SZENT ISTVÁN UNIVERSITY
DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCE

INVESTIGATION OF HEAVY METALS SOLUBILITY AND REDOX PROPERTIES OF SOILS

Ph.D Thesis

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1. INTRODUCTION

During January and March 2000, two serious mine tailings dam failures occurred, both originating in northern Transylvania (Romania); both polluted the rivers Szamos and Tisza. The Bozanta-Aural tailing pond dam failure occurred on 30th of January, 2000 releasing cyanide and mainly Cu and Zn ions into Lapus and Szamos rivers. The highest values recorded for these two contaminants were 15.8 mg/L and 0.5 mg/L respectively, at Olcsvaapáti, just before entering the Tisza river (HUNGARIAN GOVERNMENT, 2000), therefore contaminating the River Tisza. In a tailings management facility a dam overflowed on March 10, 2000 and released 100.000 m^3 of water and 20.000 tons of tailing sludge, containing heavy metals. Some of this material was retained in the lower dams but most of it flowed downstream and entered the Viseu and finally the Tisza rivers (OSAN et al., 2002). The flood, which was contaminated by sludge containing lead, zinc, copper reached the Hungarian border at the river segment of Tiszabecs on 11th March. Concentrations of copper in the first incident (cyanide and heavy metal), and Copper, Zinc and lead, in the second (heavy metal sludge), exceeded the Hungarian standard limit values for the most severely polluted waters (CSENGERI et al., 2002). The river Tisza is the second of the most important rivers in Hungary with a section of 579 km in the country. In the last few years, the river has left its bed causing various floods and depositing great amount of sludge and sediments on the flood area (BUZÁS et al., 1999). The soil heavy metals concentrations recorded for all heavy metals in the flood zone of the Tisza were higher than the reference data for the particular soils of the country, such values were found in the contemporary flood zones, and also in the 10 km band along the river. The concentration of heavy metals in the environment has increased due to, among other reasons, the influence of human activity. This increase in concentration is not the same for all metals and depends mainly on the amount and the method of transmission, as well as the source of pollution. The build up of large amounts of heavy metals through a long period of time in the organic area of the soil brings about contamination of organisms in the soil that have a significant role in the development and maturity of the soil. One must keep in mind that the content of heavy metals and their negative effect is closely related to the pE and pH values, as well as the amount of clay and organic matter in the soil

(ATANASSOV et al, 1999). The solubility and mobility of heavy metals contaminants in soils depend on chemical properties such as chemical speciation of the trace element, soil pH and redox potential, and water movement. For example, metal cation solubility typically increases with decreasing pH, and is related to pH-dependent sorption on various soil minerals and organic matter (SAUVÉ et al., 2000; SUKREEYAPONGSE et al., 2002). Redox potential is an important parameter in environmental quality research, it indicates the tendency of an environment to receive or give electrons. Redox potential is, together with pH, a driving variable for speciation of heavy metals (SALOMONS and STIGLIANI, 1995), and it describes the potential for degradation of organic substances. Changes in redox potential are the result of the combined effects between many chemical, physical and biological processes in the soil. Soil oxidation and reduction depend on soil respiration, diffusion of oxygen and carbon dioxide in soil and on changes in biochemistry of the system (NEMECEK et al., 1990). The most common ions creating redox couples of soil are following: NO_3^-/NO_2^-, Fe^{3+}/Fe^{2+} and Mn^{4+}/Mn^{2+} (BOHREROVA et al., 2004).

Except for the simple cyanide compounds consisting of a single metal ion in combination with CN^-, all readily soluble cyanide complexes are of different types, considering their solubility. The metal-cyanide complexes, which are commonly formed in mining effluents: zinc and cadmium cyanides (weak complexes); copper, nickel and silver cyanides (moderately strong complexes); iron, cobalt and gold cyanides (strong complexes). When metal-cyanide complexes are formed and released into the near surface environment, they begin to decompose at varying rates. This breakdown releases cyanide into the soil or water, generally at relatively low concentrations (WWF, 2002). Those complexes that most readily decompose are referred to as weak complexes; those most resistant to decomposition are called strong complexes. Some of the strong complexes do not break down in the presence of strong acids, but will decompose when exposed to various wavelengths of light, releasing cyanide ions. The water, temperature, pH, total dissolved solids and complex concentrations affect the decomposition rates of these complexes (MORAN, 1998). Modelling and computer simulation of geochemical processes is a valuable tool, which can be used to gain a greater understanding of heavy metals and cyanide processes where it is difficult to conduct realistic laboratory experiments.

1.1. Objectives

The overall aims of the work presented in this thesis was to gain a better understanding of some properties of soils and concentrations of heavy metals in flood-plain, with Gergelyiugornya and Tivadar as study areas. Specific objectives were:

- To develop a computer controlled redox titration laboratory measurement of soil redox potential (Eh) and to determine an equilibrium value by a non-equilibrium method (from Titration method) and to investigate the redox buffering capacity of soils as a function of measuring time.

- To compare the heavy metals concentrations of soils obtained from contaminated sites (Gergelyiugornya) and from a flood protected area (Tivadar) of the floodplain of River Tisza after three years of contamination using extraction methods, aqua regia, nitric acid (HNO_3), Ethylenediaminetetraacetic acid (EDTA) and to compare the three extraction procedures, by using atomic absorption spectrophotometer (AAS).

- To determine how extractable soil Fe, Mn, Cu, Zn are related to flooded conditions of the soil and at the same time see if there are any differences in concentrations between two soils under incubation experiment conditions.

- To use calculation tools to evaluate modelled data and predict the concentration of heavy metals and the effect of cyanide as a function of pH and pE using a geochemical equilibrium model (MINTEQ).

2. MATERIALS AND METHODS

2.1. Samples and its locations

Soil samples were collected in the east-central Hungary (Tisza river area) in the middle of August 2003. Eight soil samples were used in this study, which will be referred to as Soil 1 to Soil 8. Tivadar is a small village close to the River Tisza that has a low degree of anthropogenic impact, upstream from Szamos mouth. Gergelyiugornya is in a direct line from the Szamos-Tisza connection (about 100 m in the flow direction). The River Szamos is extremely relevant because there has been very harmful cyanide and heavy metal pollution in its channel. Therefore, it is intended to compare the "clear" Tisza sites with the "polluted" area. The Tiborszállás site is far from the rivers, but it is vitally, it is a water affected soil. In its former name -Ecsedi láp-, the word "áp" refers to the fact that it is a continously water-covered soil. The soils from Tivadar and Gergelyiugornya belonged to the high clay category.

Sample No. 1. This soil sample has been taken from outside the dam. This area is not covered by water during normal flow and is used for wheat crop. It is a clay soil with reductive marks. The sample comes from Tivadar, an unpolluted area of Tisza, situated above the Tisza-Szamos connection.

Sample No. 2. This soil sample was collected directly from the river bank. At this place there is a sandy river bank, but the sample doesn't originate from the sand. Instead, it has been taken from the clay layer directly above the sand. Normally, the river is at this level in the winter-spring period. The sample is from Tivadar, a non-polluted area of Tisza, situated above the Tisza-Szamos connection.

Sample No. 3. This soil sample is from the flood plain of River Tisza. The River flows over these soils three-five times per year. The frequent flooding of the river (in autumn and spring) means continuous sealing by water which covers the chosen sample sites. Normally, the river is at this level in the winter-spring flooding period. The plant in this study site was Alfalfa (*Medicago sativa L.*), which is in clay soil with reductive marks.

The exact origin of the sample is Tivadar, a non-polluted area of Tisza, situated above the Tisza-Szamos connection.

Sample No. 4. This is a soil sample taken directly from the river bank. At this place there is a sandy river bank, however, the sample does not originate from the sand; rather, it has been taken from the clay layer directly above the sand. Normally, the river is at that level in the winter-spring period. This sample is from Gergelyiugornya, a polluted area of the River Tisza, right at the bottom of the Tisza-Szamos connection.

Sample No. 5. This is a soil sample taken from the flood plain of River Tisza, therefore, in the case of normal flow the area is covered by water. Normally, the river is at this level in the winter-spring flooding period. The flora at this site was grass and the soil is clay with reductive marks. The exact origin of the sample is from below the inflow of River Szamos (near Gergelyiugornya). The sample is from a polluted area of Tisza, situated at the bottom the Tisza-Szamos connection. Gergelyiugornya Szamos mouth is where the supply of cyanide and heavy metals took place.

Sample No. 6. This soil sample was collected outside the dam, which means that in the case of normal flow the area is not covered by water. The area is dominated by turf and clay soil with reductive marks. The sample is from Gergelyiugornya, a polluted area of Tisza, situated at the bottom the Tisza-Szamos connection.

Sample No. 7. The soil sample which originates from the Tiborszállás site is far from the rivers, but it is a water affected soil. In the former name of the area, -Ecsedi láp-the word "láp" means a soil continuously covered with water. At this place corn (*Zea mays L.*) was planted as a crop. The sample was collected from a deeper layer of the soil profile and more precisely it is from the mineral layer of the soil.

Sample No. 8. This soil sample is from the Tiborszállás site which is far from the rivers, but it is a water affected soil. In the former name of the area, -Ecsedi láp- the word "láp" means a soil continuously covered with water. At this place corn was planted as a crop. This sample is from the deeper organic rich layer of the soil profile.

2.2. Chemical analysis of soil samples

Soil samples were air-dried and rootlets were sorted out. Then samples were crushed and sieved through a 2-mm sieve. Laboratory analyses of 8 samples from 8 locations were taken on pH (pHKCl), K_A (Upper limit of plasticity), $CaCO_3$ % (Scheibler-method), organic material % (heating), humus % (Tyurin-method) and exchangeable cations (K, Na) in the laboratory of the Department of Soil Science and Agro-chemistry at Szent István University, according to BUZÁS (1988). The Sulphur content of the soils was determined by atomic emission spectroscopy by inductively coupled plasma (Jobin-Yvon JY-24 Atomic Emission Spectrophotometer). Extraction of different iron forms (oxalic iron, dithionic iron and pyrophosphatic iron) were measured by the methods reported by BLAKEMORE et al. (1981).

Nº	Place	K_A	PH$_{KCl}$	Humus %	CaCO$_3$ %	Total S mg/kg	K µg/g	Na µg/g
1	Tivadar outside-dam	43	5.20	2.15	0	160	26.55	4.50
2	Tivadar bank	58	6.74	3.29	0.72	371	8.75	24.85
3	Tivadar flood-plain	37	5.30	0.64	0	95	6.15	2.35
4	Gergelyiugornya bank	48	6.14	1.34	0.19	256	6.65	21.25
5	Gergelyiugornya flood-plain	53	6.20	2.43	0.35	494	25.85	8.25
6	Gergelyiugornya outside-dam	34	6.87	0.37	4.95	190	3.3	7.05
7	Tiborszállás clay	55	6.48	10.28	0.26	627	2.2	8.7
8	Meadow organic soil	49	6.19	8.90	0.13	633	22.65	13.05

Table 1. Sampling places, properties and the features of the eight soil samples

For different extraction procedures, (EDTA, HNO$_3$ and Aqua-regia) the concentrations of heavy metals were digested using the Lakanen-Erviö method according to the Hungarian standard methods (MSZ 21470-50: 1998). The soils are acidic clay and varied in their origin, selected soil properties are summarized in Table 1.

2.3. Methodology

2.3.1. Electrochemical redox titration

During our investigations platinum electrode was used for measuring of the redox potential. As a reference electrode an Ag/AgCl electrode of a pH electrode was used. Since the potential of the platinum electrode strongly depends on both the redox potential, and the pH, it is completely unsuitable for measuring the redox potential. Since the potential of the glass electrode depends only on the pH-value and on the redox potential is practically independent, in the case when the signs of both electrodes are known, the redox potential (calculated with respect to zero pH-value) can be calculated. This potential can be expressed by use of the Nernst equation:

$$\varepsilon = \varepsilon^{\circ} + \frac{RT}{zF} \ln \frac{[ox]}{[red]}$$

where: ε is the electrode potential under given conditions (V)
ε^o standard electrode potential (V) (at 25 ºC; at 0.1 MPa)
R universal gas constant; 8.31434 $Jmol^{-1}K^{-1}$
T temperature (K)
z number of e^--s participating in the redox process
F Faraday's constant; 96 486 $Cmol^{-1}$
[ox] concentration of the oxidated form (M dm^{-3})
[red] concentration of the reduced form (M dm^{-3})

Connecting this measuring electrode to an $Ag^+/AgCl$ reference electrode, the potential of the Pt electrode sinking into soil suspension can be calculated on the base of the electromotive force (E.M.F.) of the galvanic cell, i.e.:

E.M.F. = $\varepsilon_{cathode}$ - ε_{anode}
where **$\varepsilon_{cathode}$** is potential of the $Ag^+/AgCl$ reference electrode ($\varepsilon^o = 0.222V$)
ε_{anode} is the electrode potential of Pt sinking into soil suspension

We can measure the E.M.F. of the system with a special electrical circuit but because of the difficult technique we measure only the terminal voltage instead of E.M.F. During the electric current production the measurable terminal voltage (E_K) is put, which is always smaller than the E.M.F.

$\varepsilon_{anode} = \varepsilon_{cathode} - E_K$

By applying the previous methods to the following redox reactions accompanied by pH-changes, we have:

$A_{red} + H_2O = A_{ox} + H^+ + e^-$
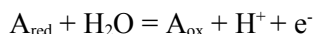
where A_{red} and A_{ox} denote the reduced and oxidated form of a redoxi pair, respectively, and the potential of a platinum electrode sinking into solution is

$$\varepsilon = \varepsilon^\circ + \frac{RT}{zF} \ln \frac{[A_{ox}][H^+]}{[A_{red}]}$$

Performing measurement at 25 °C, substituting the constants (R, F), applying of *lg* instead of *ln*, and by rearranging the equation, the following form can be obtained:

$$\varepsilon = \varepsilon^\circ + \frac{0.059}{z} \lg \frac{[A_{ox}]}{[A_{red}]} + \frac{0.059}{z} \lg [H^+]$$

and then, introducing the definition of pH into it (pH = -lg [H^+]), an informative form of this equation can be obtained:

$$\varepsilon = \varepsilon^\circ + \frac{0.059}{z} \lg \frac{[A_{ox}]}{[A_{red}]} - \frac{0.059}{z} pH$$

i.e., it is necessary to correct the redoxi potential (calculated from the measured value) of a system for 59 mV pro pH unit. The electrode potential of hydrogen and oxygen is represented as a function of the pH value, varying along two straights and its gradient is:

$$\frac{0.059}{z}$$

If the value of electrode potential indicated by the lower line is more negative, then H_2 evolution occurs. If the value of electrode potential indicated the upper line is more positive, then O_2 evolution occurs. Oxidation-reduction processes taking place in soils belong to the water stable territory, i.e. they remain within the domain inside the area between two straight lines; their change similar to those of the pH value is also postulated. In some cases the changes of redox potential with the pH can also be at quick redox processes -200 mV/pH. At most measurements however 59mV/ pH use of modulus is practical, since the redox potentials are medley potentials. It is not necessary to give more precise value than ±10 mV.

Investigations were performed in a 200 ml glass where 10 ml 1 molar hydrochloric acid was added to about 100 ml distilled water in order to ensure the acidic pH necessary for oxidation. Then a wet, possibly frozen soil sample of the exactly known mass of 2g was added to this system, the suspension was continuously mixed and the oxidizer was portioned at equal time intervals. The values obtained from the soil samples were simultaneously measured for content of the dry matter and at the evaluation corrected for the wet matter content, too. The glass electrodes produced by RADELKIS (RADELKIS, 1952) were calibrated at two points with RADELKIS buffer solutions of 2.2 and 9.3 pH values. In order to calibrate the Pt-electrode produced by RADELKIS at a lower value we used zinc powder spread into hydrochloric acid solution while making sure that the zinc did not to touch the surface of the platinum. In this way it was practically a hydrogen electrode. It was possible to set up the apparatus so that the voltage was measured to mV accuracy with the theoretical potential of the reference electrode (i.e. the potential of the platinum electrode was equal to zero volts corresponding to normal hydrogen). For the upper calibration an oxidant used at titration, 0.05 molar $KMnO_4$ solution, and 1 molar hydrochloric acid solution were used and the measured voltage values in this case agreed up to ±5 mV with the summarized values of the $KMnO_4$ solution (to be found in the tables)

with given concentration and the voltage values of the reference electrode which can be found in the literature. The data was led through an amplifier and an AD converter into a PC, where a specific program prepared for this purpose stored the voltage signal of the platinum and glass electrode (with respect to a reference electrode), stored the time and in given time intervals portioned oxidant to the continuously mixed soil suspension. Then, the measured data was presented in the function of time. At the end of the measurement, the stored data was evaluated by a specific program prepared for this purpose, which in the first step calculated the genuine pH and redox potential values via calibration values. The titration curve obtained was smoothed by the program via a sliding average method of adjustable size, since some measured values are inevitably loaded by faults, because the soil grains dashing on the electrodes may cause instantaneous potential fluctuations on the surfaces of electrodes.

The software used for evaluation of the experimental data works as follows: The earlier saved measurement results can be loaded by the command „Open" from the „File" menu. Then, on the top of the figure, the curve representing measured data appeared, while on the bottom its derivative (with and without smoothing, too), as well as the point representing the maximal value in the form of a vertical line. In order to determine the inflexion point correctly, it may be possible to apply different smoothings depending on the steepness of „S". The number of numerical values to be taken into account simultaneously by the slipping average can be adjusted in the smooth menu. The first 3-4 results are for technical reasons absent or misleading, therefore in default calculations will not be taken into account. In the „max" menu it is possible to search for the curve peak, and the result can also be copied into an Excel compatible spreadsheet. Representation of data in tables is available from the „window" menu, where the concrete numerical values of curves in the figure are also shown.

To begin with the titration was performed by 0.5 molar $KMnO_4$ solution, but since the nascent manganese II ions notably modify the soil surface, we switched over to the NaOCl solution, whose decomposition products are the Na^+, Cl^- ions and water, which do not significantly influence the surface of the soil. Unfortunately, since this is an unstable material, we could not have known its exact concentration at the measurement – and have produced it by dilution of the commercial HYPO solution. Due to this condition, every

day, before we began use of the solute, it was necessary to perform factorization. Factorization was performed by the procedure used during the measurement, but instead of soil a $Fe(NH_4)_2(SO_4)_2$ – Mohr salt - solution of known quantity and concentration was put into the glass (this solution is also used at the determination of humus for the titration of the remnant K_2CrO_4). The exact concentration value of the titration solution was calculated from the amount of the measured Mohr-salt and on the base of decrease corresponding to the crossover point calculated from the titration curve obtained for this solution. The titration was also carried out in a reduction direction, for which 0.05 molar hydrazin solution was used, factorized by 0.05 molar $KMnO_4$ solution and therefore it was possible to determine the redox buffer capacity in a reduction direction, i.e. the behaviour of the soil in the case of moistening. The destination program has stored the potential difference sign of the glass electrode in conformity with the reference electrode and has stored the different partition time. At first, another destination program has calculated the actual pH- and redox potential values by means of calibrations values from the stored data. Then it has plotted this against the time.

2.3.2. Incubation experiment of two flood plain soils

In this experiment we used Tivadar and Gergelyiugornya flood plain soil samples (3 and 5) because we found a significant difference between the two soils in the conducted laboratory chemical analyses. Our hypothesis is that we can find heavy metal pollution of River Szamos in Gergelyiugornya soil during the incubation experiment. Selected soil properties are summarized in Table 1. Samples were air dried at a laboratory temperature of 25°C for approximately 7 days. The samples were powdered and passed through a 2-mm sieve to remove gravel and rocks. During the incubation periods of both soils the cation exchange capacity (CEC) was determined according to BUZÁS (1988).

From each soil we made four samples in three replications, 10 g of soil were put in separate plastic bags and 10 ml of distilled water was added to each sample, the samples 1;2;3;4 were incubated for 1;7;14 and 21 days, respectively, and in the laboratory all incubations were carried out at 25°C in the dark. Finally every sample was analyzed at the time of passing its incubation day. After each incubation time, each sample were mixed well individually and prepared for chemical analysis. All chemicals used in this experiment

were buffer solution from (acetic acid, sodium acetate) and nitric acid solution (2M HNO_3). The buffer solution was prepared in such a way that 12.5 ml of 1 mole CH_3COONa solution was added to 12.5 ml of 0.1 mole CH_3COOH solution. In three replications 2.5 g of soil extraction is made with 25 ml of buffer solution, also 25 ml of 2 mole HNO_3 was added to same amount of soil extraction in such a way that the soil is shaken with for about 15 minutes. After filtering the Fe, Cu, Zn and Mn were determined by means of an atomic absorption spectrophotometer and extraction for the chemical analysis was taken according to the Hungarian standard methods (MSZ 21470-50: 1998).

2.3.3. Modeling of metal concentration

The modeling was performed using a geochemical equilibrium model MINTEQ, developed by U.S. EPA that calculates values on the basis of physico-chemical equilibriums. The database of the program contains the equilibrium parameters of practically all perceivable inorganic substances in solution or precipitation forms. From this data it calculates the parameters of the ingredients present in the given case with iteration. During the iteration process the aggregation of the over-saturated solutions was allowed, therefore the concentration of the solutions that originally had a higher concentration than the measured value, decreased to equilibrium values. The models were run with different combinations of parameters in order to be able to determine the effect the alterations of pH and pE.

Methodology - A program was created that changed the input file of MINTEQ, based on the change of the variables. Consequently, MINTEQ was run, and the essential concentration values were collected from the results file. These served as a basis for drawing the concentration curves. For a better understanding a three-dimensional plot was made by Surfer 6 (GOLDEN SOFTWARE, 1983) based on the calculated database.

2.3.4. Statistical analysis

In the case of the titration method we used regression analysis for the reduction buffer capacity results of Tivadar and Gergelyiugornya flood plain soil samples. The standard deviation of different extraction methods and heavy metals was calculated by using Excel statistical functions. Using Microsoft Excel macros we performed two-factor analysis of variance (ANOVA) for different incubation periods and soil samples (TOLNER, 2008).

3. RESULTS AND DISCUSSION

3.1. Electrochemical redox titration of eight soil samples

The received titration was smoothed with the program by dint of sliding average method of adjustable size, since the measured values were loaded with error caused by soil granules impinging upon the surface of electrodes and generating instantaneous potential fluctuation sign. By numerical differentiation of the smoothed curve the program has calculated the derived curve and has determined its maximum value. Later, this was taken as the crossover point, i.e. exactly this potential value was set up by the concentration ratios of the oxidized and reduced pairs, which really determine the redox state of the soil. At this point there is the biggest rise of the curve so it has determined the quantity of oxidant with the least error plotted against the redox potential.

Time/Soil	1	2	3	4	5	6	7	8	Average
0.5 min	1.44	5.19	0.96	3.46	1.66	1.23	2.60	2.17	2.34
1 min	1.54	5.39	0.98	2.69	1.93	1.07	3.75	2.46	2.48
2.5 min	2.38	5.21	0.88	3.26	2.46	1.00	2.36	2.69	2.53
5 min	1.99	8.67	0.90	3.96	1.97	1.00	8.84	3.63	3.87
10 min	3.36	6.17	0.86	4.20	3.32	0.70	7.71	2.75	3.63
20 min	2.48	6.17	0.92	6.23	9.90	0.94	18.47	3.14	4.78
Average	2.20	6.13	0.92	3.97	3.54	0.99	5.62	2.81	

Table 2. Values of the Oxidation Buffer Capacity mmol/kg Soil

Time/Soil	1	2	3	4	5	6	7	8	Average
0.5 min	4.65	5.03	5.93	5.63	5.10	4.13	4.58	3.98	4.88
1 min	4.73	5.10	4.80	2.93	3.60	3.45	3.38	3.83	3.98
2.5 min	4.13	3.53	3.68	3.23	3.15	2.70	2.78	2.55	3.22
5 min	3.00	3.15	3.08	6.08	2.78	3.08	3.60	2.78	3.44
10 min	2.55	2.63	2.93	2.33	2.70	2.78	3.23	2.70	2.73
20 min	2.40	2.63	2.78	2.78	2.48	2.25	2.40	2.40	2.51
Average	3.58	3.68	3.86	3.83	3.30	3.06	3.33	3.04	

Table 3. Values of the Reduction Buffer Capacity mmol/kg Soil

As can be seen from Table 2 and Table 3, in the case of processes directed towards reduction, the measured values are shown to be decreasing, while in the case of processes towards oxidation they show a general increase tendency in average, this means, that by advancing towards an equilibrium system (with increasing waiting time intervals between successive partitions) in the case of the oxidation direction, the expected results are obtained, i.e. the oxidation determining materials from the soil grain surfaces depart in increasing rates. In order to explain the decreasing tendency in the reductive direction more investigations are necessary. The results corresponding to waiting times of 5 minutes in both cases do not follow the tendency suggested by other data, because in the case of oxidation there is a linear increase, while at reduction an exponential decrease is characteristic for the system. With regard to this tendency, some exceptions were found dependant on soil type: redox titration of soil number 4 displays a decreasing trend that occurred at 0.5-2.5 partition frequency. Between 2.5-5 an increasing tendency was found, then a decreasing tendency was experienced again from 5. The increasing trend of soil number 7 emerged from the others. Significant differences were not found between the oxidation buffer capacity of soils marked 3 and 6. In the case of soil 2, increasing tendency was found at 0.5-2.5 partition frequency and then a decreasing trend occurred in the buffer capacity. The average values of measurement results relevant for different time moments are presented in Table 2 and Table 3. It can be seen in these tables that while for oxidation investigation the values obtained for separate samples differ significantly, in the case of reduction experiments, the values are very similar.

3.1.1. Results of redox buffer capacity of two (3, 5) flood plain soil samples

The oxidation buffer capacity of Tivadar soil sample is almost constant in partition times. There is an increase for Gergelyiugornya soil sample but not linearly in greater partition time (20 min), which means there are some slow processes adjusting the buffering properties of the Gergelyiugornya soil sample. Therefore, there are some reduced adsorbed ions in the deeper layers of the soil pores, and for its diffusive removal, that the ions require a lengthier period of time.

For Tivadar soil sample there are reduced compounds in the deeper layer of their pores, but there is no oxidized compounds existing. Compare to the reduction buffer capacity in different partition times between the two soil samples, there is a linear correlation between the two soil samples where the two values are increasing and the Tivadar soil sample always has a higher value than the Gergelyiugornya soil sample. The reduction buffer capacity results of Tivadar and Gergelyiugornya flood plain soil samples show a significant correlation between the different partition time data. It means there is a linear ratio between the concentration of reduced compounds and the speed of their removal from the deeper layer of pores.

3.1.2. Relationship between buffer-soluble iron and redox buffer capacity

The trend of the buffer-soluble iron concentration is the same compared to the redox buffer capacity and there is strong correlation to suggest that the change of the buffer-soluble iron concentration causes the redox buffer capacity changes. As shown in the normal oxidative soils there are iron compounds and the ratio of HNO_3-soluble iron is higher than in buffer-soluble iron and as we reduce the soil in the absence of oxygen, the reduction potential will decrease and a higher amount of HNO_3-soluble iron will transform to buffer-soluble iron. Buffer-soluble iron concentration can be used as indicator for oxidation buffer capacity. If we found high values of oxidation buffer capacity that means there is high concentration of HNO_3-soluble iron in the soil.

3.1.3. Conclusion

By using this method, the errors mentioned in the case of redox potential measurements can be eliminated and a soil redox buffer capacity can be measured. As a result of evaluating the redox buffering capacity of the analysed soil samples we have found that the redox potential of the samples largely depends of the timing of analysis, where the increased waiting periods between doses have definitely resulted in higher values. Comparing the redox potentials of a polluted soil sample (Gergelyiugornya) with an unpolluted one (Tivadar) coming from areas situated near to each other, significant differences have been traced in the oxidation buffering capacity values. The values were higher in the polluted sample, especially in the case of long-term examinations nearer to

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the balance level. The buffer-soluble iron content of the given materials shows significant differences, while the buffering capacities have identical tendencies. For the oxidative redox-buffer capacity measurements we have found that with increasing time between adding the next dose, the buffer capacity increased, while it decreased at the reductive measurements. This suggests a different mechanism for the direction of the two processes.

3.1.4. Extraction results of two (3, 5) flood plain soil samples

The results obtained by determining the extractable elements are dependent on the extraction procedure applied. In general and compared to the Tivadar soil all the measured parameters (K_A, pH, Humus, $CaCO_3$, S, K and Na) in the Gergelyiugornya soil were greater (Table 1). We studied the different methods for extracting heavy metals for each of the elements and compared the concentrations of each element obtained by the three different methods for two soil samples.

Table 4 and Table 5 show that the aqua regia method extracted larger quantities of iron, copper, zinc and manganese than EDTA and HNO_3 methods, by using the EDTA extraction method the heavy metal content from the Gergelyiugornya soil is significantly higher than from the Tivadar soil. The difference between the two soils is displayed by the HNO_3 extraction method as well. A much higher content of heavy metal was retrieved by using the Aqua Regia extraction method compared to the two previous methods.

	EDTA	HNO_3	Aqua regia
Fe	255.2 ± 1.8	3791.3 ± 23.9	23360.0
Cu	6.7 ± 0.3	12.8 ± 0.2	32.6 ± 0.8
Zn	0.9 ± 0	7.8 ± 0.3	19.1 ± 0.5
Mn	311.3 ± 3.8	298.4 ± 3.9	588.3 ± 5.8

Table 4. Heavy metals concentrations (mg/kg) and standard deviations at Tivadar flood plain study site using different extraction methods

	EDTA	HNO₃	Aqua regia
Fe	608.9 ± 7.9	5562.1 ± 111.5	28910.0 ± 1353.0
Cu	56.8 ± 1.0	61.1 ± 1.8	97.1 ± 3.9
Zn	140.8 ± 7.3	239.9 ± 12.5	225.0 ± 2.0
Mn	443.6 ± 6.9	741.2 ± 12.5	712.2 ± 6.9

Table 5. Heavy metals concentrations (mg/kg) and standard deviations at Gergelyiugornya flood plain study site using different extraction methods

Strong acid digestion (e.g. by boiling HNO_3 or aqua regia) is often claimed to yield the total metal concentration or sometimes the quasi- or pseudo-total concentration (e.g. ANDERSON et al. 2000; MADRID et al., 2002). The Zn and Pb accumulation was typical in the samples from the region of Gergelyiugornya (ONCSIK-BIRONE and CSENGERI, 2006). The heavy metal content shows a significant difference between the two soils by using the three extraction methods. The higher heavy metal content in the Gergelyiugornya soil using aqua regia extraction method shows this soil to be contaminated with the deposition of the wave of pollution. For the Tivadar soil, the heavy metal content retrieved using EDTA extraction method is similar to that of the using HNO_3 extraction method, while by applying Aqua Regia extraction method the heavy metal content is much higher compared to the other extraction methods. In the Gergelyiugornya soil samples the three applied extraction methods results display the same trend compared to the Tivadar soil results with some exceptions.

The higher concentration of heavy metals retrieved by the Aqua Regia method compared to the other two extraction methods (EDTA, HNO_3) could be a result of the Aqua Regia method being more effective in the extraction of heavy metals (ZEREMSKI-SKORIC et al., 2006). ONCSIK-BIRONE and CSENGERI (2006) studied the heavy metal contents of the soil obtained from contaminated sites and from flood protected areas (control sites) of the River Tisza floodplain in the year of contamination and in the following year. By using EDTA-soluble heavy metal contents, Cu concentration reached 30 mg/kg. The highest Zn concentration was 80 mg/kg in the case of the soils from the contaminated area and the highest levels of these elements of soil from the uncontaminated arable land had the following values: Cu: 4 mg/kg, Zn: 32 mg/kg.

ADRIANO et al. (2006) analysed metals (Cd, Co, Cr, Pb, Cu, Mn, Ni and Zn) from similar contaminated areas and indicated that Cd and Zn are particularly concerning as their bioavailable (NH4OAc-EDTA extractable) fraction in most sites exceeded the allowable threshold values (0.50 mg/kg for Cd and 40 mg/kg for Zn) established by Hungary and WHO/FAO. They also stated that high accumulation of metals (Cd, Zn, Pb, and Cu) occurred in surface (0-30 cm) soils. ALAPI and GYŐRI (2002) in 2000-2001 studied the difference between the element (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) contents of the grey layer (contaminated soil) and the surrounding light layer (uncontaminated soil) in Tivadar and Gergelyiugornya areas by using different extraction methods. They show that the grey layer contained copper, lead and zinc in higher quantities than the light layers whereas the total heavy metal content of the grey layer in the sample from 2000 is higher (Cu 170-185 mg/kg, Zn 515-550 mg/kg) than of the surrounding light mud (Cu 40-100 mg/kg, Zn 150-340 mg/kg), while 2001 was similar to that of the light layer in the previous year's sample (Cu 30-55 mg/kg, Zn 100-165 mg/kg), they concluded that the soil concentration values reflected the element content ratios of the cyanide spill and sludge pollution. This is consistent with the result of KELE et al. (2002) who analysed the elemental constituents (Cd, Pb, Zn, Cu, As, Ni, Cr) of soil samples from flood area of the Tisza in February, 2000. They also found that the range of Cu content is 100-200 mg/kg and 30-60 mg/kg compared to the background limit in Hungary of 30 and 60mg/kg for Cu and Zn respectively. The results of these extraction methods show the heavy metal content (mainly Cu and Zn) of the flood plain soils to be much higher in the Gergelyiugornya than in the Tivadar soil sample. The study showed similar results in agreement with the various authors mentioned above.

3.1.5. Conclusion

By using different extraction methods the metals analysed (Fe, Cu, Zn and Mn) are particularly concerning as their concentrations at the Gergelyiugornya study site were much higher compared to the Tivadar study site. For the Gergelyiugornya soil the amounts of Cu and Zn extracted with aqua regia, HNO_3 and EDTA far exceeded the amounts of the same metals at the Tivadar soil. It may be noted that the increased concentration of heavy metals in the Gergelyiugornya flood plain soil (contaminated site) was due to the two

pollutions events while the Tivadar flood plain soil (control site) had heavy metal contamination that was within the normal range for agricultural soils. The three extraction procedures were compared through analysis for each element. All elements were analysed by the atomic absorption spectrophotometer method (AAS). Aqua Regia-extractable metals of both soils showed a high and significant correlation for all the examined metals. The other two extracting procedures are only partially effective for most of the measured heavy metals in soil.

3.2. Incubation results of two (3, 5) flood plain soil samples

While both soils (Tivadar and Gergelyiugornya) displayed a low concentration of the studied metals by using buffer solution (weak acid) except for the Mn which was 76.0 mg kg as an average of the incubation times compared to Tivadar soil, Fe, Cu, Zn and Cu concentrations in Gergelyiugornya soil were much greater by using nitric acid solution whereas the concentrations of all metals increased initially and then decreased after approximately 2 weeks for all measured metals without exception (see Table 6, Table 7, Table 8 and Table 9). There was no difference between the two soils in CEC which was 28.62, 27.49 for Tivadar and Gergelyiugornya, respectively.

Tivadar (3)					Gergelyiugornya (5)				
Fe	Buffer		HNO₃		**Fe**	Buffer		HNO₃	
Days	Av.	Sd	Av.	Sd	**Days**	Av.	Sd	Av.	Sd
1	8.5	4.26±	619.8	65.9±	1	19.8	1.9±	1132.1	153.3±
7	9.0	1.07±	613.7	49.6±	7	14.9	2.3±	1291.8	143.3±
14	15.6	1.86±	702.4	68.3±	14	19.3	0.9±	1582.8	203.2±
21	10.9	1.81±	692.5	43.8±	21	25.9	2.6±	1212.9	143.9±
	10.9	0.69±	657.1	6.0±		19.9	0.3±	1304.9	14.3±
	0.0	0.0±	5.5	0.0±		1.0	0.0±	1.0	0.0±

Sd: standard deviation; Av: average.

Table 6. Iron concentration (mg/kg) of incubation periods using HNO₃ and buffer solution for Tivadar and Gergelyiugornya flood plain soils

	Tivadar (3)					Gergelyiugornya (5)			
Cu	Buffer		HNO$_3$		**Cu**	Buffer		HNO$_3$	
Days	Av.	Sd	Av.	Sd	**Days**	Av.	Sd	Av.	Sd
1	4.9	0.4±	10.1	1.2±	1	1.5	0.4±	42.9	6.6±
7	5.3	1.4±	12.5	1.1±	7	1.9	0.6±	52.9	8.3±
14	5.4	0.6±	14.7	1.2±	14	2.3	0.3±	60.1	10.2±
21	5.9	1.9±	12.7	1.3±	21	1.1	0.2±	47.1	5.9±
	5.3	0.3±	12.4	0.0±		1.8	0.0±	50.8	1.0±
	0.4	0.0±	0.2	0.0±		1.0	0.03±	1.0	0.0±

Table 7. Copper concentration (mg/kg) of incubation periods using HNO$_3$ and buffer solution for Tivadar and Gergelyiugornya flood plain soils

	Tivadar (3)					Gergelyiugornya (5)			
Zn	Buffer		HNO$_3$		**Zn**	Buffer		HNO$_3$	
Days	Av.	Sd	Av.	Sd	**Days**	Av.	Sd	Av.	Sd
1	6.9	3.0±	25.8	9.8±	1	10.3	1.3±	99.7	15.8±
7	6.8	0.2±	16.9	0.3±	7	10.1	0.9±	113.7	16.2±
14	11.8	1.8±	31.3	12.1±	14	8.0	2.1±	134.2	24.0±
21	10.1	2.3±	9.7	0.4±	21	4.0	0.3±	102.6	9.9±
	8.9	1.0±	21.0	3.1±		8.1	0.0±	113.0	2.9±
	0.4	0.0±	0.1	0.0±		1.0	0.0±	1.00	0.0±

Table 8. Zinc concentration (mg/kg) of incubation periods using HNO$_3$ and buffer solution for Tivadar and Gergelyiugornya flood plain soils

	Tivadar (3)					Gergelyiugornya (5)			
Mn	Buffer		HNO$_3$		**Mn**	Buffer		HNO$_3$	

Days	Av.	Sd	Av.	Sd	Days	Av.	Sd	Av.	Sd
1	2.0	1.1±	34.8	5.0±	1	59.6	7.7±	250.0	46.3±
7	3.0	0.9±	31.9	3.4±	7	148.7	27.0±	494.0	135.4±
14	4.4	0.7±	33.7	2.7±	14	86.0	56.0±	480.3	167.2±
21	3.4	0.3±	33.5	0.6±	21	9.8	1.4±	217.3	23.5±
	3.2	0.1±	33.4	1.0±		76.0	12.0±	360.4	34.6±
	0.1	0.0±	0.0	0.0±		1.0	0.1±	1.0	0.0±

Table 9. Manganese concentration (mg/kg) of incubation periods using HNO_3 and buffer solution for Tivadar and Gergelyiugornya flood plain soils

The Humus content of the Gergelyiugornya soil was greater than the Tivadar soil (Table 1). In contrast to the pH (5.3) of the Tivadar soil, the Gergelyiugornya soil had a pH of 6.2 and calcium carbonate percentages were 0 and 0.35 for both soils respectively. The small difference in these parameters can not be responsible for the different behaviours of Fe, Cu, Zn and Mn observed in these soils. Therefore, here we find proof that the high concentration of the metals in the Gergelyiugornya soil was because of the cyanide and heavy metal pollution effect as mentioned previously.

Concentrations of heavy metals by nitric acid solution of both soils have a similar trend with incubation times whereas Fe, Cu, Zn and Mn increased gradually until 14 days of incubation, then decreased again. However, the opposite trend was observed for Cu where the concentration in the Tivadar soil after incubation times of 14 and 21 days raised from 5.5 to 5.9 as an average using buffer solution. Concentrations of Zn and other metals in Gergelyiugornya soils using buffer solution were inversely related during incubation. STAUNTON and WANG (2005) reported that the correlations between Zn solubility and other soil parameters were very different for aerated and flooded soils, suggesting that different processes are active. They also found a good positive correlation between Cu and Fe solubility, suggesting that Cu released as iron oxides were dissolved due to changing redox and pH conditions. Therefore the relationship between Fe and Cu concentrations by nitric acid solution in both soils may reflect the actual concentration of those metals in the soils without remarkable influence of the soil's properties.

By applying nitric acid solution and taking an average from the incubation times, the total Mn concentration in the Gergelyiugornya soil was about 10 times greater than that in the Tivadar soil (Table 9). STAUNTON and WANG (2005) found more soluble Fe and Cu in flooded soils than aerated soils. It was observed that the amount of Cu by HNO_3 extraction for Gergelyiugornya soil increased gradually with increasing incubation time, reaching a maximum (60.1 mg/kg) after 14 days of incubation before declining after 21 days to the amount of 47.1 mg/kg while by using buffer extraction the maximum was 2.3 mg/kg at day 14 of incubation and decreased to an average of 1.1 mg/kg after 3 weeks of incubation. WANG and STAUNTON (2003) stated that there is a tendency for water soluble Cu content to increase then decrease with time. MA and DONG (2004) divided the changes in metal mobility with incubation time into two groups: Pb and Cu decreased with incubation whereas As and Fe increased.

The exception in our incubation was for Gergelyiugornya soil where the Zn concentration decreased gradually with increasing incubation time when we used buffer solution. There was no significant increase for the Zn by using nitric acid solution for the same soil. The inverse relationship between concentrations of Zn and other metals in buffer solution is that the Zn concentration decreased gradually from 10.3 mg/kg after the first day of incubation to 8.0 mg/kg after 14 days of incubation before reaching the minimum (4.0 mg/kg) after about 21 days of incubation (Table 8). However, the Zn concentrations by using nitric acid solution and buffer solution did not show significant differences in both soils in the incubation times. STAUNTON and WANG (2005) noticed that the soluble Zn fluctuated over a 5-month period and was initially greater in moist soil than in flooded soil. However, the opposite trend was observed for Zn concentrations in the two soils and the Zn concentrations by using nitric acid solution and buffer solution did not show significant differences with incubation times. Also they indicated that for flooded, reduced soils, Zn solubility decreased with increasing pH as is usually observed together with increased Fe solubility. They also found a slight decrease in Zn solubility with increasing Mn dissolution, but there is probably not a causative link. This may suggest the importance of Fe and Mn oxides in controlling metal solubility in soils.

The concentration of buffer-soluble iron does not correlate with the duration of incubation. Gergelyiugornya soil has significantly higher amounts than Tivadar soil. This

difference is not significant for the middle of the incubation period. In cases where samples were compared before and after incubation the correlation is significant. It is well known that flooding induces reductive dissolution of Fe oxides, and thus leads to increasing Fe^{2+} concentrations in the soil solution (PONNAMPERUMA, 1972). It is noticeable that in Tivadar soil the Fe concentration increased with incubation time which may be because of the reductive Fe dissolution. Our results were in agreement with the observation of REUTER and BELL (2001) who stated that ferrous iron is far more soluble than ferric iron, thus creating an increase in Fe mobility. In the case of the concentration of HNO3-soluble iron which occurred independently from the duration of the incubation (Table 6), the Gergelyiugornya sample contains a significantly higher concentration than the Tivadar sample. The concentration of HNO_3-soluble iron is a sign of heavy metal pollution and thus significant differences can be suspected between the samples.

The copper content of the Tivadar sample is significantly higher than the Gergelyiugornya sample in the case of using weak acid solution (Table 7). The phenomena can not be explained by the increasing effect of the sediment delivered by the River Szamos. It is rather a consequence of pollution decreasing the amount of copper concentration at least that measured in closely neutral pH. This can be explained by ion exchange effects on the surface of the soil particles where only strongly attached copper forms could remain because of the cyanide pollution. This is proved by the almost equal amount of measured copper concentration in the Tivadar sample. On Table 7 and Table 8 it can be seen that in the case of a slightly acidic solution, the copper and the zinc concentration in the Gergelyiugornya sample is significantly higher than in the Tivadar sample. The phenomena can be explained by the increasing effect of the pollution carrier - The River Szamos. During the examination of the manganese, buffer and the HNO_3 solutions were used, the expected phenomena can be seen. In the case of both solutions the manganese concentration in the Gergelyiugornya sample is almost an order of magnitude higher than in the Tivadar sample (Table 9). The results of the study are in agreement with the authors mentioned above.

By performing two-factor ANOVA analysis for different incubation periods and soil samples and in the case of using the buffer solution, the differences between the two soils is significant for iron, copper and manganese while for the zinc it isn't significant

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(SD$_{5\%}$=1.4) and the difference of zinc averages between the two soils is 4.4 and 4.0 for Tivadar and Gergelyiugornya soil samples, respectively. For the incubation time (weeks) there is a significant difference between averages for iron and manganese, however there isn't a significant difference for zinc and copper, where the incubation time has no effect on averages of concentrations. In the case of using nitric acid solution the differences between the two soils is significant for all investigated heavy metals. For the incubation time (weeks) there isn't a significant difference between the weekly averages except for manganese where the first weekly average is (135.4) significantly higher than the third week (63.1) average (SD$_{5\%}$=65.8) There is a significant difference between the two soil samples for the investigated heavy metals except for the zinc but the incubation time isn't significant.

3.2.1. Conclusion

In the incubation experiment with the slightly acid solution (buffer) it was found that the iron and manganese concentrations were significantly higher in the Gergelyiugornya sample, below the inflow of River Szamos in River Tisza while the copper concentrations are significantly higher in Tivadar sample, above the inflow of River Szamos. There were no significant differences in the zinc concentrations of the two samples, below and above the inflow of the River Szamos. In the case of the strongly acidic solution (HNO$_3$) all the measured heavy metal concentrations were an order of magnitude higher in Gergelyiugornya sample, below the inflow of River Szamos. The obtained data showed the affects of reduction on the solubility of heavy metals under different incubation periods and this affect was less pronounced after lengthier incubation periods (21 days) in comparison to shorter incubation periods (14 days). This result is in harmony with the manganese decrease of the incubated condition as was shown in the available literature data.

3.3. Modelling of metals concentration

3.3.1. Modelling in case of pure treatment system (without cyanide)

The concentrations of Fe, Cu, Mn and Zn as a function of pH and pE and it can be observed that Fe(III) concentration is high at low pH values as was found in the literature and that Fe is more soluble at a low pH and considered pH dependent. i.e. RÖMHELD and MARSCHNER (1986) stated that the concentration of Fe(III) is related to pH, increasing from 10^{-8} to 10^{-20} M as pH increases from 4 to 8. The concentration of Fe(II) reached its peak at relatively higher pE and pH values. The model shows sensitivity of pH and redox potential to Fe(III) solubility. SMITH et al. (2003) mentioned that above pH 4.0 the ferrous iron spontaneously oxidizes to ferric iron, which in turn reacts with water to release three hydrogen ions for every ferric ion reacted, driving the pH further down. CRAWFORD (1999) stated that most heavy metals have a field of minimum solubility somewhere between pH 7 and 11. At pH levels below 7 and above 11, the heavy metal solubility tends to increase dramatically. Heavy metals that exhibit this kind of behaviour with increased solubility at both high and low pH values are often referred to as being amphoteric. This means that they are able to react both as acids and bases. The model results for Fe(III) and Fe(II) were in agreement with the literature data about the influence of pH which indicated that the acidic pH cause increasing in ferric and ferrous iron concentrations. BODEK et al. (1988) reported that iron solubility may be significantly affected by the formation of other iron compounds, such as phosphates, sulfides, and carbonates. Beside pH, redox status is another factor affecting metal solubility in soil (CHUAN et al., 1996). Also U.S.EPA (2003) reported that manganese and copper are oxidizing agents that convert ferrous irons to the more insoluble ferric form. They also found that changes in soil properties, such as pH or redox status, can bring more insoluble iron into soil fractions.

The decreasing in the pH causes an increase in the concentration of the copper as was mentioned in literature data. STEHOUWER and MACNEAL (2004) found that the Solubility of Cu decreases with increasing pH. When pH is greater than 8.0, the solubility of Cu increased sharply, probably because of an increase in dissolution of organic complex copper at high pH (TACK et al., 1996). Our results are in agreement with McLEAN and BLEDSOE (1992) who stated that copper has behaved differently from the other cations, actually decreasing with increased pH. This behaviour is the opposite of the typical

relationship between metal adsorption and pH. The explanation is that at low pH, H^+ competes with the Cu for complexation with the organic matter.

The concentration of Zn is pE independent and increases at lower pH values. GAO (2007) stated that the calculated Zn concentrations are rather constant over a wide pE range, but are strongly dependent on pH. Increases were observed (McBRIDE and BLASIAK, 1979) in soil solution for Zn at pH values >7.5, due to the formation of soluble-Zn organic-matter complexes. GUPTA et al. (1987) suggested that at high pH, precipitation reactions control Zn solubility, whereas at neutral to acidic pH, specifically adsorbed Zn may control Zn solubility. Depending on the soil and soil properties, different Zn precipitates may form in soils and control Zn solubility at different levels, the solubility of Zn and the mechanisms that control Zn solubility may vary with soil properties, such as pH, organic matter content and clay content McBRIDE et al. (1997). ZHANG et al. (2003) stated that the copper and zinc contents in surface soil directly influence the movement of Cu and Zn in the soil system.

The manganese is pH dependent as was mentioned by TATE (1995) who stated that Mn is more soluble at a low pH. This is in agreement to what was found in the literature i.e. GREEN et al. (2003) reported that the higher observed maximum Mn concentrations seem to be found alongside lower pH values. He also observed increase in soluble Mn when Eh became less than approximately 450 to 500 mV. Other authors i.e. SPOSITO (1989) stated that the solubility of Mn in soils is known to be highly sensitive to changes in soil redox conditions. We are in agreement with the mentioned observations and with DONG et al. (2000) who stated that understanding the relationship between heavy metal solubility and Fe chemistry in a dynamic soil system may provide important information for assessing potential mobility of heavy metals in soil environments, which cannot be modelled successfully at the present time.

3.3.1.1. Conclusion

In this model the observed relationship between metal concentrations and the effect of pH and pE changes corresponded with our understanding of the system. Both high

pH and low pH values can increase the solubility of heavy metals. The model fit for Cu, Zn and Mn was fairly good and this was in agreement with the literature. The poorer fits for FeIII, FeII indicate some other influence, presumably added chemical materials to the model system. However, concentrations of the heavy metals can vary significantly even within localized areas due to soil types and presence of other sources. The models do not include the organic matter effect in an adequate way and there is a need for further refinement of the tools.

3.3.2. Modelling in case of cyanide-affected system

The different concentrations of metals with cyanide and without cyanide show the effect of cyanide on heavy metal concentration as a function of pH and pE. At a pH range of 5-6 there is a big difference which means the concentration is moving towards a lower pH. This can be the effect of added cyanide. Cyanide is a strong complex ligand which can dissolve the ferric iron and with cyanide ions the ferric iron can be increased at relatively higher pH. KÓNYA and NAGY (2003) stated that the main mineral components of soil (primary silicates, clay minerals, oxides) have negative charges at pH values of around 8.5, preventing the adsorption of negative cyanide ions. We expect high differences of ferric iron at the zone of original high concentration and at lower pH values the differences of cyanide iron curves show decreasing in ferric iron solubility. MEEUSSEN et al. (1994, 1995) stated that iron–cyanide complexes are becoming more soluble with increasing soil pH and increasing redox potential.

We have found a high variation in the area of high pH and pE values. This result is in agreement with the available literature. Theoretically the copper is pE independent but in this model system other chemical ions may enhance the pE to change the copper concentration. Copper has a small and linear effect in all ranges of pH and pE, a greater positive effect when the concentration is originally increased. CHRISTL and KRETZSCHMAR (2001) reported that at a pH > 6 Cu sorption was reduced significantly due to increasing concentrations of dissolved metal–organic complexes. KÓNYA and NAGY (2003) stated that copper and zinc ions have no effects on the cyanide adsorption. They also reported that in the presence of Zn(II) and Cu(I) ions HCN is at its greatest amount at pH=7-9, because the dominant complex form is the 1:3 complex both in the

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cases of Zn(II) and Cu(I). Our model results show a maximum effect at low pE and medium pH values. At low pH and low pE there is competition between ions and cations to attach the cyanide as ligands. The cyanide reduces zinc concentration at areas of low pH and high pE which may be because of the oxidation or the high zinc concentration which was in dissolved form. This complexity can be caused by the cyanide effect. Various studies have shown that there may be changes in Zn solubility with other soil properties. Iron, Mn, and Al oxides contain surface-hydroxyl functional groups that may strongly bind metals with increased adsorption at high pH (SPOSITO, 1989). GUPTA et al., 1987; SINGH and ABROL, 1985, mentioned that there are some studies which have noted that precipitation at high pH and adsorption at low pH may occur with Zn in soils. The high concentration at relatively high pH and high pE might be a result of the complex solubility effect of cyanide. Mixing or equilibrium may also exist with other phases such as manganese iron cyanide, in that case leading to lower solubility (GHOSH et al., 1999). We are in agreement with the observations of the authors mentioned above.

3.3.2.1.Conclusion

Thermodynamic models indicate that the dissolved cyanide complexes are a function of pH and pE conditions. There is an increasing variation in the concentration by decreasing the pH and pE for Fe III and Cu. The decreasing of pH when the pE is increasing causes a maximum concentration for ferrous iron, while there is a decrease in the variation concentration by decreasing of the pH and pE for Zinc. The low pH has reduced the manganese concentration. In this model we highlighted the multi ions-soil system. Theoretically and from the experimental data there are facts about the single ion of soil system, these facts may be not valid in our modelling system because of the competition of cations on cyanide ligands and soil surface. The modelling methods have shown some effect of cyanide on examined heavy metals concentration and it has predictive value in case of cyanide contamination on the mobility of different metal ions and this is the significant of the model calculations.

4. THE NEW SCIENTIFIC RESULTS

- The developed electrochemical redox titration method can be used to measure the soil redox buffering capacity. By using this method there is an exponential decrease in reduction and linear increase in oxidation buffering capacity as a function of time.

- This study has confirmed the fact that the heavy metal concentrations of the sampled soils from the study areas are different and showed significant differences between the Fe, Cu, Zn and Mn concentration of polluted (Gergelyiugornya) and non-polluted (Tivadar) site. Aqua regia-extractable metals of both soils showed high and significant correlation for all examined metals compare to HNO_3 and EDTA which are only partially effective for most of the measured heavy metals in soil.

- Under incubation experiment Fe, Cu, Zn, Mn concentrations were much higher in Gergelyiugornya soil than Tivadar soil. Concerning to how reduction affects the solubility of heavy metals, the maximum concentration was reached within about 15 days, afterwards, decreasing soluble heavy metal concentrations could be observed again. In the reducing experiment, the extractable heavy metal concentration did not increase linearly as a function of time.

- A new visualization method of modelled concentrations by using a new model program which can make the Minteq program run with different pH and pE parameters pairs, for the evaluation of the modelled data the result can be presented as 3D graphical map. The modelling methods have shown some effect of cyanide and it can be useful in prediction of cyanide/heavy metal contamination.

5. SUMMARY

Soil samples taken from different areas of the river Tisza's banks have been analysed in the present survey. One sample stems from Tivadar that is above the Szamos site of the Tisza River, the other from directly under the river site. The greatest differences were found in the samples taken directly from the river bed near the bank. The Fe, Cu, Zn and Mn concentrations of the samples have been examined with EDTA, HNO_3 and Aqua Regia extraction. We have developed a variable time titration method in order to analyse the redox buffering capacity of the soil samples and all samples have been examined by these means. An incubation experiment was conducted to detect the possible effects of periods of sustained flooding on the soluble heavy metal concentration. The relevant point of the experiment was to incubate soil samples hermetically closed for 1, 7, 14, 21 days at room temperature while regularly measuring their heavy metal concentration week by week. As we did not have a sufficient amount of experimental data to measure and evaluate effects, we have conducted computer-based modelling using the MINTEQ program at various pH and pE levels, and calculated the balance of heavy metal concentrations with and without cyanide content.

A titration method has been worked out for measuring the redox capacity. This method offsets most of the disadvantages of the conventional measuring methods because more than just the actual redox potential is detected. During the measurement, the redox property samples are changing continuously by the addition of a reductant or an oxidant. Using this procedure, the sampling and measuring errors can be decreased. To avoid the problems associated with the pH-E_h cross effect error, both values are measured in a parallel way, and the evaluating software can calculate the theoretical corrections automatically. For the oxidative redox-buffer capacity measurements, we have found, that with increasing time between adding next dose, buffer capacity increased, while the reductive measurements decreased. This suggests a different mechanism for the direction of the two processes. This method was elaborated for determining the redox buffer ability of soil samples. Its relationship to the redox potential is similar to that of the acidity values to pH. The acidity value depends on the analytical methods. If the applied oxidant does not buffer the redox potential, it can be substituted by acidity, otherwise by hydrolytic acidity. Therefore, it is an extensive quantitative feature of soil, which shows the quantity of

oxidants that makes it possible to bring the soil into a given, strongly oxidised state. By use of this method, the errors mentioned in the case of redox potential measurement can be eliminated, and moreover, a characteristic feature of soil, that changes to a far lesser extent as a function of time and conditions, can be measured.

As a result of evaluating the redox buffering capacity of the analysed soil samples we have found that the redox potential of the samples largely depends on the timing of analysis, that is, the small reaction speeds of redox processes had a significant influence on the final results. Increased waiting periods between two doses have definitely resulted in higher values (which means that oxidation values were increased while reduction buffering capacity values were decreased). Mathematically, it means that the kinetic relationships can be best described with a linear curve in the case of oxidation and with an exponential curve in the case of reduction. At a waiting time of approximately five minutes between two doses, the values were nearly equal. Comparing the redox potentials of a polluted sample (Gergelyiugornya) with an unpolluted one (Tivadar) coming from areas situated near to each other, significant differences have been traced in the oxidation buffering capacity values. The values were higher in the polluted sample, especially in the case of long-term examinations nearer to the balance level. Furthermore, the reduction buffering capacity values at various speeds had a good correlation and the rise of the curve was near to 1, which means that there is not a significant difference between the two samples regarding their reduction. This might be due to the fact that this sample contained a larger amount of reduced material, e.g. a heavy metal. Another evidence for this is that the buffer-soluble iron content of the given materials similarly shows significant differences, while the buffering capacities have identical tendencies.

In regards to the concentrations extracted with different methods, we experienced significantly higher concentration values in the case of the polluted samples that were taken from under the Szamos site than in the case of unpolluted samples taken from above the site. Regarding Cu and Zn, the concentration of pollution did not depend on the extracting materials. Therefore, we can assume that the examined metal is in an easily mobilised form in the sample. Hermetically closed incubation experiments have been conducted in order to decide how reduction affects the solubility of heavy metals. As opposed to our expectations, instead of permanently increasing concentration values, the

maximum concentration was reached within 15 days, afterwards, decreasing soluble heavy metal concentrations could be observed again. This phenomenon could not be explained with simple chemical processes, so most probably, microbiological processes are of influence. We have also examined the effect of pH and pE on the solubility of the analysed heavy metals in the soil solution, and the effect of conditionally added cyanide ions, all by means of computer modelling based on thermodynamic balances and 3D demonstration of the concentration values. The results of the models run without the addition of cyanide and correspond with the values described in the available literature, which served as a basis for checking the application. By observing the changes in concentration, that is the difference between the two measured values, as a result of cyanide ion addition, we have gained new results that have not been described in previous literature and may be of relevant informative value for the estimation of the effects of cyanide contamination as part of the heavy metal concentration.

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