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LITHIUM AND HEAVY METAL CONCENTRATION ANALYSIS IN SAJÓ VALLEY

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Abstract *The Sajó valley was a blooming industrial area 20-25 years ago, but in the early 1990s most of the factories closed down, but relatively little attention was paid to the pollution left behind. The Green Action Association carried out a comprehensive monitoring of the Sajó Valley in the early 1990s. This gave us the idea to carry out our work, as significant heavy metal and lithium pollution was found in the areas surveyed. It is very likely that this was mainly caused by heavy industry from the 19th century until the 1980s. Our aim was to investigate how the lithium and heavy metal contamination might be found in some of the areas studied by the association more than 20 years later. Six areas were selected as study sites for the soil samples, between Ónod and Muhi (3 areas) and near Tiszaszederkény and Tiszagyulaháza (3 additional areas). Our soil samples were collected from the floodplains of the Sajó, Hernád and Tisza rivers at a depth of 0-40 cm. After proper storage, we started the analysis by preparing and digesting the samples.The pH-value and dry matter content of the sieved (2 mm) samples were determined. Digestion of the finely sieved samples (0.45 mm) with nitric acid using a Milestone 1200mega microwave digestion system allowed the samples to be analyzed with an "ATI UNICAM 939 AAS" atomic absorption spectrometer for seven elements: cadmium, copper, zinc, lead, manganese, iron and lithium. The results of the measurements were converted to mg/kg dry matter. The results obtained showed that there are still areas where some elements, such as Cd, are contaminated above the limit values (Joint Decree 6/2009 (IV. 14.) of the Ministry of Agriculture, Forestry, Environment and Water Management). The measured pH values are slightly alkaline and slightly acidic, which means that the contaminants are immobile in the soil. Statistical evaluation was performed by use of the three-factor random block analysis variance method using SPSS 14.0 for Windows software package. After performing analysis of variance, it was shown that the heavy metal content of soil samples was significantly related to the sampling location. Based on the data obtained in our work, we propose to carry out a study of similar magnitude to the monitoring carried out in the 1990s and to clean up the contaminated soils*

Keywords: *Lithium, Heavy metals, Heavy Industry, Soil contamination*

INTRODUCTION

We often hear: protecting the environment is also protecting future generations [1]. But to imagine, influence and shape the future without knowledge of the present is a futile attempt. It is therefore not surprising that the collection of data on the state of the environment is as old as the birth of environmental protection [2].
Nowadays, as pollution becomes more widespread, more and more are being said about potentially toxic substances and more and more attention is being paid to the hazards associated with heavy metals. Industrial installations in favorable geographical locations and mineral-rich areas have been producing and releasing pollutants into the immediate environment in an uncontrolled manner for centuries. Scientific research and new technological tools are increasingly enabling us to assess and evaluate these pollutants [3].

In this paper, we focus on the heavy metal and lithium pollutions concentrated in the Sajó valley over decades by the heavy industry of Borsod-Abaúj-Zemplén county. The Sajó valley was a flourishing industrial region 20-25 years ago, but in the early 1990s most of the plants were closed down. But the soil contamination left behind has hardly been dealt with.

The heavy industry is a part of the industry. Basically, it produces those type of products, which are not necessary for everyday consumption, but also durable ones, and produce other products, which are necessary to produce machines. Low labor demand and substantial energy, raw materials and capital requirements are characterized. The „heavy" word refers to the weight of the final product (mechanical engineering) and complexity of the production of (chemical industry) as well [4].

The North Hungarian Chemical Company in Sajóbábony was started in the late 1940s. Until the 1950s, the factory produced mainly military products and explosives, and later pharmaceutical and pesticide active ingredients, chemical raw materials and polyurethane foams [5].

In 1965, the production of active battery masses was started, the only technology of the factory that determined the cadmium contamination of the Sajó and even the Tisza.

According to a 1974 study, 13 tons of cadmium were being discharged into the Sajó every year during that period.

Most of the cadmium that entered the river settled out and became embedded in the bottom sediment, which was mobilized by the tidal waves and spread the contaminated sediment in the lower stretches of the river.

The polluting part of the plant was closed down in 1998, but the cadmium deposited in the Bábony stream and in the factory's sewage system continues to pollute the Sajó.

The Ózd steelworks produced pig iron, steel and rolled products. The company's effluent was discharged into the river Sajó via the Hagony stream, causing significant heavy metal pollution. The Borsodnádasd sheet metal factory had a history of almost 130 years before its closure, where it was mainly engaged in the production and metal coatings. The company's waste water was not treated until 1975, when it was discharged into the Hódos stream and from there via the Hangony stream into the Sajó. Construction of the factory began in the 1950s, formerly known as Borsod Chemical Combine [6].

Until the 1970s, the factory's plants discharged their effluents untreated into the Sajó river due to a lack of environmental controls. The company came to the center of attention mainly because of the small amount of mercury discharged during the production of large quantities of chlorine gas and caustic soda, and the chlor-alkali electrolysis plants which caused significant pollution over the years. Some 850 tons of mercury were removed from the three plants in the period 1963-1989, from which mercury-containing effluents were discharged untreated into the River Sajó until the late 1970s. According to WHO/UNDP/OVH Water Quality Protection Project studies, approximately 1.7 tons of mercury were discharged into the river with these effluents in 1974. The plant started operations in 1960. It mainly discharged pollutants, which have been significantly reduced by the environmental protection measures introduced in the meantime.

According to the available data, the heavy metal pollution of Tisza Chemical Group [7] is not noteworthy.

The plant started operations in 1960. It mainly emitted pollutants, which have been significantly reduced by the environmental protection measures introduced in the meantime. According to available data, Tisza Chemical Group's heavy metal pollution is not important. Iron metallurgical plant which from 1989 operated under the name DIMAG RT [8].

After its privatization in 1991, it was split into 30 different legal entities, after which the plants went bankrupt and then merged under a government decision as another name (DNM Ltd.). The company's wastewater, which also contains heavy metals, is discharged into the Sajó river via the Sinava stream.

4 December Wire Works was a steelwork producing high-strength steel wire and stranded steel wireproducts. As a result of this production technology, the process effluents, surface preparation sludges were largely contaminated with zinc, lead, iron and to a lesser extent chromium, nickel and cadmium. Prior to 1987, the effluents were discharged into the Sajó after minimal treatment and neutralization. During this period, the company was the most significant heavy metal polluter of the Sajó.

Heavy metal contamination [9] in the Sajó Valley was brought to our attention by the Green Action Association [10] when the so-called "mercury scandal" broke out on 23 August 1990, and in December 1990**,** the association drew up a program to investigate heavy metal contamination in the area. A map of the contamination in the area was completed in 1992, and has been available to us ever since, providing a good

basis for examining the topicality of the issue.
Our aim was to assess the concentration of some heavy metals (Zn, Mn, Fe, Cu, Pb, Cd) and lithium in the soil of part of the area. Our work was divided into two main areas, the floodplain of the Hernád and Sajó rivers between Ónod and Muhi and the floodplain of the Sajó and Tisza rivers between Tiszagyulaháza and Tiszaszederkény.

MATERIALS AND METHODS

Soil sampling principle

Sampling is the collection of a sufficient number of samples from a typical soil section or from individual levels or layers of soil for laboratory analysis. Soils vary in their horizontal and depth extent even over small areas. This means, that it is not possible to classify a large area on the basis of the results obtained by point sampling and analysis. A basic rule for the selection of sampling sites when investigating soils is that they should be representative of the soil or area for which the results are to be used [11].

Sampling of linear emission areas

Sampling is the collection of a sufficient number of samples from a typical soil section or from individual levels or layers of soil for laboratory analysis. Soils vary in their horizontal and depth extent even over small areas. This means, that it is not possible to classify a large area on the basis of the results obtained by point sampling and analysis. A basic rule for the selection of sampling sites when investigating soils is that they should be representative of the soil or area for which the results are to be used [11].

Sampling of linear emission areas

For the heavy metal analysis of floodplain sediments, the standard MSZ 21470-1:1998 was used. According to the standard methods, the "banded sampling system" (Figure 1) was used for sampling. According to the standard, rectangular sampling grids should be established at 5, 10, 20, 50 m distances from linear pollutant sources. The intersection of the diagonals of a given rectangle best represents that rectangle, so this is where we took our soil samples on both sides of the rivers.

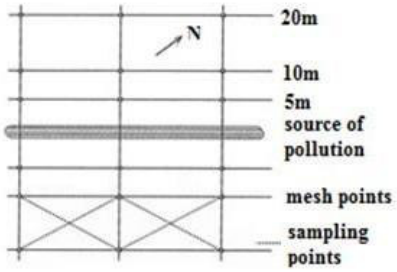

Figure 1. Band sampling system [12]

Other small area sampling

After the sampling units have been selected, the soil grid should be drawn on a sketch. A minimum of 4-6 sampling units is recommended, so that 8-12 average samples can be obtained. The average samples are obtained by taking 20 to 20 right and left transects along the diagonals of the quadrilaterals for surface sampling [12].

Field sampling

Our samples were collected in two transects in the Sajó valley in Borsod-Abaúj-Zemplén county in northern Hungary. Firstly, in the area bounded by Ónod - Muhi - Sajóhídvég, approximately 14 km as the crow flies from Miskolc. Within this, 3 smaller areas were identified (Figure 2). The River Sajó (area 1), River Hernád (area 2), River Sajó after the Hernád inlet (area 3). It was designed using the Google Earth program:

Figure 2. Sampling areas (areas 1 to 3)

The sampling grid we constructed is a stretched rectangular grid with grid points spaced 5, 10, 20, and 50 m from the river on either side of the river. The distance between adjacent mesh points is 30 m (Figure 1.).
The sampling points are red marked, and their GPS coordinates were read using the Google Earth program (Figure 2. and 3.). Soil samples were taken at the sampling points with the sampler at a depth of 0-40 cm. The excavated soil was placed into a plastic bucket and a 1 kg average sample was taken according to the standard and placed in a labelled plastic bag. The bagged soil samples were kept in a cool place until laboratory work.

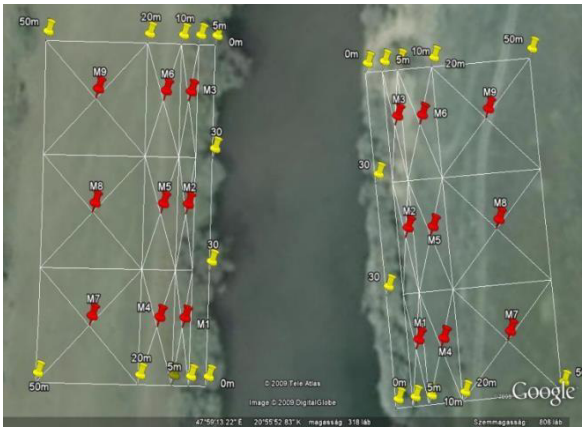

Figure 3. Sampling grid in Google Earth

Preparation of soil samples

The collected soil samples were cleaned from stones, plant parts and roots and poured into plastic containers and dried in the laboratory for one week at room temperature. The resulting "air-dry" soil samples were pulverized in a pestle and mortar and sieved through a sieve with a 2 mm mesh to obtain a sample of approximately 150 grams. The resulting sample was further sieved through a 0,2 mm sieve. Samples of around 50 grams were placed in small paper bags, numbered and stored in cardboard boxes.
Then, approximately 5 g of the soil sieved through a 0.2 mm sieve was weighed into weighing bottles for the determination of the absolute dry matter content according to standard MSz-08-0205-1978. The samples were dried in a drying oven at 105 ºC to constant weight.
The % dry matter content of the soil samples was calculated according to the following formula: n=(v/b)*100
Where: n= dry matter %, v=mass of the soil dried at 105 ºC (g), b=mass of air-dried soil (g)

Measurement of soil pH

The measurement was performed according to the standard MSZ-08-0206/2-1978. [13] 6 grams of each air-dry soil sample was weighed on a dial balance and 15 ml of distilled water or 15 mL of 1 mL potassium chloride solution was added to the samples in the test tubes and the samples were mixed thoroughly. The

samples were left to stand for 12 hours in the cork-film sealed tubes and then measured with a Corning NE 1604 pp3 pH meter set to a so-called two-point calibration.

Digestion of soil samples with a Milestone 1200 mega microwave digestion device

Procedure for digestion: 0.5 g of soil was measured from the air-dry soil samples into Teflon bombs, then 5 ml of 65% nitric acid and 2 ml of 30% hydrogen peroxide were added. The samples were then allowed to stand for half an hour, and the bombs were sealed and placed in a Milestone 1200 mega in which the program according to Table 1 was set.

Table 1. Program of digestion

Number of steps	Requires time	Operation
1.	5 minutes	Digestion, 250 Watt
2.	2 minutes	Ventilation
3.	5 minutes	Digestion, 400 Watt
4.	5 minutes	Digestion, 250 Watt
5.	7 minutes	Digestion, 700 Watt
6.	5 minutes	Ventilation

After destroying, the samples were cooled in a water stream for half an hour and then opened in a gas mask in the open air. The liquid from the Teflon bombs was filtered through a funnel and 0.45 μm pore size filter paper into 25 mL flasks and filled to the mark with deionized water. After homogenization, the solutions were transferred to plastic containers and stored in the refrigerator until measurement.

Determination of the concentration of the elements under test using a UNICAM 939 atomic absorption spectrometer

Emission mode (to measure the concentration of lithium ions)

Flame photometry is a branch of emission spectroscopy where the sample is excited by the thermal energy of a flame at an appropriate temperature. It exploits the phenomenon that excitation of certain elements with low excitation energy is possible at hot flame temperatures.

The solution under test is injected into the flame in the form of an aerosol by means of high-pressure gas atomization. The temperature of the flame must be high enough to ensure the evaporation, atomic dissociation and excitation of the solid after the solvent has evaporated; temperatures of 2000-3000^{o}C. However, the flame temperature must not be so high that metal atoms with low ionization energy are highly ionized, because this will reduce the emission of the substance. The excited elements emit a characteristic linear or banded spectrum in the flame. Linear flame colors are produced by the excited atoms (e.g. alkali metals), while banded flame colors are produced by the molecules (e.g. alkaline earth oxides).

By spraying the solution under test into the flame at a constant velocity, the intensity of the wavelength emission characteristic of each element can be used to infer the concentration of the substances, as the emission depends on the number of atoms excited. If we know the relationship between emission and concentration, i.e., the credibility function, the concentration can be calculated from the measured emission [14]. In my measurements, I first prepared a series of calibration solutions containing the element to be measured, 4-5 depending on the element. In all cases, distilled water was used as the blank solution. After preparing these, the wavelength characteristic of lithium (Li: 670.8 nm) was set on the machine.

Atomic absorption mode (to measure the concentration of the heavy metal under test)

In the single light path setup, the light from the cathode lamp passes directly through the atomizing field and enters the detector after the monochromator. In this arrangement, the measurement starts by setting the initial light intensity I_o. During the measurement, the reduced light intensity I due to atomic absorption is compared to this initial value I_o. The absorbance measured in this way is can be calculated using the formula [15]:

$$A = \lg \frac{I_o}{I}$$

In our measurements, we first prepared a series of calibration solutions containing the element to be measured, 4-5 depending on the element. In all cases, double distilled water was used as the blank solution. After preparing these measurement procedures, we set the wavelength of the elements on the machine. Theseare Zn: 213.9 nm., Cd: 228.9 nm., Pb: 217.0 nm., Mn: 279.5 nm., Cu: 324.8 nm., Fe: 252.3 nm.

RESULTS AND DISCUSSION

We have divided the area into left (B) and right (J) sides according to the course of the rivers. The letter "M" was used to mark the samples. They are numbered from 1 to 9. According to the results of the pH measurements (Table 2.) of the soils, most of the samples are neutral, some of them are weakly acidic and some are weakly alkaline at the time of analysis. The measured pH values indicate that the mobilization of heavy metals is low.

Table 2. pH values (MSZ-08-0205:1978): [13] at the time of soil sampling, weakly alkaline and weakly acidic, therefore heavy metals were not mobile in the soil

	pH average	
	KCl	H_2O
max	7.61	7.805
min	5.66	6.315

The statistical analysis of the data is intended to answer the following question:
1. Does the concentration of the soil samples depend on the location of the sampling site along the river? (X factor)
2. Does the concentration of soil samples depend on the distance of the samples from the river (perpendicular to the river)? (Y factor)
3. Does the concentration of soil samples in the samples depend on their location parallel to the river (see sampling grid)? (Z factor)
The answers to these questions were sought using a three-factor random block design analysis of variance and the analysis was performed using the program "SPSS FOR WINDOWS 14.0" at P=5%. The factors of analysis of variance were as follows:
Factor X: twelve levels of the right and left bank of the Sajó, the right and left bank of the Hernád, the right and left bank of the section after the inflow of the Sajó Hernád, the right and left bank of the Tisza, the right and left bank of the section before the inflow of the Sajó into the Tisza, the right and left bank of the section of the Tisza where the Sajó has already flowed into the Tisza.
Y factor: three levels 5 m-10 m- 20 m
Z factor: three levels 0m-30 m-60 m
The values measured by the GA [15] in 1992 are not comparable with our results, as the average samples were formed differently (the GA [15] averaged samples taken at a depth of 0-60 cm), but they are indicative. Our analyses were carried out from average samples of soil samples taken to a depth of 0-40 cm.

Lithium concentration measures in soil samples

According to Figure 4. the average lithium content in Area I is 11.96 mg/kg of dry matter weight (hereinafter d.w.). There is no contamination limit for lithium in soils. The average lithium content of the samples taken from the right bank of the river is 11.71 mg/kg d.w. The average lithium content of the samples taken from the left bank of the river is 12.20 mg/kg d.w. The average lithium concentration in the GA [15] soil samples taken at Ónod was 10.62 mg/kg d.w. The average lithium content of the samples taken from the right bank ofthe river was 25.66 mg/kg d.w. The average lithium content of the samples taken from the left bank of the river was 25.28 mg/kg d.w.
The average lithium content of the samples from the right bank of the river is 24.20 mg/kg d.w. The average

lithium content of the samples from the left bank of the river is 23.10 mg/kg d.w. The average lithium concentration of the ZAE soil samples taken at Muhi was 10.75 mg/kg d.w. The average lithium content of the samples taken from the right bank of the river was 9.84 mg/kg d.w. The average lithium content of the samples taken from the left bank of the river was 5.01 mg/kg d.w. The average lithium content of the samples taken from the right bank of the river is 23.24 mg/kg d.w. The average lithium content of thesamples taken from the left bank of the river is 21.71 mg/kg d.w. Average lithium content in Area VI: 36.56 mg/kg d.w. Average lithium content in samples from the right bank of the river: 35.32 mg/kg d.w. Average lithium content in samples from the left bank of the river: 37.80 mg/kg d.w.

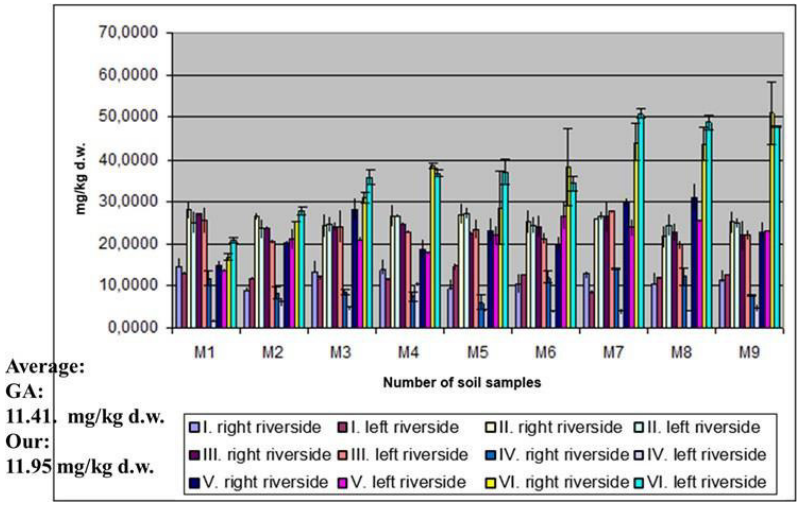

Figure 4. Lithium concentration in the soil samples tested

Cadmium concentrations measured in soil samples

Figure 5. shows that the average cadmium content in Area I is 8.21 mg/kg d.w. The contamination limit for cadmium in soils is 1 mg/kg d.w. according to Joint Decree 6/2009 (IV. 14) [16] of the Ministry of Agriculture, Forestry, Environment and Water Management, which was exceeded in all (18) samples. The average cadmium content of the samples taken from the right bank of the river was 6.20 mg/kg d.w. The average cadmium contentof the samples taken from the left bank of the river was 10.21 mg/kg d.w. The average cadmium concentration of the GA [15] soil samples taken at Ónod was 6.21 mg/kg d.w.

The average cadmium content in Area II was 5.74 mg/kg S.A. All samples (18 samples) exceeded the contamination limit for cadmium in soils. The average cadmium content of the samples from the right bank of the river was 6.04 mg/kg S.A. The average cadmium content of the samples from the left bank of the river was 5.43 mg/kg S.A.

The average cadmium content in Area III was 0.95 mg/kg of soil d.w. The contamination limit for cadmium in soils was exceeded in 9 samples, mainly from the left bank. Samples from the right bank of the river had an average cadmium content of 0.24 mg/kg d.w. Several of the samples from the right bank were below the measurement threshold. Samples from the left bank of the river had an average cadmium content of 1.66 mg/kg d.w. The average cadmium concentration of the GA [15] soil samples taken at Muhi was 2.13 mg/kg d.w.

The average cadmium content in Area IV was 0.52 mg/kg d.w. The contamination limit for cadmium in soils was exceeded in 12 samples. Samples from the right bank of the river had an average cadmium content of 1.32 mg/kg d.w. Several of the right bank samples were below the measurement threshold. The average cadmium content of the samples from the left bank of the river was 1.84 mg/kg d.w. The average cadmium content in Area V was 1.97 mg/kg soil d.w. The contamination limit for cadmium in soils was exceeded in 16 samples. Samples from the right bank of the river had an average cadmium content of 1.64 mg/kg d.w. Several of the right bank samples were below the measurement threshold. The average cadmium content of the samples from the left bank of the river was 2.31 mg/kg d.w. All samples in Area VI were below the measurement limit.

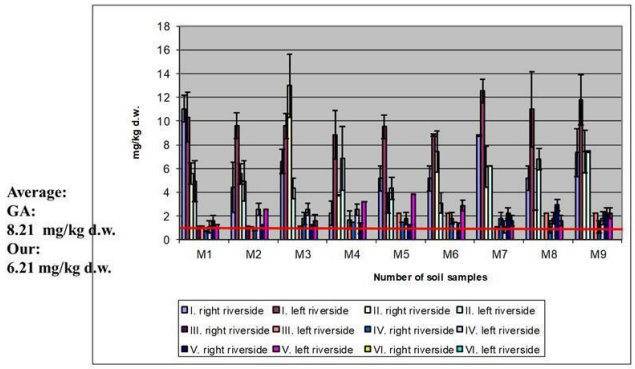

Figure 5. Cd concentration in soil samples

Zinc concentrations measured in soil samples

According to Figure 6. the average zinc content in Area I is 281.48 mg/kg d.w. The contamination limit for zinc in soils is 200 mg/kg d.w., which was exceeded in 12 samples, according to the joint decree 6/2009 (IV. 14) of the Ministry of Agriculture, Forestry, Environment and Water Management. The average zinc content of the samples taken from the right bank of the river was 296.97 mg/kg d.w. The average zinc content of the samples taken from the left bank of the river was 265.99 mg/kg d.w. The average zinc concentration of the ZAE soil samples taken at Ónod was 403.30 mg/kg d.w.

The average zinc content in Area II was 64.21 mg/kg d.w. No sample exceeded the contamination limit for zinc in soils. Samples from the right bank of the river had an average zinc content of 63.63 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 64.79 mg/kg d.w.

The average zinc content in Area III is 61.42 mg/kg d.w. of soil. Samples from the right bank of the river had an average zinc content of 60.21 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 62.63 mg/kg d.w. The ZAE soil samples taken at Muhi had an average zinc concentration of 90.00 mg/kg d.w.

The average zinc content in Area IV was 17.28 mg/kg d.w. No sample exceeded the contamination limit for zinc in soils. Samples from the right bank of the river had an average zinc content of 17.87 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 16.68 mg/kg d.w.

The average zinc content in Area V is 147.75 mg/kg d.w. The contamination limit for zinc in soils was exceeded in 2 samples. Samples from the right bank of the river had an average zinc content of 161.05 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 134.44 mg/kg d.w.

The average zinc content in Area VI was 197.12 mg/kg of soil d.w. The contamination limit for zinc in soils was exceeded in 9 samples. Samples from the right bank of the river had an average zinc content of 179.94 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 214.30 mg/kg d.w.

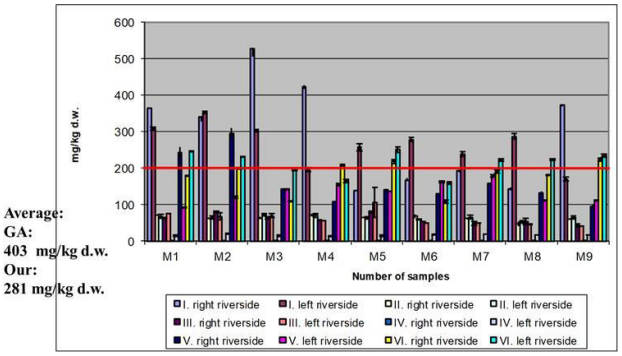

Figure 6. Zinc concentrations measured in the soil samples tested

Lead concentrations in soil samples

According to Figure 7, the average lead content in Area I is 45.71 mg/kg d.w. The contamination limit for lead in soils is 100 mg/kg d.w. according to the joint decree 6/2009 (IV. 14) of the Ministry of Agriculture, Forestry, Environment and Water Management, which was not exceeded by any sample. Samples from the right bank of the river had an average lead content of 36.95 mg/kg d.w. Samples from the left bank of the river had an average lead content of 54.47 mg/kg d.w.

The average lead concentration of the GA [15] soil samples taken at Ónod was 253.72 mg/kg d.w.

The average lead content in Area II was 65.84 mg/kg d.w. Only 1 sample exceeded the contamination limit for lead in soils. The average lead content of the samples from the right bank of the river was 79.23 mg/kg d.w. The average lead content of the samples from the left bank of the river was 52.44 mg/kg d.w.

The average lead content in Area III was 95.23 mg/kg d.w. The contamination limit for lead in soils was exceeded in all (9) samples from the right bank. Samples from the right bank of the river had an average lead content of 128.42 mg/kg d.w. Samples from the left bank of the river had an average lead content of 62.04 mg/kg d.w.

The GA [15] soil samples taken at Muhi had an average lead concentration of 35.85 mg/kg d.w.

The average lead content in Area IV was 48.89 mg/kg d.w. No sample exceeded the contamination limit for lead in soils. Samples from the right bank of the river had an average lead content of 73.05 mg/kg d.w. Samples from the left bank of the river had an average lead content of 24.73 mg/kg d.w.

The average lead content in Area V was 71.62 mg/kg d.w. The contamination limit for lead in soils was exceeded in 3 samples. Samples from the right bank of the river had an average lead content of 92.38 mg/kg d.w. Samples from the left bank of the river had an average lead content of 50.87 mg/kg d.w.

The average lead content in Area VI was 111.74 mg/kg d.w. The contamination limit for lead in soils was exceeded in 8 samples from the right bank. Samples from the right bank of the river had an average lead content of 151.31 mg/kg d.w. Samples from the left bank of the river had an average lead content of 72.17 mg/kg d.w.

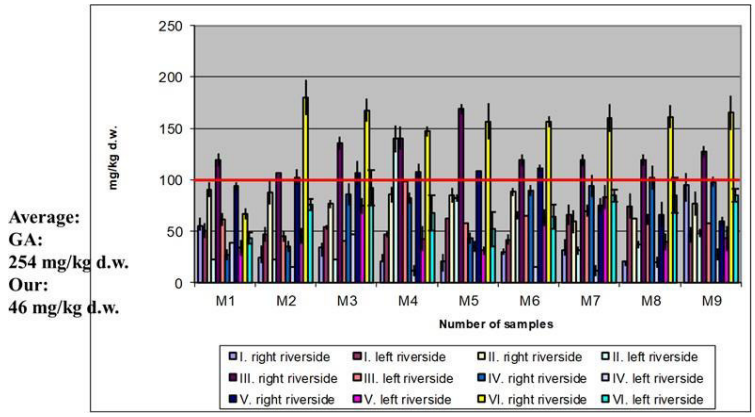

Figure 7. Lead concentration in soil samples tested

Manganese concentration in soil samples

According to Figure 8, the average manganese content in Area I is 584.66 mg/kg d.w. There is no contamination limit for manganese in soils. The average manganese content of the samples taken from the right bank of the river is 617.01 mg/kg d.w. The average manganese content of the samples taken from the left bank of the river is 552.31 mg/kg d.w. The average manganese concentration in the GA [15] soil samplestaken at Ónod was 1030.00 mg/kg d.w.

The average manganese content of the samples taken from the right bank of the river was 190.90 mg/kg d.w.

The average manganese content of the samples taken from the left bank of the river was 194.36 mg/kg d.w.

The average manganese content of the samples taken from the right bank of the river is 468.68 mg/kg d.w.

The average manganese content of the samples taken from the left bank of the river is 479.49 mg/kg d.w.

The average manganese concentration of the GA [15] soil samples taken at Muhi was 1059.00 mg/kg d.w.
The average manganese content of the samples taken from the right bank of the river was 602.42 mg/kg d.w.
The average manganese content of the samples taken from the left bank of the river was 535.76 mg/kg d.w.
The average manganese content of the samples taken from the right bank of the river was 447.58 mg/kg d.w.
The average manganese content of the samples taken from the left bank of the river was 433.70 mg/kg d.w.
The average manganese content of the samples from the right bank of the river was 714.28 mg/kg d.w.
The average manganese content of the samples from the left bank of the river was 795.85 mg/kg d.w.

Iron concentration in soil tested

According to Figure 8, the average iron content of Area I is 12086.94 mg/kg d.w. There is no contamination limit for the iron content of soils. The average iron content of the samples taken from the right bank of the river is 12088.63 mg/kg d.w. The average iron content of the samples taken from the left bank of the river is 12085.25 mg/kg d.w.
The average iron content of the samples taken from the right bank of the river is 10299.61 mg/kg d.w. The average iron content of the samples taken from the left bank of the river is 10204.48 mg/kg d.w. The average iron content of the samples taken from the right bank of the river is 6219.72 mg/kg d.w.

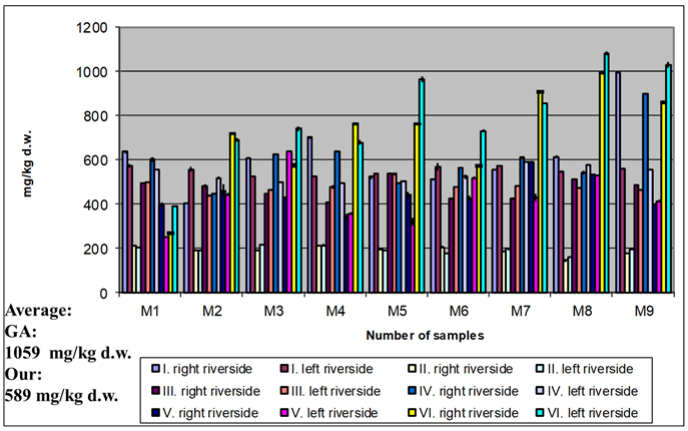

Figure 8. Manganese concentration in soil samples tested

Iron concentration in soil tested

According to Figure 9, the average iron content of Area I is 12086.94 mg/kg d.w. There is no contamination limit for the iron content of soils. The average iron content of the samples taken from the right bank of the river is 12088.63 mg/kg d.w. The average iron content of the samples taken from the left bank of the river is 12085.25 mg/kg d.w.
The average iron content of the samples taken from the right bank of the river is 10299.61 mg/kg d.w. The average iron content of the samples taken from the left bank of the river is 10204.48 mg/kg d.w.
The average iron content of the samples taken from the right bank of the river is 6219.72 mg/kg d.w.
The average iron content of the samples taken from the left bank of the river is 6091.66 mg/kg d.w. Average iron content in Area IV: 11806.23 mg/kg d.w. Average iron content in samples from the right bank of the river: 11757.91 mg/kg d.w. Average iron content in samples from the left bank of the river: 11854.55 mg/kg d.w.
Average iron content in Area V: 9696.70 mg/kg d.w. Average iron content in samples from the right bank of the river: 9283.40 mg/kg d.w. Average iron content in samples from the left bank of the river: 9490.05 mg/kg d.w.
Average iron content in Area VI 14901.93 mg/kg d.w. Average iron content in samples from the right bank of the river 14891.37 mg/kg d.w. Average iron content in samples from the left bank of the river 14912.50 mg/kg d.w.

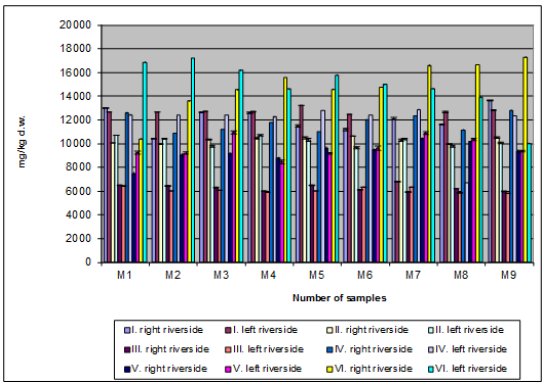

Figure 9. Iron concentration in tested soils

Zinc concentration in measured soil samples

According to Figure 10, the average zinc content in Area I is 281.48 mg/kg d.w. The contamination limit for zinc in soils is 200 mg/kg d.w., which was exceeded in 12 samples, according to the joint decree 6/2009 (IV. 14) of the Ministry of Agriculture, Forestry, Environment and Water Management [16]. The average zinc content of the samples taken from the right bank of the river was 296.97 mg/kg d.w. The average zinc content of the samples taken from the left bank of the river was 265.99 mg/kg d.w. The average zinc concentration of the GA [15] soil samples taken at Ónod was 403.30 mg/kg d.w.

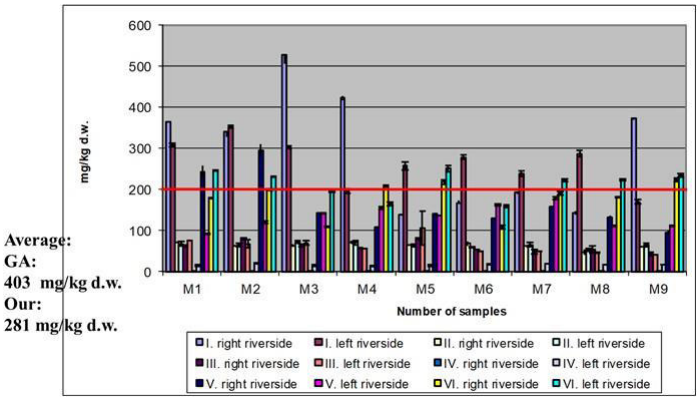

Figure 10. Zinc concentration in tested soil samples

The average zinc content in Area II was 64.21 mg/kg d.w. No sample exceeded the contamination limit for zinc in soils. Samples from the right bank of the river had an average zinc content of 63.63 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 64.79 mg/kg d.w.

The average zinc content in Area III is 61.42 mg/kg d.w. of soil. Samples from the right bank of the river had an average zinc content of 60.21 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 62.63 mg/kg d.w.

The GA [15] soil samples taken at Muhi had an average zinc concentration of 90.00 mg/kg d.w.

The average zinc content in Area IV was 17.28 mg/kg d.w. No sample exceeded the contamination limit for zinc in soils. Samples from the right bank of the river had an average zinc content of 17.87 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 16.68 mg/kg d.w.

The average zinc content in Area V is 147.75 mg/kg d.w. The contamination limit for zinc in soils was exceeded in 2 samples. Samples from the right bank of the river had an average zinc content of 161.05 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 134.44 mg/kg d.w.

The average zinc content in Area VI was 197.12 mg/kg of soil d.w. The contamination limit for zinc in soils was exceeded in 9 samples. Samples from the right bank of the river had an average zinc content of 179.94 mg/kg d.w. Samples from the left bank of the river had an average cadmium content of 214.30 mg/kg d.w.

The copper content in measured soil samples

According to Figure 11, the average copper content in Area I is 40.49 mg/kg d.w. The contamination limit for copper in soils is 75 mg/kg d.w. according to the joint decree 6/2009 (IV. 14) of the Ministry of Agriculture, Forestry, Environment and Water Management, which was not exceeded by any of the samples in this area. Samples from the right bank of the river had an average zinc content of 37.65 mg/kg d.w. Samples from the left bank of the river had an average zinc content of 43.33 mg/kg d.w.

The GA [15] soil samples taken at Ónod had an average copper concentration of 51.61 mg/kg d.w.

The average copper content in Area II was 39.66 mg/kg d.w. None of the samples exceeded the contamination limit for copper in soils. Samples from the right bank of the river had an average copper content of 39.44 mg/kg d.w. Samples from the left bank of the river had an average copper content of 39.88 mg/kg d.w.

The average copper content in Area III was 16.31 mg/kg d.w. None of the samples exceeded the contamination limit for copper in soils. Samples from the right bank of the river had an average copper content of 14.63 mg/kg d.w. Samples from the left bank of the river had an average zinc content of 17.99 mg/kg d.w.

The GA [15] soil samples taken at Muhi had an average copper concentration of 56.90 mg/kg d.w.

The average copper content in Area IV was 19.75 mg/kg d.w. No sample exceeded the contamination limit for copper in soils. Samples from the right bank of the river had an average copper content of 22.15 mg/kg d.w. Samples from the left bank of the river had an average zinc content of 17.38 mg/kg d.w.

The average copper content in Area V was 25.40 mg/kg d.w. No sample exceeded the contamination limit for copper in soils. Samples from the right bank of the river had an average copper content of 26.00 mg/kg d.w. Samples from the left bank of the river had an average zinc content of 24.79 mg/kg d.w.

The average copper content in Area VI was 60.57 mg/kg d.w. The contamination limit for copper in soils was exceeded in 4 samples. Samples from the right bank of the river had an average copper content of 52.14 mg/kg d.w. Samples from the left bank of the river had an average zinc content of 68.99 mg/kg d.w.

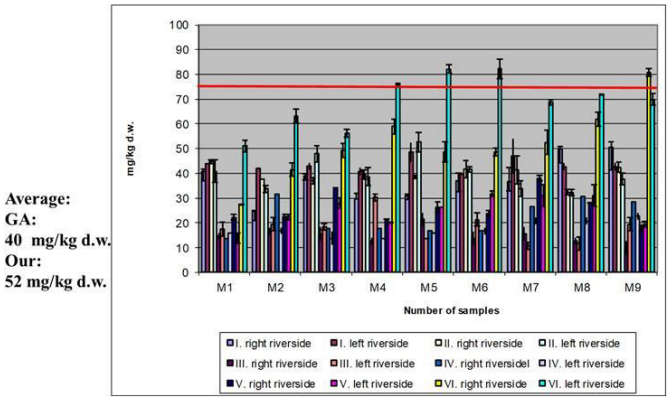

Figure 11. Copper concentration in soil samples

CONCLUSIONS AND RECOMMENDATIONS

The Green Action Association [15] carried out a comprehensive monitoring of the Sajó Valley in the early 1990s. This gave us the idea to carry out our work, as significant heavy metal and lithium pollution was found in the areas surveyed. It is very likely that this was mainly caused by heavy industry from the 19th century until the 1980s. Six areas were selected as the test sites for the soil samples, between Ónod and Muhi(3 areas) and near Tiszaszederkény and Tiszagyulaháza (3 additional areas). Our soil samples were collected from the floodplains of the Sajó, Hernád and Tisza rivers at a depth of 0-40 cm. The results obtained showed that there are still areas where some elements such as Cd, Zn, Pb, Cu are contaminated above the limit values(Joint Decree 6/2009 (IV. 14.) [16] of the Ministry of Agriculture, Forestry, Environment and WaterManagement). Due to the weakly alkaline and weakly acidic pH values measured, the contaminants are

immobile in the soil.
In our floodplain soil samples from the six sample sites, the following four heavy metals (Cd, Zn, Cu, Pb) with contamination limits exceeded the contamination limit. We measured high concentrations of cadmiumin five areas (Areas I, II, III, IV, V), high concentrations of zinc in three areas (Areas I, V, VI), lead concentrations above the limit value in three areas (Areas II, III, VI) and copper concentrations above the limit value in one area (Area VI). As floodplain areas are often used for grazing and are close to arable land,the accumulation of heavy metals can pose a serious health risk, as these heavy metals can accumulate in plants and animals and can indirectly harm the human body. Before choosing the measures to reduce the heavy metal load described above, it is necessary to analyze samples of river sediment and sludge, because itcannot be excluded that during the past continuous pollution, large quantities of heavy metals have been deposited in the sediment, which could be reintroduced into the floodplain and further polluted by flooding. Statistical evaluation was performed by three-factor random block analysis of variance using SPSS 14.0 for Windows software package. After performing analysis of variance, it was shown that the heavy metal content of soil samples was significantly related to the sampling location. On the basis of the data obtained, we propose to carry out a study on a similar scale to the monitoring carried out in the 1990s and to clean up the contaminated soils.

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