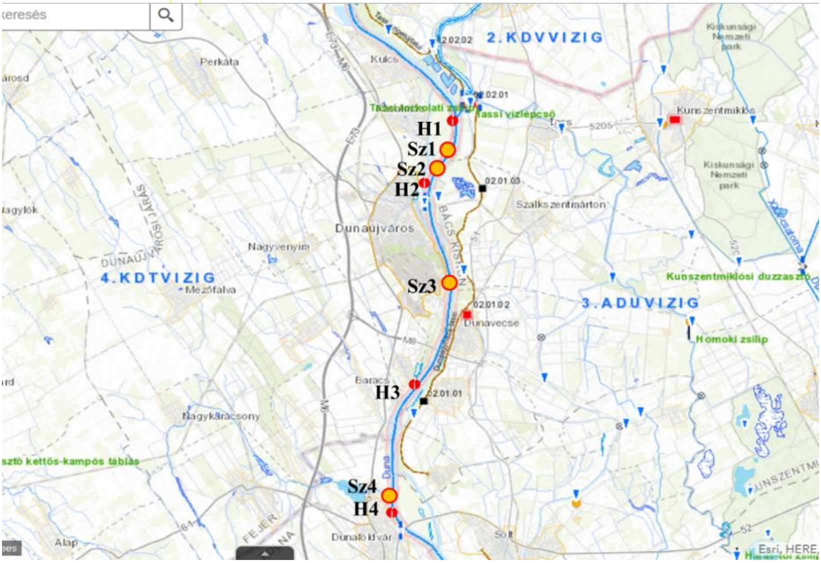

Figure 1. Sampling places along the river Danube

In Fig. 1 the orange points mean the communal or industrial sewage water plants (Sz1-Sz4).

1. Sampling sites in Veszprém

Sampling points in Veszprém were selected along the Békatói ditch which is located on the northern part of the town, along the “Házgyári Street” in Veszprém, Hungary (Figure 2). The estuary of this small creek is the middle part of Séd creek. Békatói-trench is a part of the surface drainage system of the town in which the sewage water of the northern industrial zone and the rainwater of Dózsaváros is flowing.

The toxic element content of Békatói-trench is probably due to the contamination of the nearby wastewater treatment plant. Other polluting sources can be the surrounding agricultural fields and gardens, the rainwater, which can be contaminated from the nearby industrial area, the Bakonyművek Ltd. and the nearby waste landfill at Csererdő, Jutas Car Wash and the illegal communal inlets.

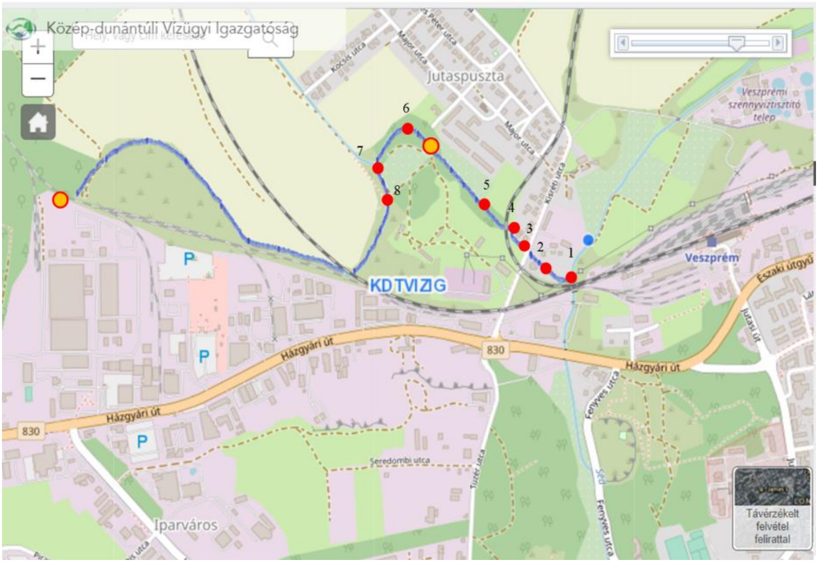

Figure 2. Sampling places along the Békatói-ditch

2. Sampling method of sediment and plant samples

Soil/sediment samples were collected from closest vicinity of each test-plants. Soil/sediments at locations were sampled from the upper horizon (0-10 cm). The sampling area was 1 m^2 in the case of each sample. Composite sub-samples were collected from 5-5 points along the two diagonals of using a stainless-steel soil sampler (Pürkhauer 5012 soil sampler). The total weight of the soil/sediment samples were between 790-870 gram/each individual plants. During transportation, they were stored at 4 °C.

In the case of plant samples, I collected 3-3 specimens from the 1 m^2 area designated for soil / sediment samples along the two diagonals, which I placed in a polyethylene bag and then provided with a sample identifier (date, location, plant type). Plant samples were stored at 4 ° C in a cooler bag during transport. In the laboratory, samples were washed with deionized water, and sediment / soil residues were removed from the roots. Then I measured the wet weight and the total length of the plant sample as well, and then cut the whole plant sample into its main parts (root, stem, leaf, flower). The samples thus obtained were dried to constant weight for acid digestion.

3. Extraction method of the toxic element from sediment samples

From 2019 instead of Heidolph rotary evaporator, I used a microwave digester (CEM Mars 6) to explore the metal content of the sediment samples. In the case of the microwave digester, it was sufficient to calibrate 0.5 g of dried and powdered sediment sample. To this I added 5 ml of hydrogen peroxide and 5 ml of concentrated nitric acid. I waited 15 minutes for the effervescence and gas evolution before sealing the Teflon container. According to the program, the extraction was made at 290-1800 W. The magnitude of the power depended on the number of samples to be extracted simultaneously (8-24). The Ramp time was 20 min, and the Hold time was 15 min. The samples were extracted at a constant 200 °C. After extraction, the samples were filtered, and their metal content was measured at five-fold dilution (2 ml sample + 8 ml distilled water + 0.1 ml yttrium internal standard) with Perkin Elmer Avio 200 ICP-OES (Figure 3).

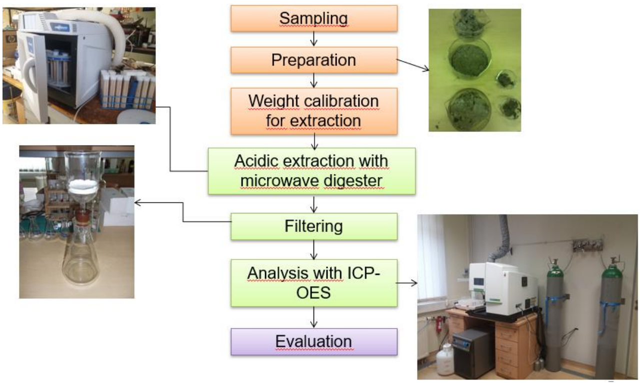

Figure 3 The steps of the extraction method for sediments/sludges

During the evaluation of data, the metal content of the sediment/sludge samples was compared to standard limits of "6/2009. (IV. 14.) KvVM-EüM-FVM Regulation".

4. Extraction method of the toxic elements from plant samples

The heavy metal content of the plant samples was also determined with concentrated nitric acid and hydrogen peroxide *(Simon, 2004; Szegedi, 2011)*. Prior to extraction, the main parts of the plant were rinsed with deionised water several times to remove sediment residues and other contaminants, and then dried to constant weight. After drying, the plant parts were cut into an average of 1 mm, and then 0.5 g of the sample was pre-treated in 20 ml of concentrated nitric acid for 12 hours at room temperature (20 ± 2 ° C).

From 2019 instead of the rotary evaporator, I used a microwave digester (CEM Mars 6) to digest plant samples. After the pre-treatment, the plant samples were transferred to a Teflon vessel and 5 mL of hydrogen peroxide was added. According to the program with the device, the destruction happened at a power of 290-1800 W, depending on the number of samples (8-24) at the same time. The Ramp time was 20 min, and the Holding time was 10 min. The samples were extracted at a constant 200 °C. After extraction, the solutions were filtered, and their metal content was measured at five-fold dilution (2 ml sample + 10 ml distilled water + 0.1 ml yttrium internal standard solution) with Perkin Elmer Avio 200 ICP-OES (Figure 4).

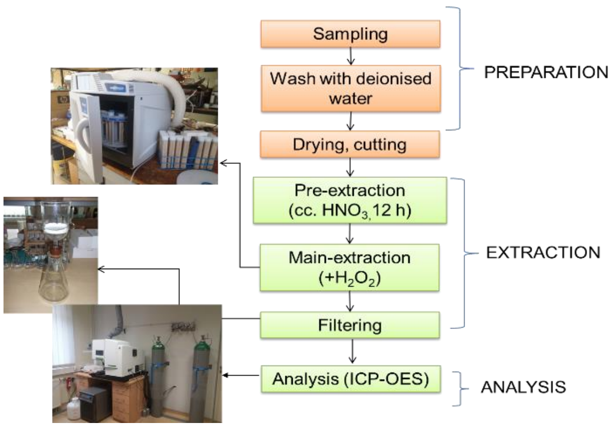

Figure 4 The steps of the extraction method for plant samples

The toxic element content of the plant samples was compared to the limit values of the related references *(Simon, 2004; Szegedi, 2011)*.

5. Steps of the seedling growth test

Seedling growth test was made by using white mustard seeds *(Sinapis alba L.)* as test plants according to MSZ 21 976-17:1993 Hungarian standard. For these experiments, 10 g dried sediment/sludge samples were calibrated into Petri dishes. After setting the moisture content 20 seeds were taken on the top of the samples. The Petri-dishes were covered and incubated for 72 hours at 20 °C in a dark place. At the end of the experiment the number of the germinated seeds and the length (mm) of radicles and plumules were counted (Fig. 5).

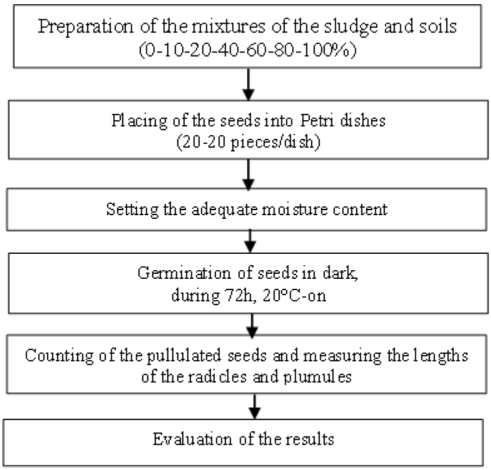

Fig. 5 The main steps of the seedling growth test

6. Laboratory planting experiments

During the experiments, I grew perennial rye-grass, wheat, basil, tagetes and winged tobacco with a plant-growing light shelf I designed. I chose a mixture of converter sludge and loess and biohumus soil.

The pots were filled with 540 grams of sludge/soil mixture according to the sludge mixing ratio (5-10-15-20%). Both the soil and the sludge were dried to constant weight. I planted the seeds to an average depth of 1 cm. The light shelf was timed with 11 hours of lighting based on the number of hours in the spring sun. The average temperature in the room was 21 °C (± 1.5 °C), the relative humidity varied between 35-42%. The average pH of the soil/sludge mixtures changed between 5 to 6.5 which was measured by the X4-Life soil tester. Watering was done twice a week, from below, the average duration of a plant growing experiment was 60 days.

7. Pollution load index (PLI)

The sediment contamination for metals was calculated of using the pollution load index (PLI).

$$\mathrm{PLI} = \frac{\mathrm{c_{sediment}}}{\mathrm{c_{reference}}}$$

where $c_{sediment}$ was the metal content of the river sediment, $c_{reference}$ was the metal content of the bottom sediment, which was determined at the site of S4. The metal content of loamy (yellow) soil was also used as $c_{reference}$. Loamy soil is the dominant soil type of the bank of river Danube at the studied sites. *(JDS3 2015; Khan et al. 2008).*

8. Factors for determination of phytoremediation potential

A. Bioaccumulation Factor (BAF)

Bioaccumulation factor (BAF) was calculated to determine the ratio of metal concentration in the plant shoots (stems and leaves) to sediment:

$$BAF = \frac{c_{shoots}}{c_{sediment}}$$

where C_{shoots} is the total metal concentration in the plant (leaves, stems) and $C_{sediment}$ are metal concentrations in the river sediment *(Lago-Vila et al. 2015; Mehr et al. 2020).*

B. Translocation factor (TF)

Metal concentrations in the sediment and plant samples were calculated on a dry weight basis. The translocation factor (TF) was estimated as the ratio between the metal content (mg/kg) in shoots of the test plants (C_{shoots}) to the roots (C_{roots}):

$$TF = \frac{c_{shoot}}{c_{root}}$$

Where c_{shoot} were calculated from the metal content of the plant-parts, grown above the surface. *(Baker and Brooks, 1989; Lago-Vila et al. 2015, Khan et al. 2008; Mehr et al. 2020).*

RESULTS

I. Reduction of heavy metal content of river sediment by phytoextraction method

Thesis 1

I confirmed that the heavy metal content of river sediment can be reduced by natural plant vegetation. Examining the phytoextraction potential of the selected six plant species, it can be stated that:

a. Based on the highest Bioaccumulation Factor (BAF) values the most suitable plant for chromium accumulation was parella (2.56); for lead uptake was water mint (9.29); for the accumulation of nickel was bistort (7,7); for zinc uptake was beggarticks (2.18) and for the accumulation of copper was creeping ivy (5,56).

b. Based on the highest Translocation Factor (TF) values, water mint was capable of translocate most of the metals into its upper parts (6.7-103.5). Examining the translocation ability as a separate element the most suitable plant was beggarticks (12.25) for Cd, bistort (9.52) for Cr, water mint (103.5) for Pb, the parella (10.73) for Ni, and water mint (6.69) for Zn.

Thesis 2

Based on my field experiments, I found that the heavy metal content of river sediments can be reduced with crops.

a. The average reduction rates measured in the sediment per element were as follows: Ni: 35-67%, Cu: 2-62% and Zn: 16-28%.

b. The test plants accumulated most of the heavy metals in their roots (TF <1).

c. In this type of contamination, elements accumulated from the sediment into radishes and green peas can mean a risk to children's health.

II. Reduction of heavy metal content of industrial sludge by phytoextraction method

Thesis 3

Based on the germination results of white mustard seeds, I determined that loess and chernozem are the best soil types for the disposal of converter sludge.

a. In the case of 20-40% converter sludge/soil mixture the germination rate was between 70-95%.
b. In the case of 20 % mixing ratio of converter sludge and loess soil, the root and stem lengths were 1.8 times and in the case of chernozem soil 1.1 to 2.7 times higher than in the case of 100% soils.

Thesis 4

The lead and zinc concentration of converter sludge and loess soil mixtures can be effectively reduced by phytoextraction. The reduction rates are:

- With wheat planting: Pb: 40-67%, Zn: 53-73%
- By planting perennial ryegrass: Pb: 16-57%, Zn: 8-55%
- With basil: Pb and Zn: 41%
- With winged tobacco: Pb: 53%, Zn: 51%
- With French marigold: Pb and Zn: 58%

III. Synergy experiments

Thesis 5

During the laboratory experiments I investigated that the accumulation of Pb and Zn within both wheat and perennial ryegrass increases in synergy.

a. The average lead accumulation increases by 80 to 85% for ryegrass and 34 to 48% for wheat.
b. The rate of zinc accumulation increases by 48% in ryegrass and 45% in wheat in case of synergy.
c. The accumulation place of these two toxic elements was mainly the root system. The distribution ratio of the elements between the root and the leaf does not change significantly in case of synergy.

Thesis 6

In the case of the coexistence of bistort and coastal sedge, rooted in a riverside environment, the metal accumulation capacity of bistort decreased by 2-10% and that of sedge by 5-37%, depending on the element.

a. As a result of coexistence, the accumulation place of heavy metals in the test plants shifts towards the upper plant parts (upper stem, leaf, flower).
b. The translocation factor (TF) increases on average 1.5 - times in bistort and 2 - times in sedge in synergy.

PUBLICATIONS

Publications in direct relation to the PhD dissertation

(1) Kovács-Bokor, É.; Domokos, E.; Biró, B. (2021): *Toxic metal phytoextraction potential and health-risk parameters of some cultivated plants when grown in metal-contaminated river sediment of Danube, near an industrial town;* ENVIRONMENTAL GEOCHEMISTRY AND HEALTH 43 : 6 pp. 2317-2330., 14 p.

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(3) Kovács-Bokor, É.; Domokos, E.; Kiss, E. (2019): *Effect of industrial sludge-soil mixtures on germination of white mustard and wheat;* JOURNAL OF APPLIED TECHNICAL AND EDUCATIONAL SCIENCES, 9: 1 pp. 66-78., 13 p.

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(4) Kovács-Bokor, É. ; Kiss, E. (2021): *Vízparti növények nehézfém-akkumulációjának meghatározása a dunai üledékekben;* In: Nagy, András; Németh, István Péter; Czifra, Sándor (szerk.) Anyagtudományi terek; Dunaújváros, DUE Press, pp. 85-101., 17 p.

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