

**Szent István University  
Doctoral School of Environmental Science**

**INVESTIGATION OF HEAVY METALS SOLUBILITY AND REDOX  
PROPERTIES OF SOILS**

**Ph.D. Dissertation**

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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 Lopus 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<sup>3</sup> 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 11<sup>th</sup> 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 sludges 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:  $\text{NO}_3^-/\text{NO}_2^-$ ,  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Mn}^{4+}/\text{Mn}^{2+}$  (BOHREROVA et al., 2004).

Except for the simple cyanide compounds consisting of a single metal ion in combination with  $\text{CN}^-$ , 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 Gergelyugornya 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 (Gergelyugornya) 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 ( $\text{HNO}_3$ ), 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. LITERATURE REVIEW

### 2.1. Heavy metals

The metals are classified as “heavy metals” if, in their standard state, they have a specific gravity of more than 5 g/cm<sup>3</sup>. There are sixty known heavy metals. Heavy metals can accumulate over time in soils and plants and could have a negative influence on physiological activities of plants (e.g. photosynthesis, gaseous exchange, and nutrient absorption), causing reductions in plant growth, dry matter accumulation and yield (DEVKOTA and SCHMIDT, 2000). There are many terms used to describe and categorize metals, including trace metals, transition metals, micronutrients, toxic metals, heavy metals. Many of these definitions are arbitrary and these terms have been used loosely in the literature to include elements that do not strictly meet the definition of the term. Metals are defined as any element that has a silvery luster and is a good conductor of heat and electricity (McLEAN and BLEDSOE, 1992).

#### 2.1.1. Fate of heavy metals in soil and environment

The incidence of heavy metal contamination from both natural and anthropogenic sources has increased concern about possible health effects. Natural and anthropogenic sources of soil contamination are widespread and variable (TAHIR et al., 2007). According to ROSS (1994) the anthropogenic sources of metal contamination can be divided into five main groups: (1) metalliferous mining and smelting (arsenic, cadmium, lead and mercury); (2) industry (arsenic, cadmium, chromium, cobalt, copper, mercury, nickel, zinc); (3) atmospheric deposition (arsenic, cadmium, chromium, copper, lead, mercury, uranium); (4) agriculture (arsenic, cadmium, copper, lead, selenium, uranium, zinc); and (5) waste disposal (arsenic, cadmium, chromium, copper, lead, mercury, zinc). Heavy metal contamination of soil results from anthropogenic processes such as mining (NAVARRO et al., 2008) smelting procedures (BRUMELIS et al., 1999) and agriculture (VAALGAMAA and CONLEY, 2008) as-well as natural activities. Chemical and metallurgical industries are the most important sources of heavy metals in the environment (CORTES et al., 2003). Industries such as plating, ceramics, glass, mining and battery manufacture are considered the main sources of heavy metals in local water systems causing the contamination of groundwater with heavy metals. Heavy metals which are commonly found in high concentrations in landfill leachate are also a potential source of pollution for groundwater (AZIZ et al., 2004). Large areas of agricultural land are contaminated by heavy metals that mainly originate from former or current mining activities, industrial emissions or the application of sewage sludge. Metals exist in one of four forms in the soil: mineral, organic, sorbed (bound to soil), or dissolved. Sorbed metals represent the third largest pool, and are generally very tightly bound to soil surfaces. Although mineral, organic, and sorbed metals are not immediately absorbed by plants, they can slowly release metals into solution (JONES, 2003). The inability to determine metal species in soils hampers efforts to understand the mobility, bioavailability and fate of contaminant metals in environmental systems together with the assessment of the health risks posed by them, and the development of methods to remediate

metal contaminated sites (D'AMORE et al., 2005). However, in some natural soils developed from metal-rich parent materials, as-well as in contaminated soils, up to 30 to 60% of heavy metals can occur in easily unstable forms (KARCZEWSKA et al., 1998). In soil, metals are found in one or more of several "pools" of the soil, as described by SHUMAN (1991):

- dissolved in the soil solution;
- occupying exchange sites in inorganic soil constituents;
- specifically adsorbed in inorganic soil constituents;
- associated with insoluble soil organic matter;
- precipitated as pure or mixed solids;
- present in the structure of secondary minerals; and/or
- present in the structure of primary minerals

In situations where metals have been introduced into the environment through human activities, metals are associated with the first five pools. Native metals may be associated with any of the pools depending on the geological history of the area. The aqueous fraction, and those fractions in equilibrium with this fraction, i.e. the exchange fraction are of primary importance when considering the migration potential of metals associated with soils (McLEAN and BLEDSOE, 1992). Heavy metals naturally occur in the environment, but may also be introduced as a result of land use activities. Natural and anthropogenically introduced concentrations of metals in near-surface soil can vary significantly due to different physical and chemical processes operating within soils across geographic regions (MURRAY et al., 2004). Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several environmental factors. The most significant environmental factors appear to be (i) soil type, (ii) total organic content, (iii) redox potential, and (iv) pH (MURRAY et al., 1999). Although heavy metals are generally considered to be relatively immobile in most soils, their mobility in certain contaminated soils may exceed ordinary rates and pose a significant threat to water quality (BUNZL et al., 2001). Organic manure, municipal waste, and some fungicides often contain fairly high concentrations of heavy metals. Soils receiving repeated applications of organic manures, fungicides, and pesticides have exhibited high concentrations of extractable heavy metals (HAN et al., 2000) and increased concentrations of heavy metals in runoff (MOORE et al., 1998). Previous studies indicate that metal constituents of surface soil directly influence the movement of metals, especially in sandy soils (MOORE et al., 1998; CEZARY and SINGH, 2001).

### 2.1.2. Behavior of heavy metals in soil

Monitoring the endangerment of soil by heavy metals is of interest due to their influence on ground and surface water (CLEMENTE et al., 2008; BOUKHALFA, 2007) and also on flora (PANDEY and PANDEY 2008; STOBRAWA and LORENC-PLUCIŃSKA, 2008), animals and humans (DE VRIES et al., 2007). The overall behavior of heavy metals in soil is said to be governed largely by their sorption and desorption reactions with different soil constituents, especially clay components (APPEL and MA, 2002). The chemical behavior of heavy metals in soils is controlled by a number of processes, including metal cation release from contamination source materials (e.g., fertilizer, sludge, smelter dust, ammunition, slag), cation exchange and specific adsorption onto surfaces of minerals and soil organic matter, and precipitation of secondary minerals (MANCEAU et al., 2000). The relative importance of these processes depends on soil composition and pH. In general, cation exchange reactions and complexation to organic matter are most important in acidic soils, while specific adsorption and precipitation become more important at near-neutral to alkaline pH values (VOEGELIN et al., 2003). EL-GHAWI et al. (2007) studied the trace metal concentrations in some Libyan soils and found that the concentrations in clay surface soil are higher than in sandy soil. The multiple regression analyses performed confirmed the importance of pH as well as other soil properties such as texture, electrical conductivity and organic matter or carbonates on the behaviour of nutrients and heavy metals (SORIANO-DISLA et al., 2008). Increased anthropogenic inputs of Cu and Zn in soils have caused considerable concern relative to their effect on water contamination (ZHANG et al., 2003). Oxidizing conditions generally increase the retention capacity of metals in soil, while reducing conditions will generally reduce the retention capacity of metals (McLEAN and BLEDSOE, 1992). Soil reduction has been shown to result in the coincident release of metals associated with minerals that are susceptible to reductive dissolution, in particular Mn and Fe oxides (CHARLATCHKA and CAMBIER, 2000; DAVRANCHE and BOLLINGER, 2000). FILEP (1998) stated that contaminants reaching the soil can be divided into two groups, namely micropollutants and macropollutants. Micropollutants are natural or anthropogenic molecules, which are toxic at very low concentration. Macropollutants are present in the environment locally and/or temporarily to a much higher degree than normal level. The main micropollutants of soils are inorganic or organic compounds. (i) Inorganic micropollutants are mainly the toxic and potentially toxic heavy metals (Pb, Cd, Ni, Cr, Hg, Cu, Zn etc.) (ii) Organic micropollutants include pesticides and certain non-pesticide organic molecules: e.g. aliphatic solvents, monocyclic aromatics, halogenated aromatics, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), surfactants, plastifiers. Frequent macropollutants are:

- Inorganic (nitrogenous fertilizers)
- Organic (crude oil and products of oil industry)

Toxic heavy metals and micronutrients utilized as metal ions exist in the soil as species with several types of mobility (Table 1) and take part in many interactions.

Species	Examples
Free metal ion	$[\text{Cd}(\text{aq})]^{2+}$ , $[\text{Cu}(\text{aq})]^{2+}$ , $[\text{Pb}(\text{aq})]^{2+}$
Ion pairs and inorganic complexes	$\text{PbCO}_3$ , $\text{PbHCO}_3^+$ , $\text{PbCl}^+$ , $\text{CdCO}_3$ , $\text{CdCl}^+$
Organic complexes	$R\left(\begin{smallmatrix} \text{COO} \\ \text{COO} \end{smallmatrix}\right)M$ ; M-fulvic acid complexes
Metal sorbed to <i>inorganic colloids</i>	Exchangeable and nonexchangeable forms (in solid phase)
Metal sorbed to <i>organic colloids</i>	Exchangeable forms and M-humic acid complexes (in solid phase)
Precipitates	$\text{PbCO}_3$ , $\text{CdCO}_3$ , $\text{CdS}$ etc. (in solid phase)

M = metal ion

Table 1. Chemical species of heavy metals in soil with respect to solubility (FILEP, 1998)

In liquid phase they exist as hydrated ions, soluble organic and inorganic complexes and as a component of fine disperse floating colloids. In the solid phase they occur as insoluble precipitates and minerals, on the surface of organic and inorganic colloids in exchangeable and non exchangeable (specific adsorbed) forms.

#### 2.1.2.1. Accumulation

ATANASSOV et al. (1999) stated that heavy metals are of interest due to their abundance in the environment, which has increased considerably as a result of human activities. Their fate in polluted soils is a subject of study because of the direct potential toxicity to biota and the indirect threat to human health via the contamination of groundwater and accumulation in food crops (MARTINEZ and MOTTO, 2000). Heavy metals are dangerous because they tend to bioaccumulate. This means that the concentration of a chemical in a biological organism becomes higher relative to the environmental concentration (KAMPA and CASTANAS, 2008). Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (GIMMLER et al., 2002). In environments with high nutrient levels, metal uptake can be inhibited because of complex formation between nutrient and metal ions (GÖTHBERG et al., 2004). Therefore, a better understanding of heavy metal sources, their accumulation in the soil and the effect of their presence in water and soil on plant systems seems to be a particularly important issue (SHARMA et al., 2004). Accumulation of heavy metals can also cause a considerable detrimental effect on soil ecosystems, environment and human health due to their mobilities and solubilities which determine their speciation (KABATA-PENDIAS, 1992). The soil to plant transfer factor is one of the important parameters used to estimate the possible accumulation of toxic elements, especially radionuclides through food ingestion (EL-GHAWI et al., 2005). Several studies have indicated that crops

grown on soils contaminated with heavy metals have higher concentrations of heavy metals than those grown on uncontaminated soil (NABULO, 2006). Heavy metals accumulating in soil directly (or through plants indirectly) enter food chains, thus endangering herbivores, indirectly carnivores and not least the top consumer humans (KÁDÁR, 1995). Compounds accumulate in living organisms any time they are taken up faster than they are broken down (metabolized) or excreted (O'BRIEN, 2008). Total levels of heavy metals have shown a trend relationship between metal concentration in soil and long term irrigation (ABDEL-AZEEM et al, 2007). The Association of American Plant Food Control Officials (AAPFCO, 2007) established rules and standards in regard to heavy metals in fertilizer. According to the Uniform State Fertilizer Bill, fertilizers that contain guaranteed amounts of phosphates and/or micronutrients are adulterated when they contain metals in amounts greater than the levels of metals established in Table 2.

<b>Metals</b>	<b>ppm per 1% P<sub>2</sub>O<sub>5</sub></b>	<b>Micronutrients</b>
Arsenic	13	112
Cadmium	10	83
Cobalt	136	2228
Lead	61	463
Mercury	1	6
Molybdenum	42	300
Nickel	250	1,900
Selenium	26	180
Zinc	420	2,900

Table 2. Maximum heavy-metal levels allowed in fertilizer (AAPFCO, 2007)

Metals such as lead, arsenic, cadmium, copper, zinc, nickel, and mercury are continuously being added to our soils through various agricultural activities such as agrochemical usage and long-term application of urban sewage sludge in agricultural soils, industrial activities such as waste disposal, waste incineration and vehicle exhausts, together with anthropogenic sources. All these sources cause accumulation of metals and metalloids in our agricultural soils and pose threat to food safety issues and potential health risks due to soil to plant transfer of metals (KHAN, 2005). Investigations of heavy metal migration and accumulation in natural conditions are very laborious as it is difficult to control all numerous factors influencing metal behaviour in the field (ERMAKOV et al., 2007).

#### **2.1.2.2.Solubility and Mobility**

Among the negative impacts related to human activities, the mobilization of heavy metals from their natural reservoirs to the aquatic and terrestrial ecosystems has become a generalized problem almost worldwide (HAN et al., 2002; KOPTSIK et al., 2003; SALEMAA et al., 2001). Heavy metal solubility and

mobility in soils are of environmental significance due to their potential toxicity to both humans and animals (CHIRENJE et al., 2003). The transfer and the chemical stability of metal contaminants in soils and sediments are controlled by a complex series of biogeochemical processes depending on variables like pH, clay content and redox potential (VANBROEKHOVEN, 2006). Trace metal mobility is closely related to metal solubility, which is further regulated by adsorption, precipitation and ion exchange reactions in soils (MA and DONG, 2004). The transfer of heavy metals from soils to plants is dependent on three factors: the total amount of potentially available elements (quantity factor), the activity as well as the ionic ratios of elements in the soil solution (intensity factor), and the rate of element transfer from solid to liquid phases and to plant roots (reaction kinetics) (BRÜMMER et al., 1986). However, changes in soil solution chemistry, such as pH, redox potential and ionic strength, may also significantly shift the retention processes of trace metals by soils (GERRINGA et al., 2001). These effects may be further complicated by ligand competition from other cations (NORRSTROM and JACKS, 1998). Soil redox status varies temporally and spatially. In a surface soil it is influenced by rainfall, bioactivity, and changes in land use, whereas in vadose zones it varies mainly with the fluctuation of water table (BOUL et al., 1997). Reduction in redox potential may cause changes in metal oxidation state, formation of new low-soluble minerals, and reduction of Fe, resulting in release of associated metals (BAUMANN et al., 2002; CHUAN et al., 1996). Metal solubility usually increases as the pH decreases, with the notable exception of metals present in the form of oxyanions or amphoteric species. Since soil solution properties might change with time (for example following sludge application), the solubility and speciation of metals might also be time-dependent (MO et al., 1999). As soil pH increases, the solubility and availability of these trace nutrients decreases (MELLBYE and HART, 2003). The solubility of most metals becomes limited around pH values of 5.5 to 6.0. Aluminum hydroxide, a white gelatinous precipitate, begins to form at pH 4.5. Ferric hydroxide forms at around 3.5, while ferrous hydroxides do not form until a pH of 8.5. Iron hydroxide and oxy-hydroxide precipitates are yellow and red in color. Immobilization of metals by mechanisms of adsorption and precipitation will prevent movement of the metals to ground water. Metal-soil interaction is such that when metals are introduced at the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded or metal interaction with the associated waste matrix enhances mobility. Changes in soil environmental conditions over time, such as the degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes may also enhance metal mobility (McLEAN and BLEDSOE, 1992).

### **2.1.2.3. Bioavailability**

Bioavailability depends on biological parameters and on the physicochemical properties of metals, their ions, and their compounds. These parameters in turn depend upon the atomic structure of the metals, which is systematically described by the periodic table (VANLOON and DUFFY, 2000). The bioavailability and mobility of metals in soil strongly depends on the extent of their sorption with solid phases. Partitioning of heavy metals between solid and aqueous phases is controlled by properties such as surface area, surface

charge (induced by the formation of organic coatings on the surface), pH, ionic strength, and concentration of complexing ligands (PETROVIC et al., 1999). The pH and redox potential affects the bioavailability of metals in solution: at high pH elements are present as anions, while at low pH the bioavailability of metal ions is enhanced (PETERSON et al., 1984). In natural systems the bioavailability of trace metals is primarily controlled by adsorption-desorption reactions at the particle-solution interface (BACKES et al., 1995). The bioavailability of some metals (Co, Ni, Cu, Zn) decreases in horizon B of the soils with clay illuviation due to their enhanced adsorption capacity. The availability of metals also decreases in the calcareous soil horizons because of the enhanced buffering capacity of these horizons (SIPOS, 2004). Soil pH will influence both the availability of soil nutrients to plants and how the nutrients react with each other. HOLLIER and REID (2005) stated that at a low pH many elements become less available to plants, while others such as iron, aluminum and manganese become toxic to plants and in addition, aluminum, iron and phosphorus combine to form insoluble compounds. In contrast, at high pH levels calcium ties up phosphorus, making it unavailable to plants and molybdenum becomes toxic in some soils. Generally, heavy metals become increasingly mobile and available as the pH decreases (TYLER and OLSSON, 2001) depend on the actual combination of physical and chemical properties of soil (SHUMAN, 1985).

#### **2.1.2.4. Toxicity**

Recently pollution of the general environment has gathered an increased global interest. In this respect, contamination of agricultural soils with heavy metals has always been considered a critical challenge in the scientific community (FARUK et al., 2006). Heavy metals are generally present in agricultural soils at low levels. Due to their cumulative behaviour and toxicity, however, they have a potentially hazardous effect not only on crop plants but also on human health (DAS et al., 1997). Even metals essential to plant growth, like copper (Cu), manganese (Mn), molybdenum (Mo), and zinc (Zn) can be toxic at high concentrations in the soil. Some elements not known to be essential to plant growth, such as arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), lead (Pb), nickel (Ni), and selenium (Se), also are toxic at high concentrations or under certain environmental conditions in the soil (SLAGLE et al., 2004). Both pH and redox potential affect the toxicity of heavy metals by limiting their availability (PETERSON et al., 1984). At low pH, metals generally exist as free cations; at alkaline pH, however, they tend to precipitate as insoluble hydroxides, oxides, carbonates, or phosphates (MAMBOYA, 2007). Chemical hazards include chemical agents such as heavy metals, nutrients such as nitrogenous compounds, phosphorus compounds, minerals, insecticides, pesticides, fertilizers, fungicides, herbicides and organic hazards (NABULO et al., 2008). Metals, unlike the hazardous organics cannot be degraded. Some metals such as Cr, As, Se, and Hg can be transformed to other oxidation states in soil, thus influencing their mobility and toxicity (McLEAN and BLEDSOE, 1992). Many of them (Hg, Cd, Ni, Pb, Cu, Zn, Cr, Co) are highly toxic both in elemental and soluble salt forms. High concentration of heavy metals in soils is toxic for soil organisms: bacteria, fungi and higher organisms (WOOLHOUSE, 1993). Short-term and long-term effects of pollution differ depending on metal and soil characters (KÁDÁR, 1995; NÉMETH and KÁDÁR, 2005). In the after-effect of heavy metal

pollutions, the role of pollutant bounding or leaching increases which determines their bioavailability and toxicity (MÁTHÉ-GÁSPÁR et al., 2005). When soil is acidified it increases the concentration of free aluminium ions in the water that is in the soil, and these are potentially toxic to the root systems of plants. The mobility of many heavy metals also increases when soil becomes more acidic. Perhaps the most serious consequence of the higher metal concentrations is their negative effect on many of the decomposers that live in the soil (ELVINGSON and AGREN, 2004). The U.S. Environmental Protection Agency (U.S. EPA, 1993) regulates nine trace elements for land-applied sewage sludge: As, Cd, Cu, Pb, Hg, Mo, Ni, Se and Zn. Only six of these elements (Cu, Ni, Zn, Cd, Pb, Se) are considered to be phytotoxic (SCHMIDT, 1997). Accounting for element speciation, complexation and the dynamic interaction of solid surfaces (soils, organic matter, and live plants) and water with trace elements, it is difficult to determine the maximum allowable total trace element concentrations that can exist in soils without becoming potentially toxic to plants or harming the environment (SLAGLE et al., 2004).

### **2.1.3. General features of the investigated heavy metals and cyanide**

#### **2.1.3.1. Iron**

Iron is the fourth most abundant element in earth's crust (after oxygen, silicon, and aluminum). The mean iron content of soil, sediment, and rocks is about 5%. Most of the iron in soils is present as iron oxides; in fact the typical soil colors (brown, red, yellow) are partly due to various iron oxides differing in their physical/chemical properties and their color. Iron, aluminum, and manganese oxide soil minerals are important sinks for heavy metals in soil and residual-amended soils (BASTA et al, 2005). Iron can occur in either the divalent ( $\text{Fe}^{+2}$ ) or trivalent ( $\text{Fe}^{+3}$ ) states under typical environmental conditions (U.S. EPA, 2003). Due to their high specific surface area, iron oxides act as important sorbents for dissolved species, e.g. heavy metals, phosphate and arsenate (ROZAN et al., 2002; APPELO and POSTMA, 2005). Some characteristic features of iron oxides include low solubility, and thereby high stability, conspicuous colours, and high surface area making them very effective sorbents for a number of dissolved species. In principle, all organic matter is thermodynamically apt to reduce Fe(III), and due to the high affinity of carboxylate groups for Fe(III) in solution or on the surface of a hydrous Fe(III) oxide, this type of process is very likely to occur in natural water, soils, and sediments (PEDERSEN, 2006). In most well-aerated soils, the minimum solubility of total inorganic iron is fixed in the range of  $10^{-8}$  to  $10^{-6}$  mol/m<sup>3</sup>. The concentrations of soluble iron measured in soil solutions are usually higher than those calculated from equilibrium reactions and in the range of  $10^{-5}$  to  $10^{-3}$  mol/m<sup>3</sup> due to the complexation of soil-Fe with soluble organic ligands (OLOMU et al., 1973).

### **2.1.3.2.Copper**

Total Copper concentration in soil solution is normally low ( $0.01-0.6 \mu\text{mol L}^{-1}$ ). It is essential to plants, animals, and microorganisms, but is toxic when its concentration exceeds a certain critical level (BAKER, 1990). Soil quality criteria and legislation on Cu levels in soils generally rely on data for total Cu content based on chemical analysis (TOM-PETERSEN et al., 2004). Copper in soils may exist in the following forms: (i) water soluble, (ii) exchangeable, (iii) organically bound, (iv) associated with carbonates and hydrous oxides of Fe, Mn, and Al, and (v) residual (SHUMAN, 1985). Copper and Zinc are two metals that are consistently added to soils in increasing quantities in the form of fertilizers, pesticides, livestock manures, sewage sludges and industrial emissions (ADRIANO, 1989). Both of these metals show moderate mobility under relatively acidic soil conditions (pH 5-7) because of increased solubility and formation of soluble complexes with organic ligands (KLAMBERG et al., 1989). Copper is adsorbed into the soil, forming an association with organic matter, Fe and Mn oxides, soil minerals, etc., thus making it one of the least mobile of the trace metals (IOANNOU et al., 2003).

### **2.1.3.3.Zinc**

Zinc is a heavy metal of much interest since it is a plant micronutrient as well as a potential contaminant in soils. In soil solution, the speciation of Zn, and thus the free Zn activity determines the availability of Zn for plants as a micronutrient and its characteristics as a heavy metal contaminant. The solubility of Zn in soil solution must be quantified to evaluate bioavailability and transport of Zn in soils (CATLETT et al., 2002). Zinc metal does not occur in the natural environment. It is present only in the divalent state Zn(II). Zinc is a transition element and is able to form complexes with a variety of organic ligands. Zinc in high concentrations can be toxic to flora and fauna, a subject of current environmental research (BARBARICK et al., 1997). KABATA-PENDIAS and PENDIAS (1992) have stated that soil chemistry of zinc is governed by the pH of the soil. In acidic soils, zinc adsorption is related to cation exchange sites, while in alkaline soils the chemistry is dominated by organic ligands. In more alkaline soils zinc can form an organozinc complex, which would also increase the metals mobility. Metal oxides influence the mobility of zinc in soils and zinc was found to be highly associated with oxides. They stated that clay is also capable of absorbing zinc. Soils that contain high levels of calcium and phosphorous immobilize the metal. Copper and Zn contents in surface soil directly influence the movement of Cu and Zn (ZHANG et al., 2003). A significant proportion of Hungarian soils are deficient in Zinc. Due to an original or induced zinc deficiency the zinc nutrition of plants may not be sufficient in about two thirds of the arable land in the country. 30% of Hungary's soils show a copper deficiency, and 60-70% show a zinc deficiency (SCHMIDT and SZAKÁL, 2007). The lack of these microelements can be restored through the soil or the foliage (SZAKÁL et. al.; 2000, 2003).

#### **2.1.3.4.Manganese**

Manganese is an essential plant nutrient, and Mn deficiencies have been observed primarily in arid regions (XIANG and BANIN, 1996). However, Mn toxicities to plants are sometimes observed in flooded soils (SMITH, 1990). Manganese in the soil is different, the solubility of each of the metals relative to Mn may be significantly different from the concentration of the metal in the Mn oxide particles. There are substantial gaps in knowledge of Mn in the bulk soil due to difficulties in studying the typically small, low-abundance, low-crystallinity Mn oxides (LATRILLE et al., 2001). The fact indicates that Mn in highly contaminated soils was also associated with fractions more easily dissolved than oxides, such as sulfides of Mn(II) (DA SILVA et al., 2002). The specific reactions responsible for the retention of Mn(II) in soils include adsorption to Fe oxides, organic matter, and layer silicate clay minerals (KHATTACK and PAGE, 1992). The reduction of Mn oxides before Fe oxides is consistent with the theoretical redox potentials under which Mn oxides vs. Fe oxides become thermodynamically unstable (SPOSITO, 1989). Manganese oxides also adsorb trace metals including Zn and Cu via specific surface adsorption. The chemical influence of Mn oxides in soil systems may be much greater than that suggested by their relatively low abundance. This is due to their surface characteristics (e.g., high negative surface charge, low point of zero charge, large surface area, low crystallinity) and dynamic redox behavior (NEGRA et al., 2005a). Manganese oxides are more susceptible to reductive dissolution under slight to moderate soil reduction than are Fe oxides, and consequently Mn dissolution precedes Fe dissolution in saturated soils (PATRICK and JUGSUJINDA, 1992). Manganese oxides may act as scavengers of trace metals (KAY et al., 2001; LIU et al., 2002) and evidence points to a catalytic role in creation of soil organic matter (BARTLETT and JAMES, 1993).

#### **2.1.3.5.Cyanide**

The term cyanide in this Toxicological Profile means a compound that contains the cyanogen (CN) radical. Since the CN portion of the compound is of concern in poisons, any reference to the amount present in air, water, soil, sediments, or other media refers only to this part of the compound. The term free cyanide refers to hydrogen cyanide and cyanide ion (CN<sup>-</sup>) (OUDJEHANI et al., 2002). Cyanide (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, or copper (I) cyanide). Anthropogenic sources are responsible for much of the cyanide in the environment. Cyanide-containing substances also occur naturally in the fruits, seeds, roots, and leaves of numerous plants, and are released into the environment by natural biogenic processes from higher plants, bacteria, and fungi (CRUTZEN and CARMICHAEL, 1993). However, an estimate of the amount of cyanide released into the environment from natural biogenic processes is not available. The major cyanide releases to water are discharges from metal-finishing industries, iron and steel mills, and organic chemical industries (U.S. EPA, 1981e).

Estimates of the amount of cyanide released to the soil from anthropogenic sources are limited. The largest anthropogenic sources of cyanide releases to soil probably result from the disposal of cyanide wastes in landfills and the use of cyanide-containing road salts (U.S. EPA, 1981e). Analogous to the fate of

cyanides in water, it is predicted that the fate of cyanides in soil would be dependent on cyanide concentrations, pH, temperature, metal content, concentration of microbes, availability of nutrients, and acclimation of microbes. Cyanide may occur as hydrogen cyanide, alkali metal salts, or as immobile metalocyanide complexes. In soil, cyanide present at low concentrations would biodegrade under aerobic conditions with the initial formation of ammonia, which would be converted to nitrite in the presence of nitrifying bacteria. Under anaerobic conditions, the cyanides ion will denitrify to gaseous nitrogen (RICHARDS and SHIEH, 1989). Cyanide ions in soil are not involved in oxidation-reduction reactions but may undergo complexation reactions with metal ions in soil (U.S. EPA, 1978c). Since cyanides are not strongly sorbed to soil and sediments (U.S. EPA, 1979) the role of sorption may not be significant in determining the bioavailability of cyanides from different soils or waters. The bioavailability of cyanide from an environmental medium is expected to increase if the cyanide is present in water-soluble forms, such as ions or soluble complexes. The pH of a medium may also be significant in determining the bioavailability because hydrogen cyanide gas may be released as the pH of the medium decreases (U.S. EPA, 1978c, 1979).

#### **2.1.4. Background values of heavy metals concentrations of Tisza flood plain soils**

Background concentrations of trace elements in soils are important due to recent interest in contamination potential and the toxic effect of these elements on humans and the environment (SLAGLE et al., 2004). By studying distribution of several toxic elements, it was surprising to see that their values on the various flood plains were higher than the national averages as well as the Hungarian limits (e.g. river Tisza). Historical soil metal data from the lower Tisza River flood plain reveals chronic heavy metal contamination dating back to the 1980s (KISS et al., 2000). The same researchers monitored flood plain soils of the lower Tisza River in spring 2000 and determined that toxic metal concentrations measured just after the flood were lower than levels measured prior to the flood. Also they indicated that a number of metals were above detectable concentrations in all soil samples with the reference site soil having the lowest concentrations. Two Tisza River flood plain soils had higher metal concentrations, with the sample from the ferry site (Nagykörü) having the highest values. Within the group of metals associated with the spill, Zn, Pb and Cu were found in the greatest quantity followed by Cd. KELE et al. (2002) indicated that the quantity of the measured toxic elements in the the Hungarian Tisza flood plain is higher than the national values. As the higher values have not only been detected in the areas flooded several times during the last decades but also in the 10-km band of the Tisza, they have concluded that the accumulation of the elements has not resulted from early, natural contaminations but from that of human interventions over recent centuries. It was conspicuous from the results of KELE et al. (2002) that the toxic element content of soils in the flood zone, especially in that of the Tisza River was higher than in the adjacent areas. By comparing the heavy metal contents of the 283 monitoring sites located at distances of 1 km, 5 km and 10 km from the river with the related data of the 322 monitoring sites located in the Great Hungarian Plain, it was concluded that the heavy metal contents of the soils in a 10 km band from the Tisza are higher than in the adjacent areas. They

concluded from the results that the heavy metal contents of the samples are consistently higher than the reference data characteristic for Hungary and in the case of certain samples, very high in heavy metal content and exceeding limit values. Acceptable toxic elements content of Hungarian soils are presented in Table 3.

Parameter	Limit mg/kg dry matter
As	15
Cd	1
$\Sigma$ Cr	75
Cu	75
Ni	40
Pb	100
Zn	200

Table 3. Acceptable toxic element content of soils, Hungary, 2001 (PÁLMAI et al., 2003)

Due to industrial and agricultural activities of mankind, soils may be contaminated with toxic metals, e.g., floodplain soils subjected to periodical flooding events. Knowledge of contaminant concentrations and release processes are necessary to estimate possible contaminant export (MEIBNER et al., 2008). A flooded soil might not be oxygen free, but the depletion of oxygen under such conditions might result in an anaerobic situation that induces facultative metabolism, anoxic metabolism, and strictly anaerobic processes (TATE, 1995). Heavy metal analysis in deposits and underlying soil taken from five arable fields showed that the levels of Cd, Zn, Pb, Cu, and As in the deposits, (82%, 51%, 42%, 36%, and 17%, respectively) were markedly higher on average than in the underlying soil and the highest heavy metal concentrations in the soils came from the most frequently flooded areas. The wide range illustrates the variation in heavy metal concentrations in the floodplain soils. For example, the heavy metal concentrations in soils with a diurnal flooding frequency varied from 11.1 to 17.7 mg/kg dry weight for As, 5.6 to 14.0 mg/kg dw for Cd, 62 to 116 mg/kg dw for Cu, 157 to 326 mg/kg dw for Pb, and from 705 to 1.239 mg/kg dw for Zn (ALBERING et al., 1999).

## 2.2. Soil properties and heavy metals

For investigating the heavy metals in soils WU et al. (2007) found that the intercorrelation between heavy metals and active soil components (such as Fe oxides, organic matter, and clay) is the major predictive mechanism and they concluded that the correlation with total Fe (including active and residual Fe) is the major mechanism. In a study conducted by CHEN et al. (1999) it was suggested that concentrations of most trace metals in Florida soils are primarily controlled by soil properties, Clay, organic C content, and CEC showed significant correlation with concentrations of most trace metals where the soil pH had significant positive correlation with concentrations of As, Cd, Cr, Cu, Mn, Se, and Zn. Adsorption of metal cations has been correlated with such soil properties as pH, redox potential, clay, soil organic matter, Fe and Mn oxides,

and calcium carbonate content (McLEAN and BLEDSOE, 1992). Heavy metal dynamics in soils are complex and influenced by numerous factors such as the pH, soil organic matter, soil texture, redox potential, and temperature (ALLOWAY, 1991). Also high calcium concentration in the treated soils can significantly hinder the metal transport, because the migration and precipitation of calcium as bicarbonates and hydroxides can clog soil pores and increase the soil buffer capacity, constraining the advance of the acid front (REDDY et al., 2006; DE GIOANNIS et al., 2007c).

### **2.2.1. Soil pH**

The link between soil pH and heavy metal threshold values reflects the complex interaction between heavy metals and the various soil properties (GAWLIK and BIDOGLIO, 2006). pH is a measure of the hydrogen ion concentration acidity or alkalinity of the soil. Measured on a logarithmic scale, a soil at pH 4 is 10 times more acidic than a soil at pH 5 and 100 times more acidic than a soil at pH 6. Alkalinity is usually an inherent characteristic of soils, although irrigation can increase the alkalinity of saline soils. Soils made alkaline by calcium carbonate alone rarely have pH values above 8.5 and are termed 'calcareous'. Under normal conditions the most desirable pH range for mineral soil is 6.0 to 7.0 and 5.0 to 5.5 for organic soil. The buffer pH is a value used for determining the amount of lime to apply on acidic soils with a pH less than 6.6. Increases in soil pH can occur as the result of organic matter decomposition, because mineralization and ammonification processes release OH<sup>-</sup> ions and consume H<sup>+</sup> ions (RITCHIE and DOLLING, 1985). Colloid and metal mobility, was enhanced by decreases in solution pH and colloid size, and increases in organic matter, which resulted in higher elution of sorbed and soluble metal loads through metal–organic complex formation (KARATHANASIS et al., 2005). Soil weathering often involves soil acidification, and most chemical immobilization reactions are pH dependent. Alkaline amendments reduce the concentration of heavy metals in soil solution by raising soil pH, thereby allowing the formation of insoluble metal precipitates, complexes, and secondary minerals (MENCH et al., 1994). The pH was reduced to 3.78 in the presence of ferrous iron. Ferrous iron acts as a Lewis acid, causing a decrease in the soil pH (REDDY and CHINTHAMREDDY, 1999). Several studies have demonstrated that pH is the most influential factor controlling sorption–desorption of heavy metals in soils.

TEMMINGHOFF et al. (1997) found that when the pH was greater than 6.6, the complexation of Cu with dissolved organic carbon comprised more than 99% of the total dissolved element. Production and accumulation of organic acid fermentation products in the presence of high organic carbon may result in a pH drop and subsequent mineral dissolution. The low pH and accumulated organic acids will also affect the composition of the microbial community (UGWUEGBU et al., 2000). The additive effect of the lower pH and excessive dissolution of Mn and Fe compounds might result in increased degradation of soil agricultural quality. In acidic environments the oxide surface is positively charged while in alkaline media it is negatively charged.

### 2.2.2.Redox Potential

Redox potential was studied mostly in anaerobic soils, where the high moisture content decreased the rate and amount of O<sub>2</sub> diffusing into the soil (SAVANT and ELLIS, 1964). Redox potential was rarely studied in aerobic soils, where O<sub>2</sub> concentration is relatively high and where Redox potential measurements do not directly reflect soil aeration (CALLEBAUT et al., 1982). The redox potential is measured as voltage between the environment and a standard reference electrode. A popular, but also criticized manual method makes use of a small tip of Pt placed on a copper wire that is placed in the soil; a reference electrode is placed in the same soil at a chosen distance (MANSFELDT, 2003). Redox potential is a measure of electron availability and is a result of electron transfer between oxidized and reduced chemical species (GAMBRELL et al., 1991). The measurements indicate the likelihood of electron donation to or loss from a chemical species and are used to assess characteristics of the soil environment (PANG and ZHANG, 1998). The redox capacity can be defined analogously to the pH buffer capacity. The concept of the redox capacity helps in understanding of many important processes in soils and soil waters (VAN BREEMEN and WIELEMAKER, 1974). The intensity of redox status can be described by redox potential in general. In surface soil it is influenced by rainfall, bioactivity, and changes in land use, whereas in vadose zones by fluctuation in the water table (BOUL et al., 1997).

Redox potential measurement is a reading of voltage difference between a working electrode such as a Pt electrode and a reference electrode inserted into the soil or various substrates. The E<sub>h</sub> of the soil solution may also be an indicator of the soil component acting as an electron acceptor during a prolonged period of anaerobic conditions (UGWUEGBU et al., 2000). The redox potential is related to the concentration of several redox pairs in the soil. Oxygen is the first acceptor that plays a large role. Oxygen diffuses into the soil, but can also be produced by plants and leak into the soil by radial oxygen loss from roots (ADEMA and GROOTJANS, 2003; ALDRIDGE and GANF, 2003). CLAY et al. (1992) observed that rainfall initially contributes a substantial amount of oxygen to the soil. Permanganate is an oxidant agent with a standard oxidation potential of about ±1.7 V. In an aqueous system the permanganate salts generate permanganate ions (MnO<sub>4</sub><sup>-</sup>). Both potassium permanganate (KMnO<sub>4</sub>) and sodium permanganate (NaMnO<sub>4</sub>) can be used for environmental applications, with similar results. Despite the relatively low standard of oxidation potential, permanganate salts are considered strong oxidizing agents, able to break organic molecules containing carbon-carbon double bonds, aldehyde groups or hydroxyl groups (BROWN et al., 2003; ITRC, 2005). The importance of the redox potential, as a master biogeochemical variable, in controlling the speciation and toxicity of a wide variety of elements and the ecology of subsurface environments can not be understated. Generally, pH and E<sub>h</sub> (pE) are considered the master geochemical variables controlling the geochemical reactions of elements in geologic and aquatic environments. The redox potential, E<sub>h</sub>, is also commonly given as pE, the measure of electron activity that is analogous to pH. Use of pE avoids the problems associated with the measurement of E<sub>h</sub>, though pE is strictly theoretical. While the form of pE is analogous to pH, there are significant differences between the two numbers that makes pE a purely theoretical value

(HOSTETTLER, 1984). Positive values of  $E_h$  and  $pE$  indicate an oxidizing environment (i.e., an environment relatively rich in oxidants –  $O_2$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ). Negative values of  $E_h$  and  $pE$  indicate a reducing environment (i.e., relatively low concentrations of oxidants and relatively high concentrations of reduced species –  $H_2S$ ,  $CH_4$ ). It is very important to know that the redox environment in order to predict the mobility of elements which have variable valences or charges and the solubility of transition metal oxides which may function as adsorbents in aquifer systems.

### **2.2.2.1.Redox buffer capacity**

VON DER KAMMER et al. (2000) stated that electrode measurements of redox potential in groundwaters can only give a current value. Regardless of the worth of the obtained number, it is impossible to make a prediction of the future development of redox conditions in contaminated soils, and therefore highly reactive aquifers. This problem is well known from the master variable pH and can be similarly treated by introducing a capacity component. While the acid or base neutralisation capacities represent a certain amount of protons that can be accepted or donated until a defined threshold limit (usually pH 4 or 10) is reached, the reduction or oxidation capacities represent the amount of electrons that can be donated or accepted. No threshold limits have been defined yet and it will have to be discussed if it is appropriate and/or possible to define certain  $E_h$ -limits. Usually the redox buffer capacities are measured against a certain strong reductant or oxidant to provide a quantitative reaction within short-term laboratory testing. Oxidation capacity (OXC) is the amount of electrons that can be accepted and TRC (total reduction capacity) is the amount of electrons that can be delivered from a sample. Within an oxic aquifer the solid matrix will have a certain OXC, but TRC will approach zero as long as natural Fe(II) or sorbed organic matter is not captured by the TRC measurement. A partially reduced aquifer matrix will have a certain decreased OXC and also a TRC if Fe(II)-components from the reduction processes are present. In strongly reduced aquifers the OXC of the matrix approaches zero (HERON and CHRISTENSEN, 1995). Like the base or acid neutralisation capacity, the reduction or oxidation capacity is mainly represented by the solid aquifer matrix, while the driving force or component (reducing reagent, mainly Dissolved Organic Carbon) is introduced in solution. The OXC-TRC concept has to be seen within the environmental context, i.e. only possible and relevant redox processes should be included (VON DER KAMMER et al., 2000).

Two of the most important variables that influence heavy metal solubility are the pH and redox state of the leachant. Solid wastes generally contain a variety of constituents which react with in-transported acidity and oxidants. Reactions that involve consumption of protons are referred to as pH buffering reactions. The amount of strong acid that can react with the waste is referred to as the pH-buffering capacity, or acid neutralising capacity of the waste. Reactions that consume oxidants, which may be present in the leachant, are referred to as redox buffering reactions. Similarly to pH buffering processes, the total amount of oxidant that can react with the waste is called the redox buffering capacity, or reducing capacity of the waste. Certain redox buffering reactions may generate protons. This can have a considerable impact upon the depletion of

the pH buffering capacity, particularly if there is a high rate of oxidant in-transport (CRAWFORD, 1999). After a period of time, under the influence of in-transported oxygen and acidity, the pH and redox buffering capacity of the waste near the surface of the landfill will become exhausted. As a result, reaction fronts may develop along the leachant flowpath. Upstream of the reaction front, the buffering capacity is depleted, whereas downstream there remains unreacted buffering capacity. There may be reaction fronts existing for both pH and redox buffering constituents in the waste (CRAWFORD, 1999). The system, which is able to stabilize the  $E_h$  value has a large redox capacity completely analogous to the buffer capacity, which decreases the changes in the acid-base states. The redox capacity is analogous to the pH buffer capacity. The concept of the redox capacity helps in the understanding of many important processes in soils and soil waters (VAN BREEMEN and WIELEMAKER, 1974) and sediments (HUTCHEON et al., 1993).

In many cases, the reducing capacity of a waste may be the result of a combination of different reducing constituents. Redox reactions can also generate acidity. This may lead to a rapid depletion in the pH buffering capacity of the waste, particularly if there is a large flux of oxygen into the system. In these reaction pathways, the amount of oxygen consumed and the amount of acidity generated depends upon the end products of the redox reactions. Here, it is assumed that the end products are fully oxidised, but this may not always be the case. Under oxidising conditions in a basic environment,  $Fe^{3+}$  ions formed as a reaction product in the oxidation of metallic Fe or Fe(II)O are rapidly precipitated as ferrihydrite ( $Fe(OH)_3$ ). As there is no net change in the cation/anion balance in the leachate, this results in no production or consumption of protons and therefore no change in the leachate alkalinity. However, in strongly reducing acidic environments, the conversion of  $Fe^{2+}$  to  $Fe^{3+}$  is hindered and the oxidation of metallic Fe may result in an increase of leachate alkalinity (i.e. protons are consumed). Under such conditions, Fe(II)O may not be oxidised at all (CRAWFORD, 1999).

Buffer solution is able to retain almost constant pE when small amount of oxidant/reductant is added. Quantitative measure of this resistance to pE changes is called buffer capacity. Buffer capacity can be defined in many ways. We may find it defined as “maximum amount of either oxidant or reductant that can be added before a significant change in the pE will occur”. This definition - instead of explaining anything - raises a question about the significant change - sometimes even change of 1 unit doesn't matter too much, sometimes - especially in biological systems - 0.1 unit change is a lot. Buffer capacity can be also defined as quantity of oxidant or reductant that must be added to change the pE of one liter of solution by one pE unit. Such definition – although have its practical applications – gives different values of buffer capacity for oxidant addition and for reductant addition (unless buffer is equimolar and its  $pE=pE_0$ ). This contradicts intuition – for a given buffer solution its resistance should be identical regardless of whether oxidant or reductant is added.

Buffer capacity definition that takes this intuition into account is given by:

$$\beta = \frac{dn}{d(pE)}$$

where n is number of equivalents of added reductant or oxidant. Note that addition of dn moles of oxidant or reductant will change pE by exactly the same value but in opposite direction.

where: pE = 16.9 E<sub>h</sub>; E<sub>h</sub> = 0.059 pE  
 E<sub>h</sub> is the redox potential  
 E<sub>0</sub> is standard redox potential  
 β is redox buffer capacity

We can define the oxidation buffer capacity as the amount of oxidizing reagents required to increase redox potential of one unit mass soil sample while reaching the inflexion point of pE – amount of oxidant curve. Dimension: mmols (removed electrons)/kg soil. The reduction buffer capacity is the amount of reducing reagent required to decrease the redox potential of one unit mass soil sample, while reaching the inflexion point of pE - amount of oxidant curve. Dimension: mmols (added electrons)/kg soil.

### 2.2.3. Effect of pH and redox potential on investigated metals in soil

JUNG (2008) showed that total metal content and soil pH in surface soils to be the dominant factors influencing metals content in plants. Measurement of the total concentration of metals in soils is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in soil metal concentration over time. However, the methods do not give an indication to the chemical form of the metal in the soil system (McLEAN and BLEDSOE, 1992). The actual concentrations and influence of metals is a direct consequence of the mobility, bioavailability and toxicity, and plant biomass and different humus fraction ranges are indirect effects (MÁTHÉ–GÁSPÁR et al., 2005). Total concentrations of metals in soils are generally a poor indicator of metal toxicity because metals exist in different solution and solid-phase forms that can vary greatly in terms of their bioavailability. Risks associated with metal contamination in soils are difficult to assess (NOLAN et al., 2003) The metal complex may be weakly or strongly adsorbed to soil surfaces relative to the free metal ion. Speciation not only affects mobility of metals but also the bioavailability and toxicity of the metal. The free metal ion is, in general, the most bioavailable and toxic form of the metal (McLEAN and BLEDSOE, 1992). Minerals, metals or metalloids, toxic or essential are present in soils in various forms with varying bioavailability, toxicity and mobility. Determination of total concentrations of these elements in solid materials is therefore considered to be of limited use in assessing potential environmental impacts. In order to assess their actual behavior, role and impact, a good understanding of the chemical forms of the elements of interest is required (SHIOWATANA et al., 2001). The total concentrations of metals in soil (determined by extracting with strong acids) are generally orders of magnitude higher than plant available metals (Table 4) Most notably,

the available Fe concentration represents less than 0.1% of the average total Fe concentration in soils (JONES and JACOBSEN, 2003).

Metal	Average total concentration (mg/kg)
Iron	38,000
Copper	30
Zinc	50
Manganese	600

Table 4. Typical total concentration of Fe, Cu, Zn and Mn in soil (Lindsay, 1979)

ZHANG et al. (2004) stated in their study that for all elements, the amounts extracted had a high dependence on pH, and the water solubility of all elements increased sharply with decreasing pH. The pH values at which a sharp increase in element concentration occurred were 4 to 5 for Cu and Zn. At pH 5.0 to 8.0, the solubility of heavy metals, including Cd, Co, Cr, Pb, Zn, and Ni, were generally low, and the released percentages of Cd, Co, Cr, Cu, Ni, Pb, and Zn at pH 5 to 8 were 3.2, 1.4, 0.3, 2.9, 2.8, 1.4, and 2.5%, respectively. Dissolution of Fe and Mn compounds, which plays a role in contaminant mobility in the soil, increases at low  $E_h$ . Redox potential and pH could be used to predict Fe or Mn speciation in soil solution (UGWUEGBU et al., 2000). Due to increased metal complexation at high pH, total extractable fractions of metals generally increased (TUKURA et al., 2007). (FRANZMEIER et al., 2004) found that soil reduction mainly depends on four factors: (1) saturation with water and depletion of  $O_2$ , (2) presence of microorganisms, (3) food for microorganisms, and (4) suitable temperatures. Due to their high degree of reactivity, Mn oxides in soil systems may exert a greater influence on trace metal chemistry (NEGRA et al., 2005a).

### 2.2.3.1. Iron

Iron in typical soil concentrations ranging from 0.2% to 55% (2000 to 550,000 ppm) (U.S. EPA, 2003) iron occurs predominantly as  $Fe^{3+}$  oxides in soils (BODEK et al., 1988). Availability of iron in the soil can be decreased up to 1000 fold for each unit increase in pH (NUNEZ, 2000). Variations in soil redox levels provide another means of increasing the solubility of iron in soils (U.S. EPA, 2003). FRANZMEIER and JENKINSON (2004) noticed that if the soil becomes anaerobic, however, iron oxides are generally reduced and dissolved. Reduction processes near respiring roots may increase  $Fe^{3+}$  reduction to  $Fe^{2+}$  and the subsequent disassociation of  $Fe^{3+}$  chelates (RÖMHELD and MARSCHNER, 1986). FRANZMEIER and JENKINSON (2004) suggested that saturation and reduction are poorly related because the water that saturates the soil might contain small amounts of oxygen. Evidence of Fe reduction is masked by other soil components. Other reasons for this poor relationship include the fact that saturation of soil with water and chemical reduction of iron (Fe) in soils are two separate processes and because many elements are involved,

reduction in soils is a continuum with no sharp breaks.  $\text{Fe}^{3+}$  can be reduced to  $\text{Fe}^{2+}$  under reducing conditions that can occur in saturated soils. Increases in soil pH or  $E_h$  (oxidizing conditions) shift iron from the exchangeable and organic forms to the water-insoluble and iron-oxide fractions (U.S. EPA, 2003). Ferric iron is dependent on the soil-water status of a particular environment. The reactions of iron in the processes of weathering are dependent largely on the  $E_h$ -pH system of the environment and on the stage of oxidation of the iron compounds involved. Iron compounds, including  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_2$  are relatively insoluble and can be precipitated at high pH because  $\text{OH}^-$  ions become more abundant when the pH rises (U.S. EPA, 2003). LINDSAY (1979) indicated that in soils, the dissolution of Fe hydroxides is generally promoted by reducing Fe (III) to Fe (II), which is sensitive to soil redox status. Research findings suggest that plants need in excess of  $10^{-8}$ -M of soluble Fe to supply their nutritional needs (SCHWAB and LINDSAY, 1983). Ferrous iron is more soluble and bioavailable to plants than ferric iron and occurs predominantly as  $\text{Fe}^{3+}$  oxides in soils (BODEK et al., 1988). JIAO et al. (2005) stated that Fe(II) oxidation is optimal at pH 6.5 to 6.9, and the mineral products of Fe(II) oxidation are pH dependent. As the redox potential and or soil pH increases, the availability of iron in soil solution decreases (U.S. EPA, 2003). The critical redox potential for  $\text{Fe}^{2+}$  reductions is between +300 mV and +100 mV at pH 6 and 7, and -100 mV at pH 8 (GOTOH and PATRICK, 1974). At pH levels below 6.0, a reduced soil can contain 5,000 ppm  $\text{Fe}^{2+}$  in the soil solution if the important solid phase is  $\text{Fe}_3(\text{OH})_8$  (U.S. EPA, 2003). JIAO et al. (2005) observed that the mineral product of Fe(II) oxidation was pH dependent. In general the pH must exceed 6 or the oxidation of ferrous iron will be slow (SMITH et al., 2003).

### **2.2.3.2. Copper**

The increase in dissolved organic carbon, potentially caused by dissolution of organic matter at alkaline pH can contribute to enhanced copper concentration in soil solution (TEMMINGHOFF et al., 1997). Cu is absorbed to a great extent by soils and soil constituents, however it has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils (McLEAN and BLEDSOE, 1992). It has been shown that an increase in pH significantly contributes to lowering the Cu toxic effect on in some fruits in natural soils (ALVA et al., 2000). MILLERO et al. (1991) stated that the kinetics of Cu(II) reduction by hydrogen peroxide were followed by measuring Cu(I) formation and it was found that rates increased with an increase in pH and  $\text{Cl}^-$ . In addition, the sorption of Cu increased with an increase in pH without the addition of dissolved organic matter, while Cu sorption in the presence of dissolved organic matter was unexpectedly decreased with an increase in pH at a pH >6.8. The higher the pH, the higher is the mobility of copper. The effect of pH on this process is sometimes called variable charge effect. This effect of pH occurs on many components of the soil such as organic matter, oxides, hydroxides, oxyhydroxides and edges of phyllosilicates (ZELAZNY et al., 1996). As the pH increases, deprotonation of the surface takes place and  $\text{OH}^-$ -ions may cover the soil surface, which may result in the soil surface being negatively charged. Another explanation of the effect of pH was given by BROWN et al. (1997) they

mentioned that when the soil pH increased the solubility of fulvic acids increased, thus giving chance for formation of more fulvic acids complexes.

### **2.2.3.3.Zinc**

The solubility of zinc is primarily determined by pH. Zinc may precipitate at pH values greater than 8.0. It may also form stable organic complexes. Acidic soils and sandy soils with a low organic content have a reduced capacity for zinc absorption. GERRITSE and VAN DRIEL (1984) concluded that pH and total soil Zn were significant predictors of total Zn in solution, while organic matter was not. Those soils that had a pH range of 4.3 to 7.9 had a total soil Zn range from 9 to 2400 mg kg<sup>-1</sup>, an organic matter range of 1 to 34%, and a total soluble Zn concentration range of 0.8 to 2200 µg L<sup>-1</sup>. For many Zn minerals, two moles of H<sup>+</sup> ions are consumed for every mole of Zn<sup>2+</sup> released by dissolution when factors other than pH and Zn<sup>2+</sup> activity are held constant (CATLETT, 2002). McBRIDE et al. (1997) indicates that total soluble Zn is not affected by organic matter. McBRIDE and BLASIAK (1979) state that different adsorption mechanisms are likely to control Zn solubility at different pH values, also they suggested that adsorption to oxide surfaces, which have a high affinity for Zn, may be important in controlling Zn solubility. Zinc adsorption by clays has been shown to be pH dependent (BAEYENS and BRADBURY, 1997). In neutral to alkaline soils, Zn(OH)<sup>+</sup> is a dominant solution species of Zn that may adsorb to soil and replace one H<sup>+</sup>. The pH value at which the change in the mechanism that controls solubility occurs will depend on the soil properties. At low pH the total soluble Zn and free Zn activity are nearly the same, but at high pH they are not the same because of hydrolysis species, organic Zn species, etc (CATLETT, 2002).

### **2.2.3.4.Manganese**

Mn minerals are quite insoluble at both alkaline and circumneutral pH values regardless of the redox potential (KRAUSKOPF and BIRD, 2003). GREEN et al. (2003) indicated that once the critical E<sub>h</sub> needed for dissolution of Mn is reached, time becomes the limiting factor that determines soluble Mn concentrations. Manganese is both weakly sorbed and is unstable under reducing conditions and at pH levels below 7.1. It can be precipitated as a carbonate species in locations where pH was 7.1 or higher (WILLOW and COHEN, 2003). Both the rate of dissolution of Mn oxides (BANERJEE and NESBITT, 1999) and also the equilibrium solubility of Mn oxides (LINDSAY, 1979) increase as pH is decreased. Furthermore, the readsorption of dissolved Mn to soil colloids is decreased under acid conditions (KHATTACK and PAGE, 1992). Manganese (Mn) availability in soil depends primarily on soil pH. The form of Mn in a soil system depends largely on the functioning of soil microorganisms and their activity depends on soil pH. As soil pH decreased, available soil Mn levels increased (RUSSELL, 1988). BEHUM and KIM (1999) demonstrated that manganese oxidation is slower than iron oxidation and does not occur in the presence of ferric iron and manganese does not precipitate until all the iron has precipitated, usually in the later stages of the wetland. Manganese oxide precipitates are unstable in the presence of ferric iron and this can cause the precipitates to

release manganese into solution (BEHUM and KIM, 1999). Mn(II) in the soil is different since the solubility of each of the metals relative to Mn may be significantly different than the concentration of the metal in the Mn oxide particles (GREEN et al., 2003). They also found that Mn concentrations are not significantly correlated with pH during reduction experiments. pH conditions conducive to oxidation of Mn (i.e., pHs of 6 to 7) could become a more important controlling variable (NEGRA et al., 2005b). There is an increase in soluble Mn when  $E_h$  became less than approximately 450 to 500 mV. This appears to be the critical Eh needed for Mn oxide dissolution in these soils. These values are slightly higher than critical Eh values of approximately 300 mV reported by PATRICK and JUGSUJINDA (1992) and also CHARLATCHKA and CAMBIER (2000). However, the  $E_h$  required to dissolve Mn oxides in some soils is less than the theoretical levels based on the solubility of Mn(IV) oxides such as birnessite ( $MnO_2$ ). BRADY and WEIL (1996) stated that the interaction of soil acidity and aeration in determining micronutrient availability is of great practical importance. Iron, manganese, and copper are generally more available under conditions of restricted drainage or in flooded soils (Figure 1). They mentioned also that very acid soils that are poorly drained may supply toxic quantities of iron and manganese. Manganese toxicity has been reported to occur when certain high manganese acid soils are thoroughly wetted during irrigation.

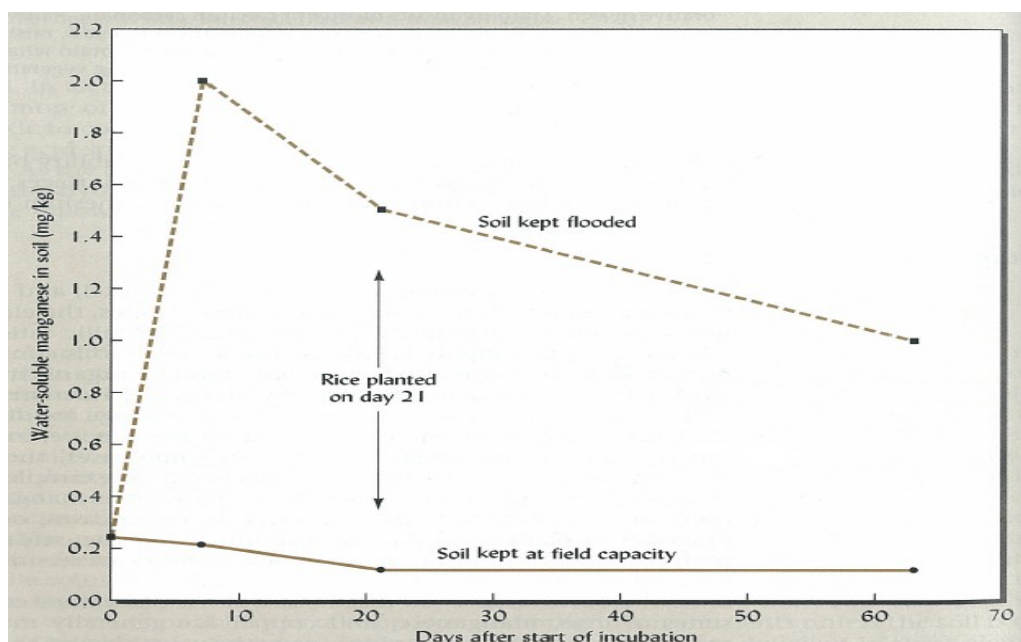


Figure 1. Effect of flooding on the amount of water-soluble manganese in soils. The data are the averages for 13 unamended Ultisol horizons with initial pH values ranging from 3.9 to 7.1. (WEIL and HOLAH, 1989)

#### 2.2.4. Organic matter

Soil organic matter is the most important indicator of soil quality and productivity and consists of a complex and varied mixture of organic substances. Commonly, soil organic matter is defined as the

percentage of humus in the soil. Humus is the unidentifiable residue of plant soil microorganisms and fauna that becomes fairly resistant to further decay. Organic matter is very important in the functioning of soil systems for many reasons (JANKAUSKAS et al., 2007). Soil organic matter increases soil porosity, thereby increasing infiltration and water-holding capacity of the soil, providing more water availability for plants and less potentially erosive runoff and agro-chemical contamination (LAL et al., 1998). Clay minerals and organic matter have a contrary effect on heavy metal retention in soils. There are factors dependent (e.g. clay minerals) on and independent (e.g. organic matter) of bedrock, of which common effect forms the actual distribution of heavy metals in soils (SIPOS, 2003). Soils with large amounts of clay and organic matter have high CECs whereas soils with sandy textures and low concentrations of organic matter have low CECs (JONES, JACOBSEN, 2003). EL-GHAWI et al. (2005) show that trace metals concentrations in clay surface soils are higher than in the sandy soils, humic and folic acid (organic matter) capture the elements. Heavy metal cations sorb to soil organic matter and other forms of humified natural organic matter. The type of sorption by natural organic matter affects the environmental fate of the heavy metal. Heavy metal cations form sparingly soluble phosphate, carbonates, sulfides, and hydroxides. Sorption and many metal precipitation processes are highly pH dependent with increased sorption with pH. The pH of the soil-residual system is often the most important chemical property governing sorption and precipitation of heavy metals (BASTA et al., 2005).

#### **2.2.5. Microbiological effect**

Microbes are arguably the most important consideration in managing the living soil. Soil microbes are responsible for the greatest percentage of nutrient recycling within the soil (FENCHEL et al., 1998). Metals play an integral role in the life processes of microorganisms, metals such as calcium, cobalt, chromium, copper, iron, potassium, magnesium, manganese, sodium, nickel and zinc. They are an essential source of micronutrients and are used for redox processes. Microbial transformations of metals serve various functions. Generally, microbial transformations of metals can be divided into two main categories: redox conversions of inorganic forms and conversions from inorganic to organic form and vice versa (TURPEINEN, 2002). Through oxidation of iron, sulfur, manganese and arsenic, microbes can obtain energy (SANTINI et al., 2000). On the other hand, reduction of metals can occur through dissimilatory reduction where microorganisms utilize metals as a terminal electron acceptor for anaerobic respiration (TURPEINEN, 2002). For example, oxyanions of chromium (QUILNTANA et al., 2001) can be used in microbial anaerobic respiration as terminal electron acceptors. Microorganisms may possess reduction mechanisms that are not coupled to respiration, but instead are thought to impart metal resistance (TURPEINEN, 2002). For example, aerobic and anaerobic reduction of Cr(VI) to Cr(III) (QUILNTANA et al., 2001). Microbiological processes can either dissolve metals, thereby increasing their bioavailability and potential toxicity, or immobilize them and thereby reduce the bioavailability of metals (TURPEINEN, 2002). In microbial systems the term redox conditions refers to the microbial terminal electron accepting processes taking place. If oxygen is present

aerobic conditions will dominate and microbial metabolism takes place with oxygen as the terminal electron acceptor. Nitrate, oxides and hydroxides of manganese (IV) and iron (III), sulfate and carbon dioxide can be used as electron acceptors in order to gain energy for microbial maintenance and growth (STUMM and MORGAN, 1996). Heavy metals are often mixed with organic pollutants in contaminated sites. In anaerobic soils Redox potential was shown to be negatively correlated with microbial activity (KRALOVA et al., 1992). Low Redox potential developed with increased soil moisture content because of the partial or complete displacement of oxygen from soil and rapid consumption of oxygen by soil microbes (SAVANT and ELLIS, 1964). Redox potential was also found to be effected by microbial activity in aerobic soils. VOLK (1993) showed that in arable soils moisture indirectly decreased redox potential by increasing bacterial activity. As in other studies (FAULKNER et al., 1989) a relationship between moisture content and redox status was observed.

#### **2.2.6. Measurements of redox potential of soils**

There are many problems with the measurement of the redox potential of soil, since only investigation on the spot can be accepted as a characteristic method, but even this method carries disadvantages, since the redox potential values also strongly depend on the actual water-content, air filling rate and even on the time of day and temperature. Dried soil samples are practically unsuitable for determining redox potential. Measurement of the redox potentials of soils is a recently discussed research topic. There are two methods accepted for measurement of the redox potential of soils. According to the first method, the concentrations of the active redox components of soils (e.g. solute oxygen, nitrate, sulphate, iron II, iron III, manganese II, manganese IV, sulphide and methane) are measured, and the redox state of the soil may be evaluated from the measured concentration values. A disadvantage of this method is that it requires careful sampling and that many relatively expensive investigations must be made. According to the other method, which uses inert electrodes (platinum or gold) and involves assembling a galvanic cell, the electromotive force can be measured, from which the redox potential can be directly calculated. The disadvantage of the method is that contact between electrode and soil grains strongly influences the result and because of its bad reproducibility this method is also strongly controversial in the literature (VEPRASKAS, 2001). Both theoretical and experimental methods give an indication of the maximum available buffering capacity of waste materials when we neglect the influence of physical heterogeneity. Experimental methods may give a better idea of the available buffering capacity, but they suffer from the disadvantage that the experimental conditions may be more aggressive than those existing in a waste landfill. This may lead to an overestimation of the buffering capacity if constituents are leached that would normally be unavailable in a landfilling environment. Experimental methods are also highly sensitive to the kinetics of pH and redox buffering processes. Short-term experiments carried out over 24 hours generally give results that differ from those that would be obtained if the same experiment was carried out for a week or more (CRAWFORD, 1999). The general approaches for the assessment of the redox status of aquifers are platinum

electrode measurements or chemical equilibrium calculations based on the chemical analysis of the main redox species (BARCELONA et al., 1989; LINDBERG and RUNNELS, 1984; HOSTETTLER, 1984). Beside the widely discussed problems of measuring redox potentials in natural waters (LINDBERG & RUNNELS, 1984), additional problems occur in contaminated aquifers due to high reactivity, disequilibrium and the distribution of reduced species (e.g. Soluble Fe(II) into the more oxic parts of the plume (LOVLEY et al., 1994). In fact, meaningful interpretation of redox potentials acquired by electrode measurements from partially oxidised soils seems to be impossible (BARTLETT and JAMES, 1995). Additionally it has to be pointed out that the measurement of redox potential as the single pH measurement is a capture of current conditions (VON DER KAMMER et al., 2000).

In order to eliminate the above-listed uncertainties, a method was elaborated by us for determining the redox-buffer ability of soil samples. This has practically the same relationship to the redox potential like the acidity values to pH. Therefore, it is an extensive quantitative feature of the soil, which is able to show how many oxidants are required to bring the soil into a given, strongly oxidated state. By use of this measurement method, the errors acquired during measurement of the redox potential can be eliminated, and such a characteristic feature of the soil can be measured, which changes to a far lesser extent in function of time and conditions. Theoretical explanation for this is the following: There are countless side by side redox systems in soils. For all systems it is required that the concentration ratio between reduced and oxidated forms determined by Nernst' law takes the value corresponding to the equilibrium redox potential formed by all such redox pairs. Within these systems, there are some quickly saturating, kinetically not blocked systems (those, which dissolve and desorb very quickly from the surface of the soil grains) fundamentally determining the redox potential of liquid phase of the soil-suspension. The errors acquired while determining the redox potential are caused by the redox pairs present in the soil in very small concentrations, which can change very quickly due to the influence of the environment and therefore in the suspension we de facto do not measure the characteristic equilibrium potential of the soil, but rather the potential of those of the easily mobilizable, and therefore quickly changing part. On the base of a redox potential curve determined by a slow, oxidating titration, the full reductive ability of the soil can also be well-estimated, while by an adequate method the redox potential value corresponding to the largest (i.e. crossover) redox potential value can also be obtained, which is characteristic for the soil, and independent on sampling conditions. MADARI et al. (1997) investigated the differences in the effect of two tillage systems - no tillage (NT) and conventional (plow) tillage (CT) - on soil organic matter (SOM), with special attention to the humic acid (HA) fraction. The data obtained from spectroscopic methods were supported by data from chemical analyses. Results show (Figure 2) that in the 0-15 cm layer of soils CT results in a more oxidized state in the soil and humic acids (HA) under CT contain relatively more acidic functional groups and less aromatic components than HAs in NT soils.

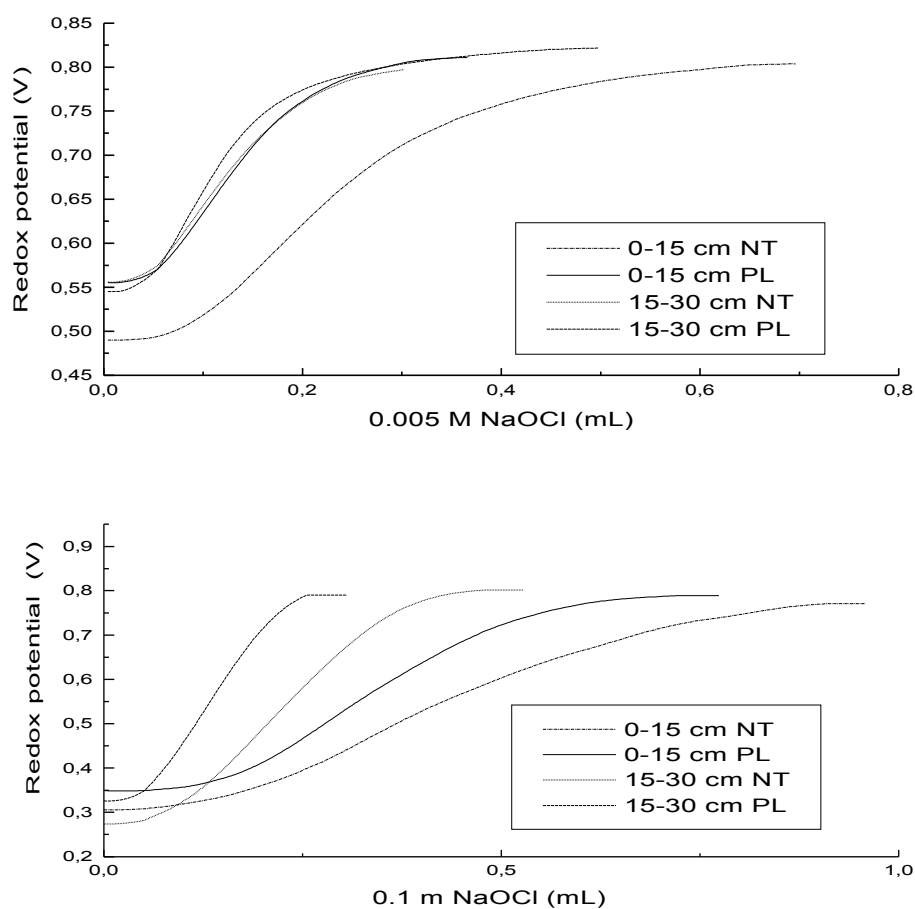


Figure 2. Redox titration curves of HAs (upper diagram) and whole soils (lower diagram) (MADARI et al., 1997)

Redox titration curves of whole soil samples and HAs are shown in Figure 2. With redox titration the redox buffer capacity of soils and humic acids (HAs) can be measured. NaOCl as a weak oxidising agent cannot oxidise the C-C and C-H bonds (both aromatic and aliphatic) but can oxidise alcohols, aldehyds, occasionally phenols and tertiary amines. The more NaOCl the material needs to reach the same redox potential change the less oxidized the material was before titration. Redox titration curves show that no tillage (NT) soils are in a less oxidised state and the same trend can be noticed in case of HAs. The HA extracted from the 0-15 cm layer of the NT soil proved to be the most reductive, hence chemically less reactive in the soil.

### 2.2.7. Heavy metal measurements

Methods for investigating heavy metal contamination in soil are time consuming and expensive (WU et al., 2007). That is why it is very important to select the appropriate method for specific studies taking into consideration the types of reactions and their relative time scales (OSZTOICS et al., 1997-2000). Complexity of soil and sediment structures (inorganic and organic components, colloidal structures, etc.), however,

makes the complete chemical speciation of metallic elements extremely difficult (HELTAI, 2005). Chemical techniques are used to analyse collected samples of soil and subsurface soil in order to determine pollutant levels and their spatial-temporal patterns (DE MATOS et al., 2001). These techniques are very expensive and they require long times for the sample chemical pre-treatment and for the elemental analysis (CAGGIANO et al., 2005). Soil is the major source through which heavy metals can be absorbed by plants via their roots or foliage (LOKESHWARI and CHANDRAPPA, 2006). Therefore, a better understanding of heavy metal accumulation at the soil surface and their leaching inside the soil seems to be particularly important in the present scenario, where pollution is spread by human activities (PALUMBO et al., 2004). Conventional analytical techniques for the analysis of soil, such as atomic absorption/emission spectroscopy, X-ray fluorescence, polarographic techniques, molecular methods, chemical analysis etc. (PALUMBO et al., 2004) require lengthy sample preparation, trained operators or chemical technicians and a long measurement time. Atomic emission spectroscopy is the method of reference for heavy metal concentration analysis. This analytical technique is employed for multi-element analysis and is suitable for routine measuring (FOURNIER et al., 1998). The dominating mineral species of heavy metals in contaminated soils can be identified by X-ray absorption fine structure (XAFS) spectroscopy, which provides information about the short-range coordination chemistry of the metal atoms (MANCEAU et al., 2000; SCHEINOST et al., 2002). However, identification and quantification of the most mobile metal species with spectroscopic tools is still difficult. Therefore, several other approaches are commonly used to estimate mobile, labile, or bioavailable pools of heavy metals in soil. The most important methods include: (i) single batch extraction of soil samples with salt solutions (e.g.,  $\text{NH}_4\text{NO}_3$  or  $\text{CaCl}_2$ ), (ii) sequential batch extractions with increasingly harsh extractants designed to dissolve metals associated with different solid phases, (iii) isotope exchange methods, (iv) the diffusive gradients in thin films (DGT) technique, and (v) column leaching experiments. Single batch extractions form the basis of environmental regulations in many countries (McLAUGHLIN et al., 2000a).

CAROLINA et al. (2007) stated that heavy metals in soil samples can be determined by highly sensitive spectroscopic techniques, such as atomic absorption spectroscopy [e.g. Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption Spectrometry (GFAAS)] and Inductively Coupled Plasma (ICP) spectrometry [e.g. ICP-Atomic Emission Spectrophotometry (ICP-AES) and ICP-Mass Spectrometry (ICP-MS)]. These techniques require the transformation of a solid sample into solution from which metal concentrations are determined. They also mentioned that heavy metals in soil samples are usually converted to a soluble form through acid digestion methods. The most important methods used for soil digestion consist of open vessel digestion by digester block and closed vessel digestion by microwave oven. Given that it is well known that different digestion methods may lead to different results, a validation process is needed to demonstrate data quality and select the most useful method according to the characteristics of the study area and particularly soil properties. Results obtained applying these digestion methods are generally used to assess the degree of pollution in soils. Therefore, the choice of the digestion

method has to be suitable in order to provide information on the total content of heavy metals in soils and consequently about the pollution levels. SLAGLE et al. (2004) measured the concentration of ten trace elements (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Se, Zn) which were determined by inductively coupled plasma-atomic emission spectroscopy (ICPAES) after microwave digestion by USEPA Method 3051 and an HF method. Trace element concentrations using USEPA 3051 were about 1.5 to 5 times lower than the amounts extracted by the HF method, except for Mn. Method 3051 of the USEPA used concentrated HNO<sub>3</sub> acid following solid waste procedure SW 846-3051 (U.S. EPA, 1997). This method involved a closed vessel using pressure and temperature-controlled microwave heating for dissolution. The HF method used a combination of three concentrated acids: HNO<sub>3</sub>, HF, and HCl with microwave digestion. The HF method should represent a “total” quantity of trace elements present in the soil because concentrated HNO<sub>3</sub>, HF, and HCl acids cause soil components to dissolve, thereby releasing the bound elements within their structures. CHEN et al. (1999) made a comparison of EPA Methods 3050 (hot-plate, HNO<sub>3</sub>-HCl), 3051 (microwave, HNO<sub>3</sub>), 3051a (microwave, HNO<sub>3</sub>-HCl) and 3052 (microwave, HNO<sub>3</sub>-HCl-HF) was thus conducted by digesting three NIST standard reference materials (SRMs) and 40 representative Florida surface soils. Fifteen trace metals (Ag, As, Ba, Be, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se and Zn), and six macro elements (Al, Ca, Fe, K, Mg, and P) were analyzed using an inductively coupled plasma spectrometer (ICP) or an inductively coupled plasma mass spectrometer (ICP-MS) except for As, Cd, Pb, and Hg, which were analyzed either by a graphite furnace atomic absorption spectrophotometer (GF-AAS) or by a cold vapor atomic absorption spectrophotometer (CVAAS). They suggested that concentrations of most trace metals in Florida soils are primarily controlled by soil properties. The most effective and useful digestion method to be applied to agricultural soils devoted to growing vegetable crops is open vessel digestion using a digester block with HNO<sub>3</sub>, HClO<sub>4</sub> and HCl and microwave-assisted digestion using HNO<sub>3</sub> and HCl (CAROLINA et al., 2007). In-situ immobilization is a promising approach that has the potential to remove metals from solutions and or stabilize metals in soils (MA et al., 1993). When using this approach, two important factors need to be considered: (i) the system must be effective under a variety of existing geochemical conditions and (ii) immobilized metals should be stable and remain nonleachable under varying environmental conditions. Generally, in-situ immobilization of metals involves minimization of contaminant mobility by transferring the metals from labile to nonlabile phases via physically, chemically, or biologically induced transformations.

A large number of sequential extraction procedures have been developed in which the element content is partitioned by sequential treatment with a series of reagents (KERSTEN and FÖRSTNER, 1995). The most widely used sequential extraction schemes are probably those proposed by TESSIER et al. (1979) and the Community Bureau of Reference (BCR) (QUEVAUVILLER, 1998). These procedures have been demonstrated to give satisfactory results for the targeted phases owing to a careful selection of reagents and detailed operating conditions (SHIOWATANA, 2001). During the extractions steps the original structures are destroyed, therefore the native species cannot be identified. The whole procedure is very time consuming

and its application requires a well-educated staff (HELTAI et al., 2001). HELTAI and FÜLEKY (1992) mentioned that the fractionation of heavy metals according to their mobility and bioavailability in the system appears to be a feasible approach for risk assessment. This approach has a long tradition in agrochemical practice where the bioavailability of nutrients in the soil is characterized by well-selected chemical extraction procedures. HELTAI et al. (2008) stated that the mobility and bioavailability of metals and their potential ecotoxicity is strongly determined by their specific chemical forms in soils and aquatic sediments. Due to the complexity of the system the total elemental speciation is impossible, therefore the fractionation of element content by sequential extraction procedures were developed for risk assessment caused by heavy metal contamination in practice. These methodologies mostly are based on the Tessier five-step procedure (TESSIER et al., 1979) which is, however, very time-consuming and labour-intensive for practical purposes. They also mentioned that the three-step sequential extraction scheme is used by which the acetic acid soluble, the reducible Fe and Mn oxide associated, and the oxidisable organic and sulfide-bound metal fractions can be distinguished by successive decomposition with a series of increasingly aggressive reagents (HELTAI et al., 2008).

Solutions of neutral salts rely on ion exchange by cations to release Zn and Cu in solutions. Acid extractants dissolve the mineral of soil samples, the chelating agent rely on the formation of water soluble complexes (LINDSAY and NORWELL, 1978). The suitability of the extractant depends on the physical and chemical characteristics of the soil, therefore, no single extractant can be recommended for all types of soils. Several extractants have been tried to measure the available forms of Cu and Zn with variable results (DE ABREU et al., 1998; ZHU and ALVA, 1993). Most laboratories in Hungary since 1978 have used KCl-EDTA solution as a routine extractant of micronutrients (MÉM-NAK, 1978) in concentration to the Lakanen Erviö extraction method used widespread internationally (LAKANEN, 1962; LAKANEN and ERVIÖ, 1971). Chelating agents can be used to convert the soil-bounded heavy metals into soluble metal complexes (AMRATE et al., 2005). Chelating agents contain two or more ligands (L) that bond with metal to form stable, ring-like coordination complexes, called chelates. Chelating agents can be particularly effective for the remediation of strongly buffered alkaline soils, in which the pH cannot be easily lowered by the addition of acid solutions (AMRATE et al., 2005). Among different chelating agents, Ethylene diamine tetraacetic acid (EDTA) has shown to be very effective for metal dissolution in soils, and it has also been extensively applied for soil washing and soil flushing (POLETTINI et al., 2006; DI PALMA and MECOZZI, 2007), being a widely available non-toxic chemical. EDTA is soluble at pH of above around 3.5 and its speciation, i.e. the degree of protonation depends on the pH (AMRATE et al., 2005). EDTA has been shown to enhance phytoextraction of some heavy metals from contaminated soil. The EDTA chelate is least effective and will remain stable up to pH 6.3 where iron deficiencies normally do not exist (SCHULTE, 2004). EDTA/NH<sub>4</sub>Ac extraction procedures reflect mobile metals which can be used and metabolised by plants (BAJO et al, 1991; GUPTA, 1991). Plants make use of loosely bound trace metals, which is just a small portion of their total amount in soil. Of many chelating agents, EDTA proved to be the best extractant (McGRATH, 1996). Strong

acid digestion (e.g. by boiling  $\text{HNO}_3$  or aqua regia) is often claimed to yield the total metal concentration or sometimes the quasi- or pseudo-total concentration (ANDERSON et al., 2000; MADRID et al., 2002). In the laboratory practice, the most frequently used chemical methods of extraction (removal, desorption) are as follows: (i) single extraction method (using a suitable extractant, e.g. a strong acid (CHEN, 1994), or a suitable complexing agent at a given pH (PETERS and SHEM, 1992), (ii) sequential extraction procedure consisting of a number of successive leaching steps (HAN et al., 2001). VEEKEN (1998) studied citric acid as an extractant, the method is applicable for the removal of Zn and Cu from some soils (e.g., sandy soil) and it does not result in high losses of the soil structure. Hot water percolation (HWP) is a soil extraction method developed by FÜLEKY and CZINKOTA (1993) and is suitable for routine analyses, i.e. to use high temperature and pressure to increase the speed and efficiency of the extraction. The element content obtained by this method could be compared with the results of conventional methods. The element contents determined by the HWP method and by the conventional methods are generally of the same magnitude. A large variety of extraction procedures has been introduced to support plant nutrition advisory systems. These procedures are mostly standardized at national levels based on internationally accepted methods (HELTAI and FÜLEKY, 1992). When cold water leaching is applied to soils or sediments, suspension formation may be significant but the effectivity of real dissolution is very low (HELTAI, 2005). Extracts gained by subcritical water may be used for estimation of ecotoxicological potential of contaminated sediments (HELTAI, et al., 2005).

Reflectance spectroscopy is a simple and nondestructive analytical method that can be used to predict not only spectral active constituents but also trace elements, which are spectrally featureless. Reflectance spectroscopy is an alternative method for assessing heavy metals, the results of using this method indicated that only at very high concentration can transition elements exhibit their inherent absorption features (WU et al., 2007). Reflectance spectroscopy within the visible and near-infrared reflectance spectroscopy (VNIRS) region (380-2500 nm) has been widely used as an inexpensive tool for rapid analysis of a wide range of soil properties (CHANG et al., 2001). For several years, with the advent of various mathematical methods such as partial least squares regression, artificial neural networks, and multivariate adaptive regression splines (WU et al., 2007), research has concentrated more on the quantitative prediction with reflectance spectroscopy of various soil constituents, most of which have absorptions within the visible and near-infrared reflectance spectroscopy (VNIRS) region, such as water (WHITING et al., 2004), Fe oxides (GRYGAR et al., 2003), carbonates (BEN-DOR and BANIN, 1990), and organic matter (FIDENCIO et al., 2002). In addition, because of the inter correlations to these spectral constituents, even spectrally featureless soil properties such as cation exchange capacity, base saturation, pH, exchangeable bases, and extractable P can be estimated, but only indirectly (BROWN et al., 2006). Soil magnetic susceptibility is a good indicator of pollutions coming from agricultural practices (CAGGIANO et al., 2005). The techniques of surface and sub-surface sensing, based on the measurements of electrical and magnetic parameters of soil, represent suitable tools for identifying innovative experimental procedures

(DESENFANT et al., 2004). In particular, the integration of traditional chemical techniques with soil magnetic susceptibility measurements may be an interesting way for monitoring of heavy metal levels in superficial soil (CHAPARRO et al., 2004; DESENFANT et al., 2004).

### 2.2.8. Environmental modeling

SCHNOOR (1996) stated that there are three reasons to build mathematical models of environmental pollutants: (1) To gain a better understanding of the fate and transport of chemical by quantifying their reactions, speciation and movement. (2) To determine chemical exposure concentrations to aquatic organisms and humans in the past, present, or future. (3) To predict future conditions under various loading scenarios or management action alternatives. In recent decades, numerous models of the fate of metals in soils have been presented in the literature. Such models are developed for different purposes and using different approaches (ÖBORN and LINDE, 2001). Mechanistic models are developed as research tools to better understand governing of processes, while functional, less mechanistic models are developed from a management perspective (ADDISCOTT and WAGENET, 1985). The approach may also differ in scale, as well as in the part of the system considered most important (ÖBORN and LINDE, 2001). DAVIS et al. (1998) discuss different modelling approaches for describing the adsorption of inorganic contaminants, e.g. metals, to natural materials. According to those authors, all such models have some basic assumptions in common: (1) The mineral surface is composed of specific functional groups that react with dissolved solutes to form surface species analogous to complexation in homogeneous solution. (2) The equilibria of metal sorption or surface complexation and surface acidity can be described by mass action equations. (3) The apparent binding constants determined for the mass action equations are empirical parameters related to thermodynamic constants by the rational activity coefficients of the surface species. (4) The electrical charge at the surface is determined by the chemical reactions of the mineral functional groups, including acid-base reactions and the formation of ion pairs and coordinative complexes. Metal concentrations determined by Atomic absorption spectrophotometers (AA) and inductively coupled plasma emission spectrometers (ICP) are often used as inputs into a thermodynamic computer program, such as MINTEQ. The MINTEQ model program was released initially by U.S. EPA in 1991 as a chemical equilibrium model for the calculation of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model can calculate the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions and gas phase partial pressures. MINTEQ comes complete with a comprehensive database, and also allows user defined parameter input (U.S. EPA, 2003). MINTEQA2 has been supported by the U.S. EPA agency and it has a wide array of choices that are available for adsorption, including the simple equilibrium distribution coefficient  $K_d$ . Most of the models (i.e. MINTEQA2) are well-documented and suitable for chemical equilibrium problems in natural waters (acid-base, precipitation-dissolution, complexation, surface complexation, and/or redox) (SCHNOOR, 1996).

### 3. MATERIALS AND METHODS

#### 3.1. Soil 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. The exact locations of the numbered sites and their GPS coordinates are provided in Table 5.

Soil	Place	Latitude °	'	''	Longitude °	'	''
1	Tivadar outside catchment	48	3	48.492	22	30	19.692
2	Tivadar bank	48	3	40.068	22	29	43.764
3	Tivadar flood-plain	48	3	41.544	22	29	50.568
4	Gergelyugornya bank	48	7	4.008	22	20	15.972
5	Gergelyugornya flood-plain	48	7	4.368	22	20	16.476
6	Gergelyugornya outside catchment	48	7	8.076	22	20	59.964
7	Tiborszállás clay	47	48	56.088	22	25	18.948
8	Meadow organic soil	47	48	56.088	22	25	18.948

Table 5. The location of each background sample identified by using global positioning system (GPS)

Tivadar is a small village close to the River Tisza that has a low degree of anthropogenic impact, upstream from Szamos mouth. Gergelyugornya 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 continuously water-covered soil. The soils from Tivadar and Gergelyugornya 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 Gergelyugornya, 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 Gergelyugornya). The sample is from a polluted area of Tisza, situated at the bottom the Tisza-Szamos connection. Gergelyugornya 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 Gergelyugornya, 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.

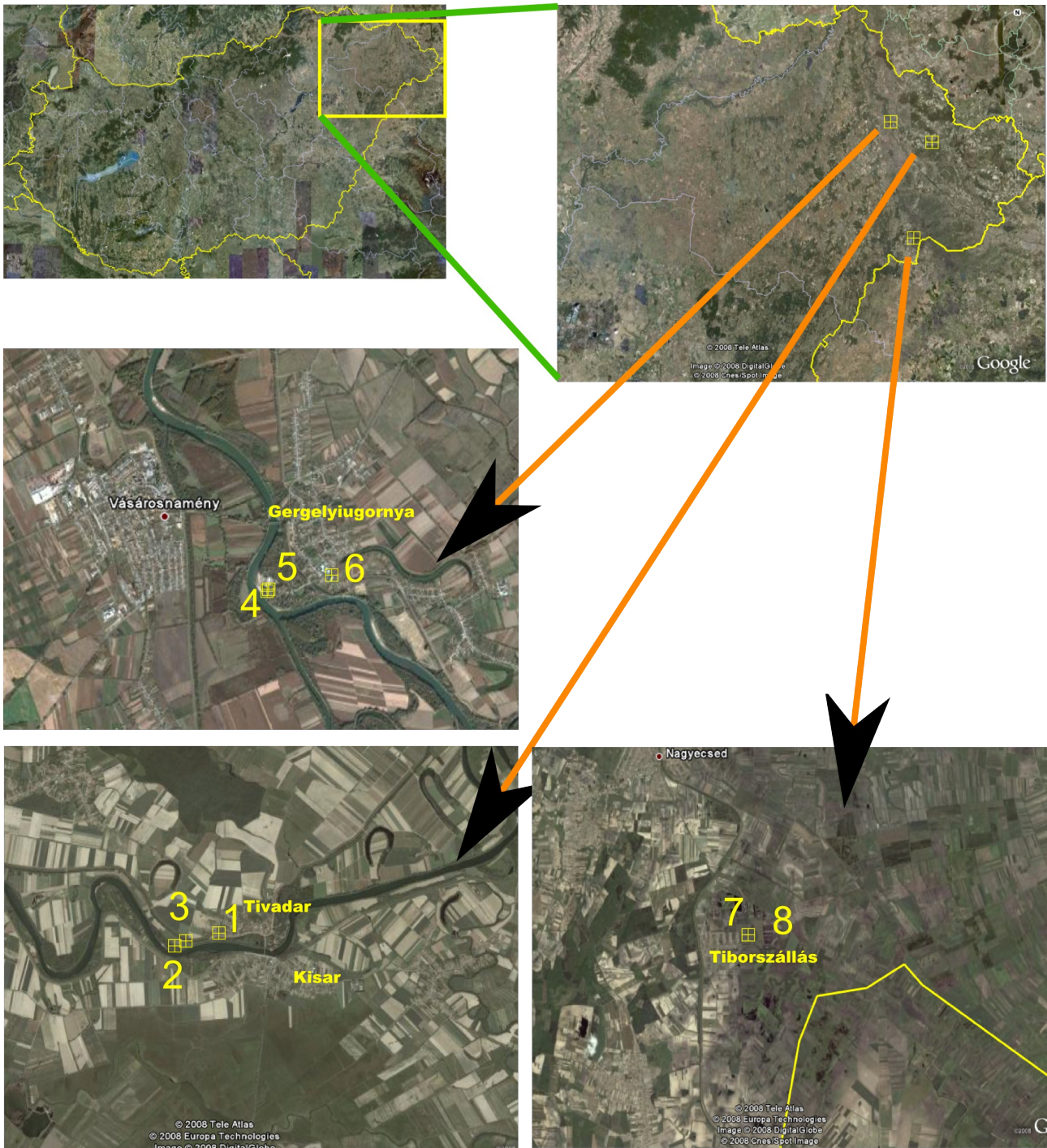


Figure 3. Soil samples sites, using Google map

### 3.2. 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 Agrochemistry 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).

For different extraction procedures, (EDTA, HNO<sub>3</sub> 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 6.

N°	Place	K <sub>A</sub>	pH <sub>KCl</sub>	Humus %	CaCO <sub>3</sub> %	Total S mg/kg	K µg/g	Na µg/g
1	Tivadar outside catchment	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	Gergelyugornya bank	48	6.14	1.34	0.19	256	6.65	21.25
5	Gergelyugornya flood-plain	53	6.20	2.43	0.35	494	25.85	8.25
6	Gergelyugornya outside catchment	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 6. Sampling places, properties and the features of the eight soil samples

### 3.3. Methodology

#### 3.3.1. Electrochemical redox titration

During our investigations platinum electrode was used for measuring of the redox potential (Figure 5). 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:  $\varepsilon$  is the electrode potential under given conditions (V)  
 $\varepsilon^\circ$  standard electrode potential (V) (at 25 °C; at 0.1 MPa)  
**R** universal gas constant; 8.31434 Jmol<sup>-1</sup>K<sup>-1</sup>  
**T** temperature (K)  
**z** number of e<sup>-</sup>s participating in the redox process  
**F** Faraday's constant; 96 486 Cmol<sup>-1</sup>  
**[ox]** concentration of the oxidated form (M dm<sup>-3</sup>)  
**[red]** concentration of the reduced form (M dm<sup>-3</sup>)

Connecting this measuring electrode to an Ag<sup>+</sup>/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.:

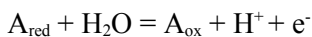
$$E.M.F. = \varepsilon_{cathode} - \varepsilon_{anode}$$

where  $\varepsilon_{cathode}$  is potential of the Ag<sup>+</sup>/AgCl reference electrode ( $\varepsilon^\circ = 0.222V$ )  
 $\varepsilon_{anode}$  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:



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 ( $\text{pH} = -\lg [H^+]$ ), an informative form of this equation can be obtained:

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

i.e., it is necessary to correct the redox potential (calculated from the measured value) of a system for 59 mV pro pH unit. The following figure, where the electrode potentials in aqueous solutions are presented as functions of the pH-value clarifies this method:

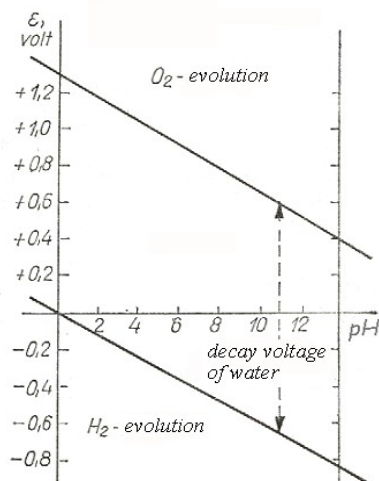


Figure 4. Hydrogen and oxygen electrode potential as a function of pH. From top to bottom: O<sub>2</sub> production; decomposition voltage of water; H<sub>2</sub> production (ERDEY-GRÚZ, 1972).

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<sub>2</sub> evolution occurs. If the value of electrode potential indicated the upper line is more positive, then O<sub>2</sub> 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 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  $\text{KMnO}_4$  solution, and 1 molar hydrochloric acid solution were used and the measured voltage values in this case agreed up to  $\pm 5$  mV with the summarized values of the  $\text{KMnO}_4$  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  $\text{KMnO}_4$  solution, but since the nascent manganese II ions notably modify the soil surface, we switched over to the  $\text{NaOCl}$  solution, whose decomposition products are the  $\text{Na}^+$ ,  $\text{Cl}^-$  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  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$  – 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  $\text{K}_2\text{CrO}_4$ ). 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  $\text{KMnO}_4$  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.

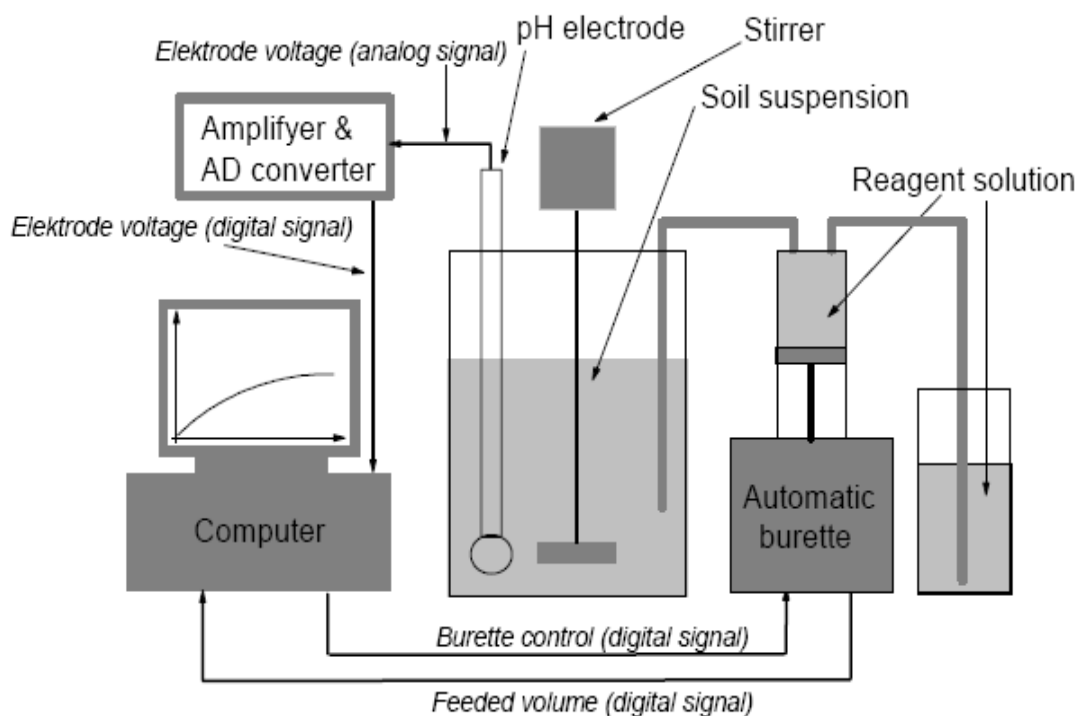


Figure 5. Theoretical outline of the redox titration equipment

### 3.3.2. Incubation experiment of two flood plain soils

In this experiment we used Tivadar and Gergelyugornya 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 Gergelyugornya soil during the

incubation experiment. Selected soil properties are summarized in Table 5. 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<sub>3</sub>). The buffer solution was prepared in such a way that 12.5 ml of 1 mole CH<sub>3</sub>COONa solution was added to 12.5 ml of 0.1 mole CH<sub>3</sub>COOH 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<sub>3</sub> 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).

### **3.3.3. 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 (Table 7). 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.

Element	Input Concentration	Redox Pair
H <sup>+</sup>	8.00	
Fe <sup>2+</sup>	.01	
Cu <sup>2+</sup>	.01	
Zn <sup>2+</sup>	.01	
Mn <sup>2+</sup>	.01	
Mg <sup>2+</sup>	.01	
Ca <sup>2+</sup>	.01	
K <sup>+</sup>	.01	
PO <sub>4</sub> <sup>-3</sup>	.01	
CO <sub>3</sub> <sup>-2</sup>	1,00E-16	
E-1	16.00	
Cu <sup>+</sup>	1,00E-16	
Fe <sup>3+</sup>	1,00E-16	
Mn <sup>3+</sup>	1,00E-16	
SO <sub>4</sub> <sup>-2</sup>	1,00E-16	
HS <sup>-1</sup>	1,00E-16	
CN <sup>-1</sup>	0.01	
		Fe <sup>2+</sup> /Fe <sup>3+</sup>
		Mn <sup>2+</sup> /Mn <sup>3+</sup>
		HS <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>

Table 7. The Input Parameters of the Visual MINTEQ 2.5 input file. The table presents all the input materials which were used in the program (concentration in mole/l.)

### 3.3.4. Statistical analysis

In the case of the titration method we used regression analysis for the reduction buffer capacity results of Tivadar and Gergelyugornya 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).

## 4. RESULTS AND DISCUSSION

### 4.1. Electrochemical redox titration of eight soil samples

The received titration (Figure 6) 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.

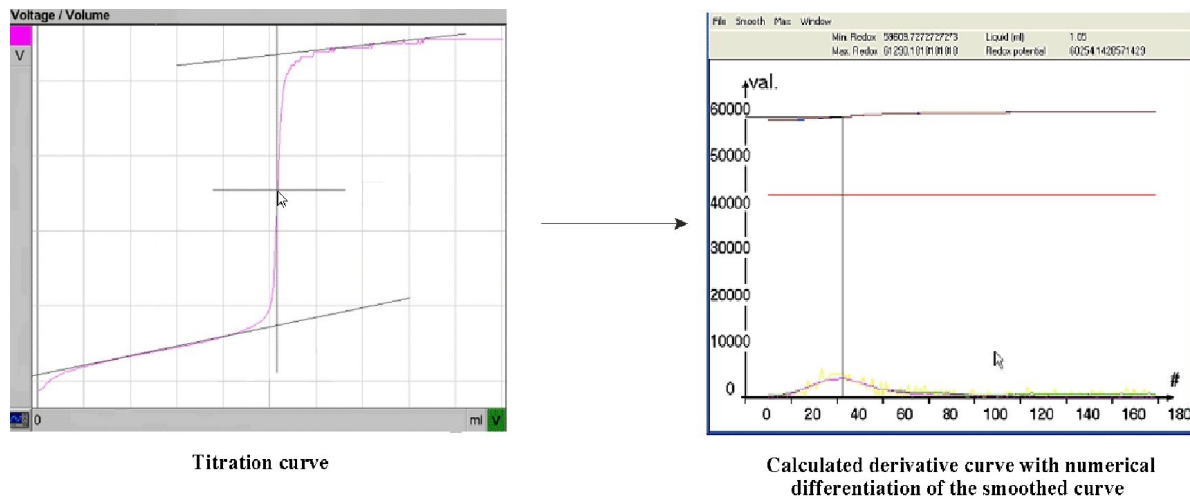


Figure 6. A measured titration curve from which the calculated derivative curve with numerical differentiation of a smoothed curve was derived

As can be seen from Table 8 and Table 9, 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 (Figure 7), 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.

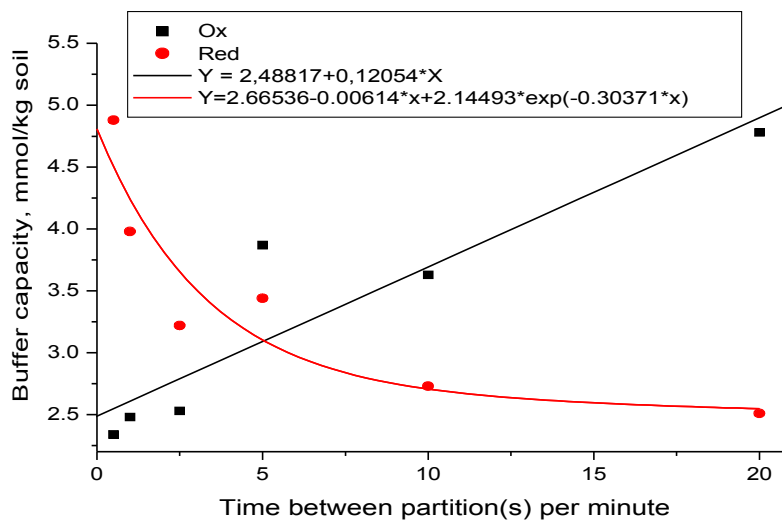


Figure 7. The calculated averages of buffer capacity values for different eight soil samples plotted against time passed between partitions

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
<b>Average</b>	2.20	6.13	0.92	3.97	3.54	0.99	5.62	2.81	

Table 8. 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
<b>Average</b>	3.58	3.68	3.86	3.83	3.30	3.06	3.33	3.04	

Table 9. Values of the Reduction Buffer Capacity mmol/kg Soil

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 8 and Table 9. 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.

#### 4.1.1. 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 (Figure 8). 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.

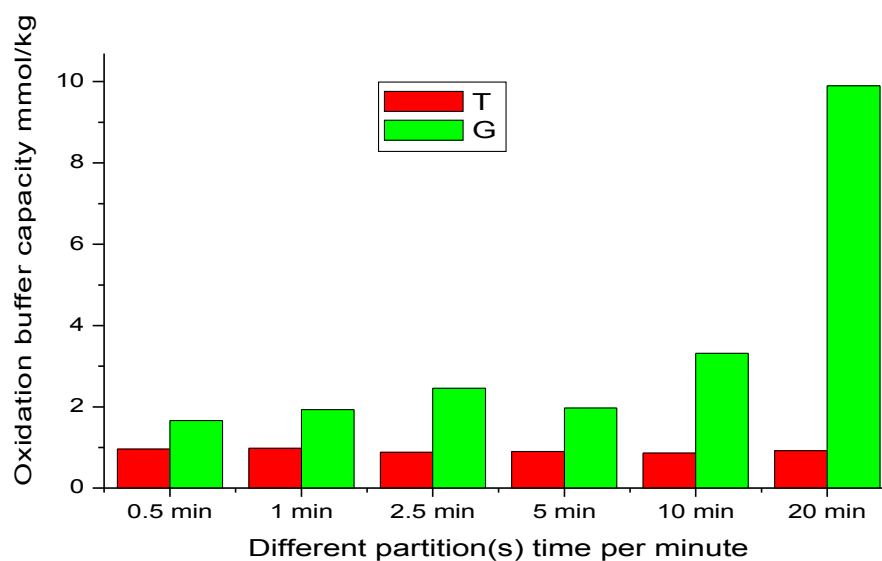


Figure 8. Oxidation buffer capacity values at different partition times for Tivadar (T) and Gergelyiugornya (G) flood plain soil samples.

For Tivadar soil sample there are reduced compounds in the deeper layer of their pores, but there is no oxidated compounds existing. Compare to the reduction buffer capacity in different partition times between the two soil samples (Figure 10), 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 (Figure 9) 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.

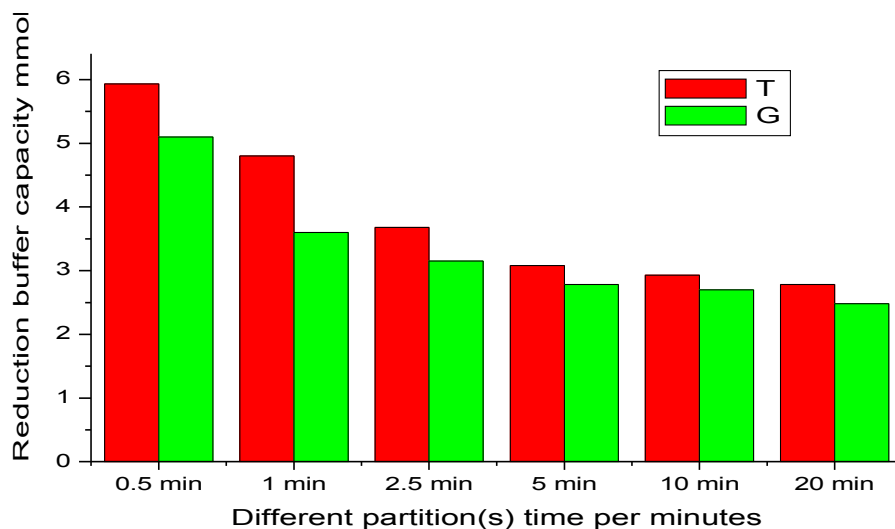


Figure 9. Reduction buffer capacity values at different partition times for Tivadar (T) and Gergelyugornya (G) flood plain soil samples.

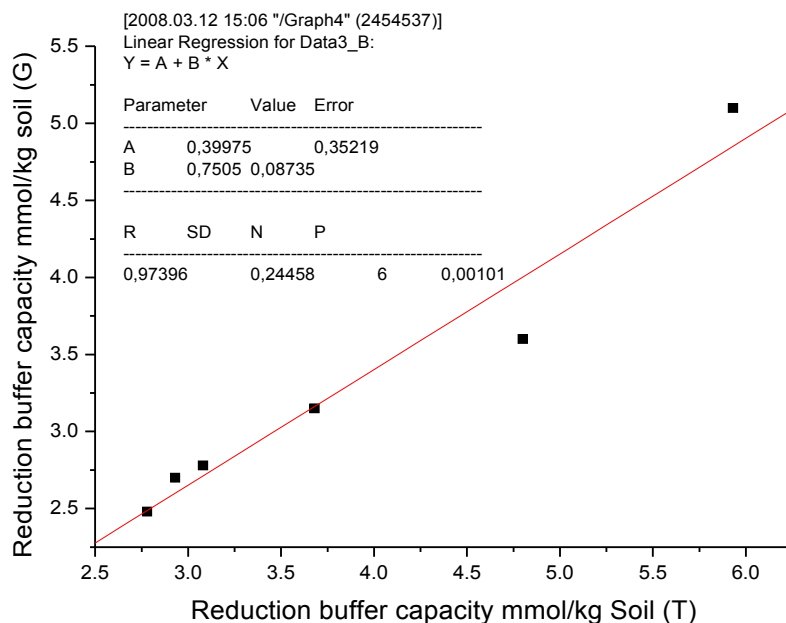


Figure 10. Comparison of reduction buffer capacity values between Tivadar (T) and Gergelyugornya (G) flood plain soil samples.

#### 4.1.2. Relationship between buffer-soluble iron and redox buffer capacity

As shown in Figure 11, 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<sub>3</sub>-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<sub>3</sub>-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<sub>3</sub>-soluble iron in the soil.

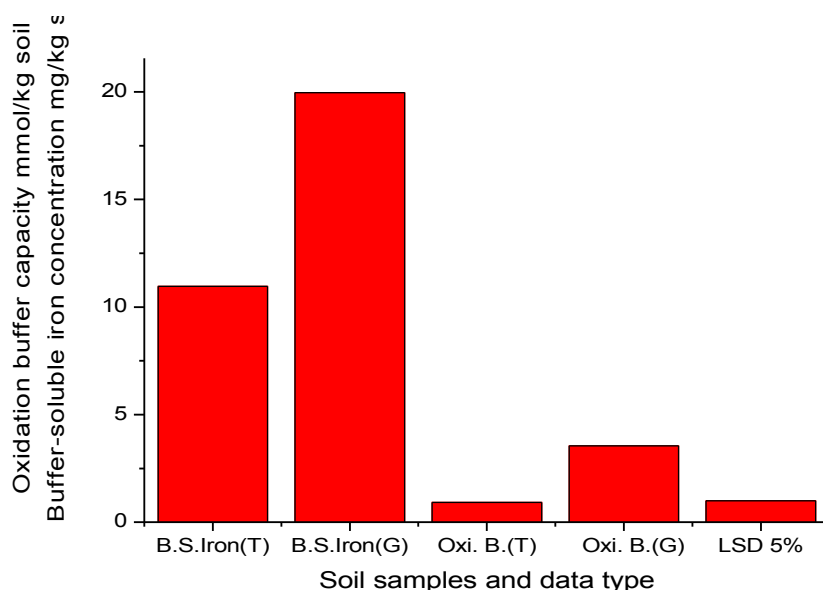


Figure 11. The relationship between buffer-soluble (B.S) iron and oxidation buffer capacity for Tivadar (T) and Gergelyugornya (G) flood plain soil samples

#### 4.1.3. 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 (Gergelyugornya) 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. 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.

#### 4.1.4. 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 Gergelyugornya soil were greater (Table 6). 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 10 and Table 11 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 Gergelyugornya 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.

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

Table 10. Heavy metals concentrations (mg/kg) and standard deviations at Tivadar flood plain study site using different extraction methods

	<b>EDTA</b>	<b><math>HNO_3</math></b>	<b>Aqua regia</b>
<b>Fe</b>	608.9 ± 7.9	5562.1 ± 111.5	28910.0 ± 1353.0
<b>Cu</b>	56.8 ± 1.0	61.1 ± 1.8	97.1 ± 3.9
<b>Zn</b>	140.8 ± 7.3	239.9 ± 12.5	225.0 ± 2.0
<b>Mn</b>	443.6 ± 6.9	741.2 ± 12.5	712.2 ± 6.9

Table 11. Heavy metals concentrations (mg/kg) and standard deviations at Gergelyugornya 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 Gergelyugornya (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 Gergelyugornya 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<sub>3</sub> extraction method, while by applying Aqua Regia extraction method the heavy metal content is much higher compared to the other extraction methods. In the Gergelyugornya soil samples the three applied extraction methods results display the same trend compared to the Tivadar soil results with some exceptions (see Figure12, Figure 13, Figure 14 and Figure 15).

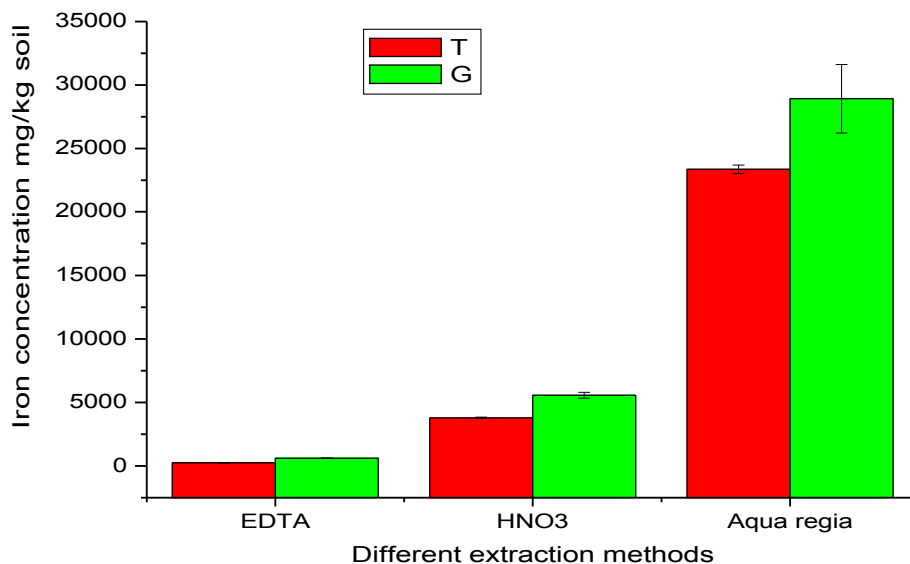


Figure 12. Iron concentration (mg/kg) soil using EDTA, HNO<sub>3</sub> and aqua regia extraction methods of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

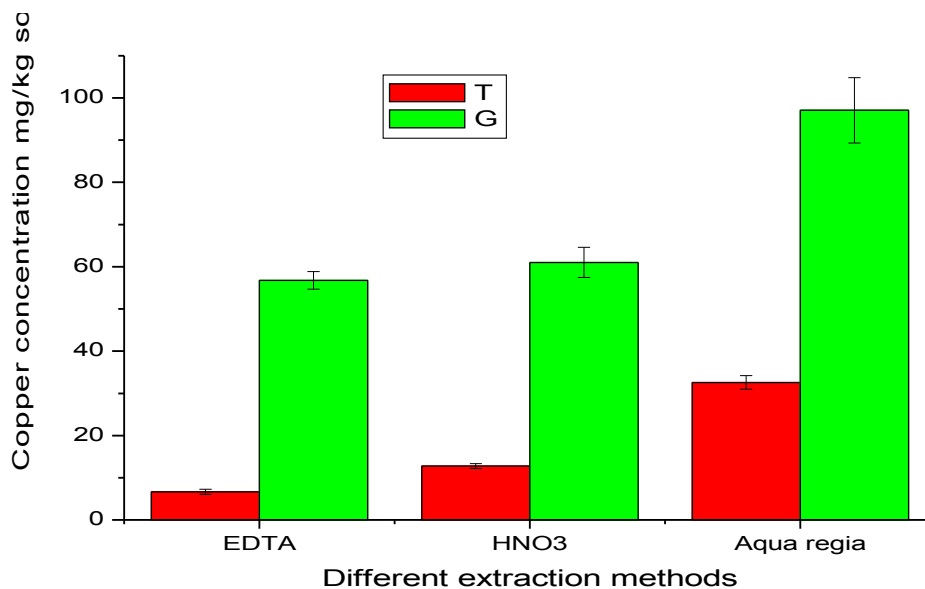


Figure 13. Copper concentration (mg/kg) soil using EDTA, HNO<sub>3</sub> and aqua regia extraction methods of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

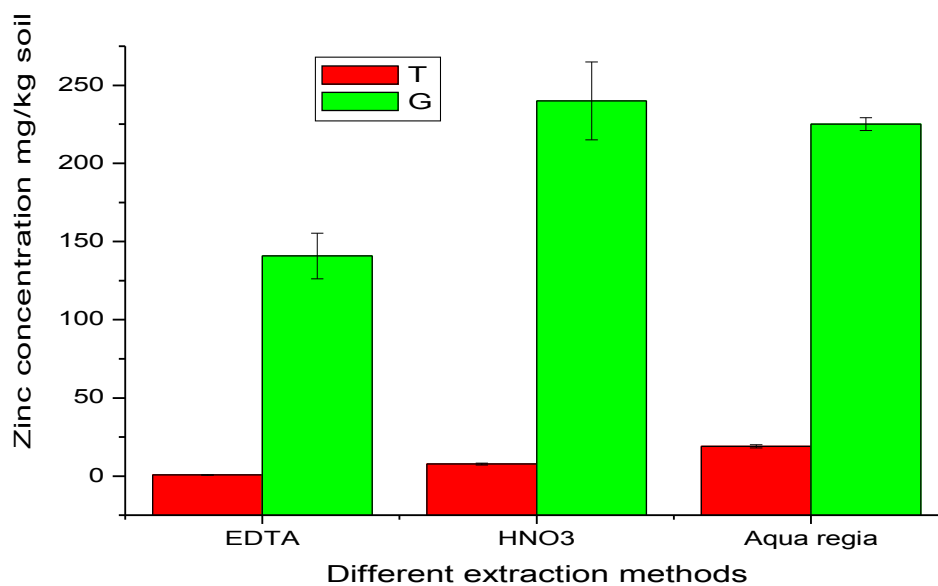


Figure 14. Zinc concentration (mg/kg) soil using EDTA, HNO<sub>3</sub> and aqua regia extraction methods of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

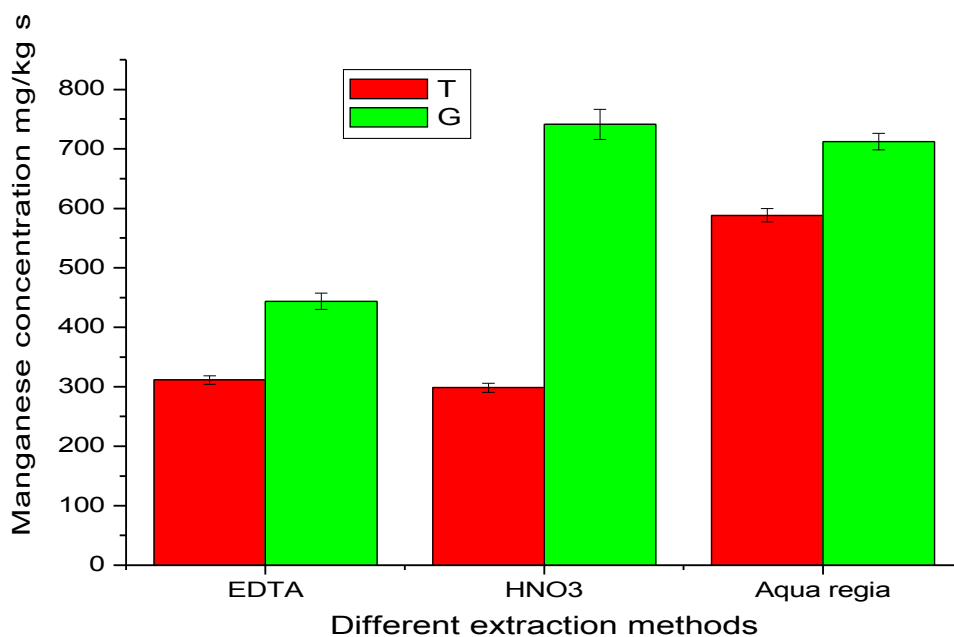


Figure 15. Manganese concentration (mg/kg) of soil using EDTA, HNO<sub>3</sub> and aqua regia extraction methods of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

The higher concentration of heavy metals retrieved by the Aqua Regia method compared to the other two extraction methods (EDTA, HNO<sub>3</sub>) 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 (NH<sub>4</sub>OAc-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 GYÓRI (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 Gergelyugornya 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 Gergelyugornya than in the Tivadar soil sample. The study showed similar results in agreement with the various authors mentioned above.

#### **4.1.5. Conclusion**

By using different extraction methods the metals analysed (Fe, Cu, Zn and Mn) are particularly concerning as their concentrations at the Gergelyugornya study site were much higher compared to the Tivadar study site. For the Gergelyugornya soil the amounts of Cu and Zn extracted with aqua regia, HNO<sub>3</sub> 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 Gergelyugornya 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.

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

While both soils (Tivadar and Gergelyugornya) displayed a low concentration (see Figure 16, Figure 18, Figure 20 and Figure 22) 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 (Figure 22) compared to Tivadar soil, Fe, Cu, Zn and Cu concentrations in Gergelyugornya 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 12, Table 13, Table 14 and Table 15). There was no difference between the two soils in CEC which was 28.62, 27.49 for Tivadar and Gergelyugornya, respectively.

Tivadar (3)					Gergelyugornya (5)				
Fe	Buffer		HNO <sub>3</sub>		Fe	Buffer		HNO <sub>3</sub>	
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 12. Iron concentration (mg/kg) of incubation periods using HNO<sub>3</sub> and buffer solution for Tivadar and Gergelyugornya flood plain soils

Tivadar (3)					Gergelyugornya (5)				
Cu	Buffer		HNO <sub>3</sub>		Cu	Buffer		HNO <sub>3</sub>	
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 13. Copper concentration (mg/kg) of incubation periods using HNO<sub>3</sub> and buffer solution for Tivadar and Gergelyugornya flood plain soils

Tivadar (3)					Gergelyiugornya (5)				
Zn	Buffer		HNO <sub>3</sub>		Zn	Buffer		HNO <sub>3</sub>	
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 14. Zinc concentration (mg/kg) of incubation periods using HNO<sub>3</sub> and buffer solution for Tivadar and Gergelyiugornya flood plain soils

Tivadar (3)					Gergelyiugornya (5)				
Mn	Buffer		HNO <sub>3</sub>		Mn	Buffer		HNO <sub>3</sub>	
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 15. Manganese concentration (mg/kg) of incubation periods using HNO<sub>3</sub> and buffer solution for Tivadar and Gergelyiugornya flood plain soils

The Humus content of the Gergelyiugornya soil was greater than the Tivadar soil (Table 6). 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 (see Figure 17, Figure 19, Figure 21 and Figure 23) 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.

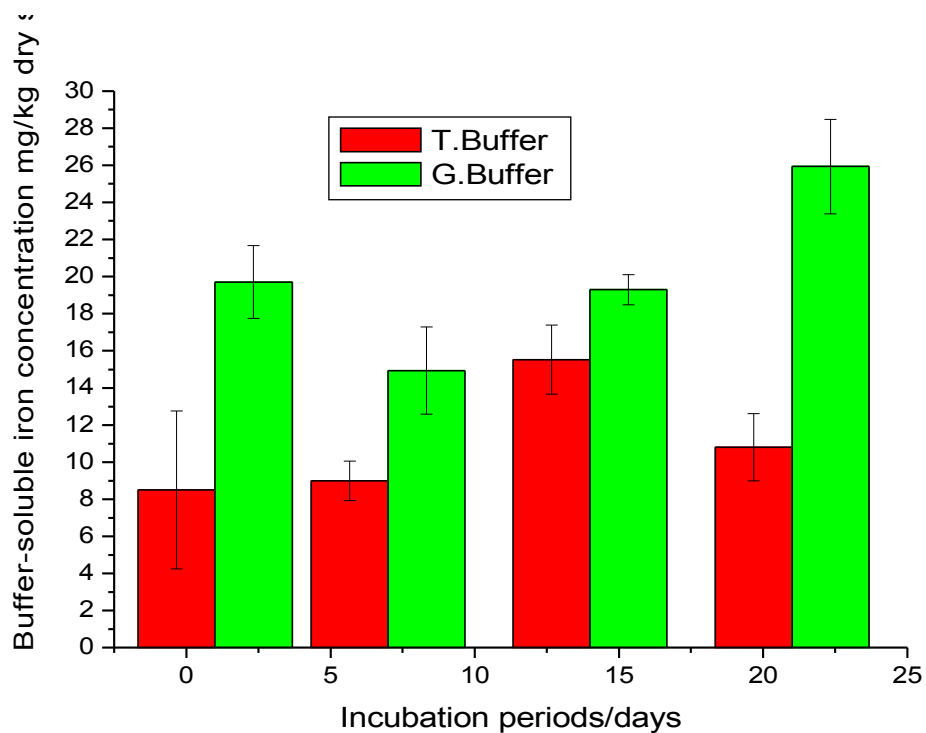


Figure 16. Buffer-soluble iron concentration (mg/kg dry soil) of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

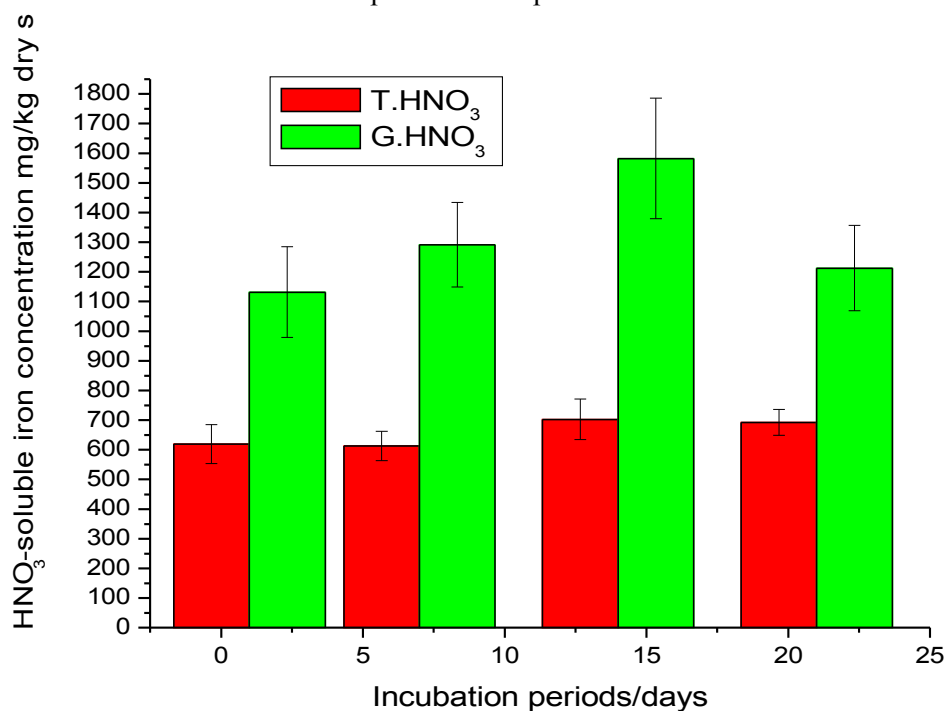


Figure 17. HNO<sub>3</sub>-soluble iron concentration (mg/kg dry soil) of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

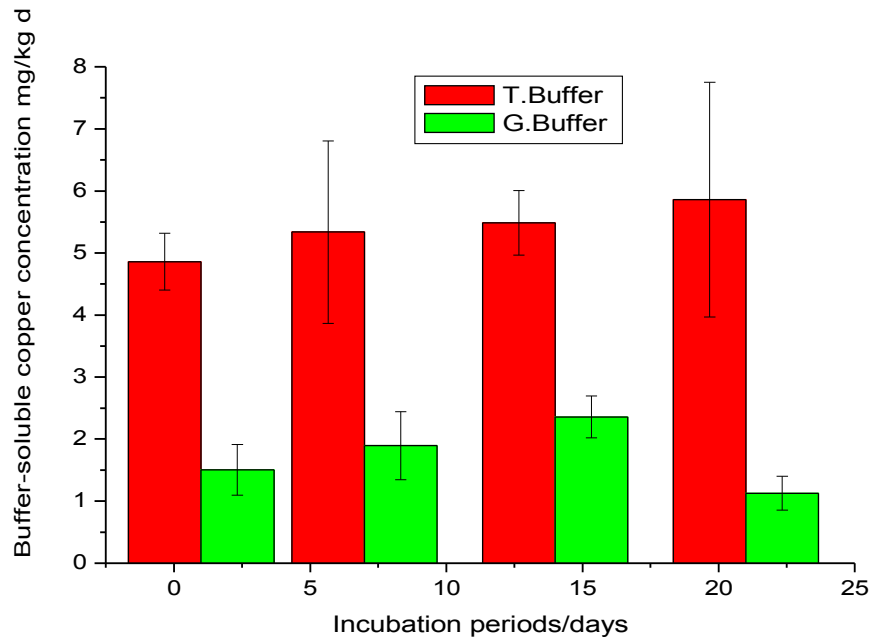


Figure 18. Buffer-soluble copper concentration (mg/kg dry soil) of Tivadar (T) and Gergelyiugornya (G) flood plain soil samples

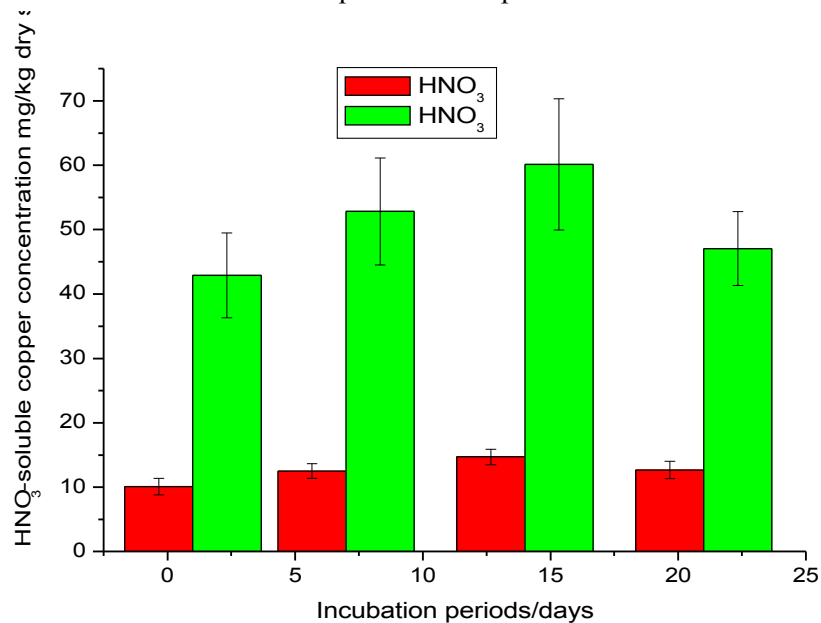


Figure 19. HNO<sub>3</sub>-soluble copper concentration (mg/kg dry soil) of Tivadar (T) and Gergelyiugornya (G) flood plain soil samples

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.

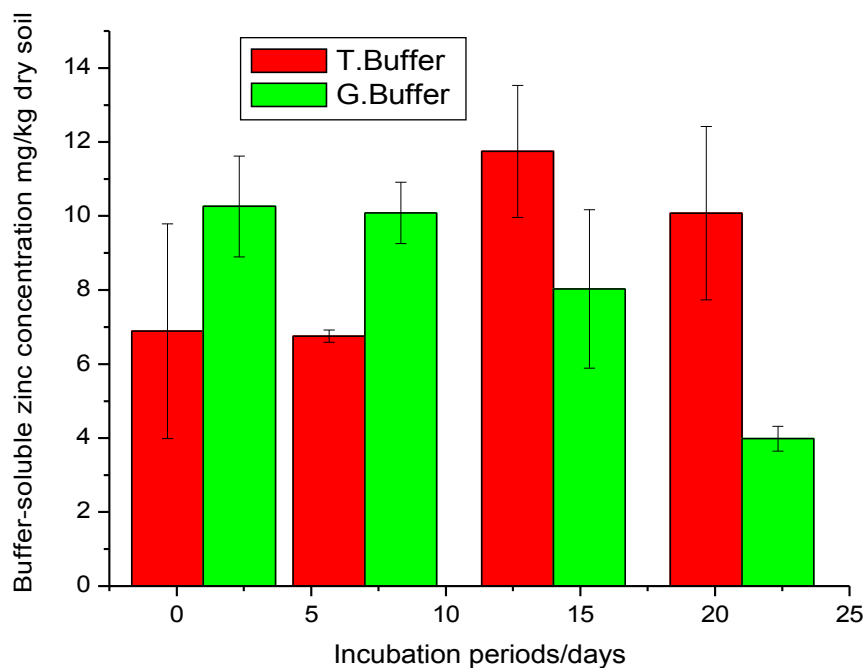


Figure 20. Buffer-soluble zinc concentration (mg/kg dry soil) of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

By applying nitric acid solution and taking an average from the incubation times, the total Mn concentration in the Gergelyugornya soil was about 10 times greater than that in the Tivadar soil (Table 15). 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<sub>3</sub> extraction for Gergelyugornya 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 Gergelyugornya 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 14). However, the Zn concentrations by using nitric acid solution and buffer solution did not show significant differences in both soils in the incubation times.

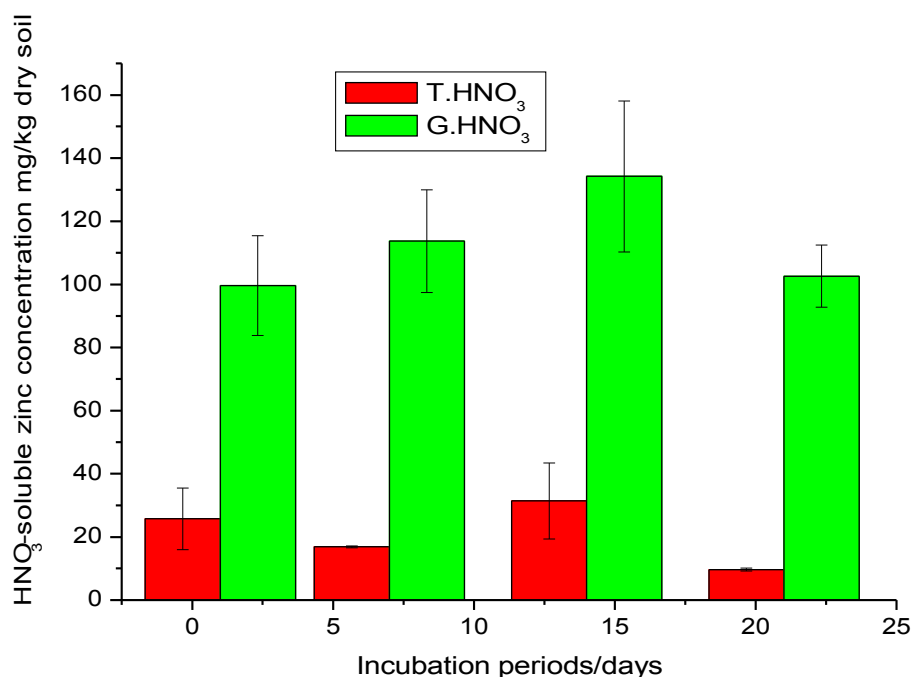


Figure 21. HNO<sub>3</sub>-soluble zinc concentration (mg/kg dry soil) of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

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.

As can be seen from Figure 16, the concentration of buffer-soluble iron does not correlate with the duration of incubation. Gergelyugornya 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<sup>2+</sup> 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 HNO<sub>3</sub>-soluble iron which occurred independently from the duration of the incubation (Figure 17), the Gergelyugornya sample contains a significantly higher concentration than the Tivadar sample. The concentration of HNO<sub>3</sub>-soluble iron is a sign of heavy metal pollution and thus significant differences can be suspected between the samples.

On Figure 18 an interesting phenomena can be seen: the copper content of the Tivadar sample is significantly higher than the Gergelyugornya sample in the case of using weak acid solution. 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 Figure 18 and Figure 20 it can be seen that in the case of a slightly acidic solution, the copper and the zinc concentration in the Gergelyugornya 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<sub>3</sub> solutions were used (see Figure 22 and Figure 23). The expected phenomena can be seen. In the case of both solutions the manganese concentration in the Gergelyugornya sample is almost an order of magnitude higher than in the Tivadar sample. The results of the study are in agreement with the authors mentioned above.

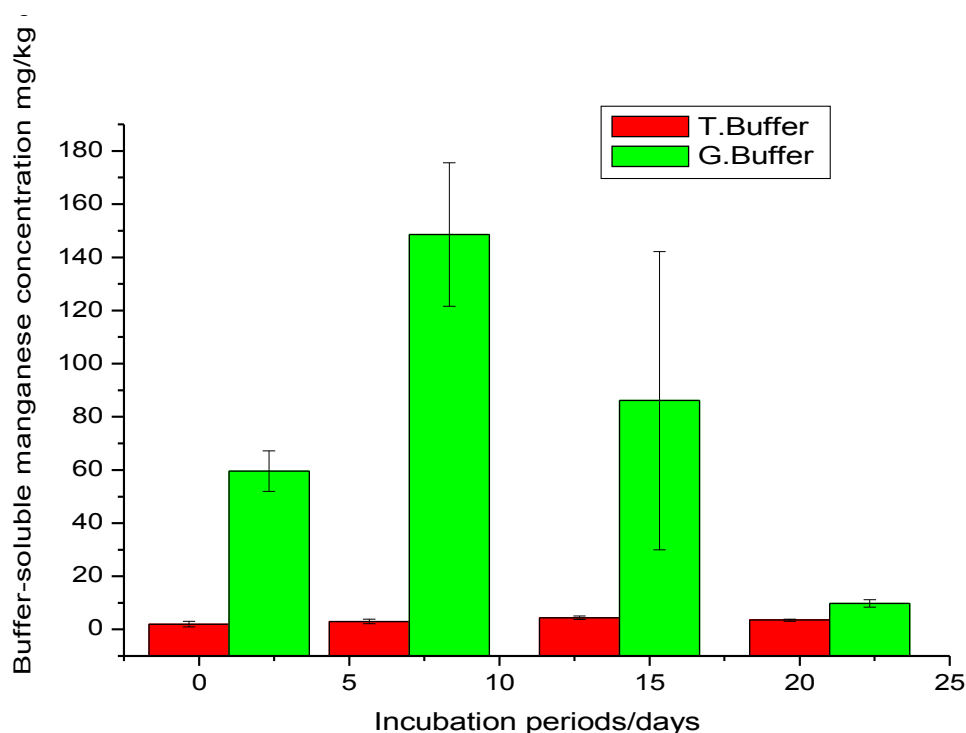


Figure 22. Buffer-soluble manganese concentration (mg/kg dry soil) of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

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 ( $sd(5\%)=1.4$ ) and the difference of zinc averages between the two soils is 4.4 and 4.0 for Tivadar and Gergelyugornya 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.

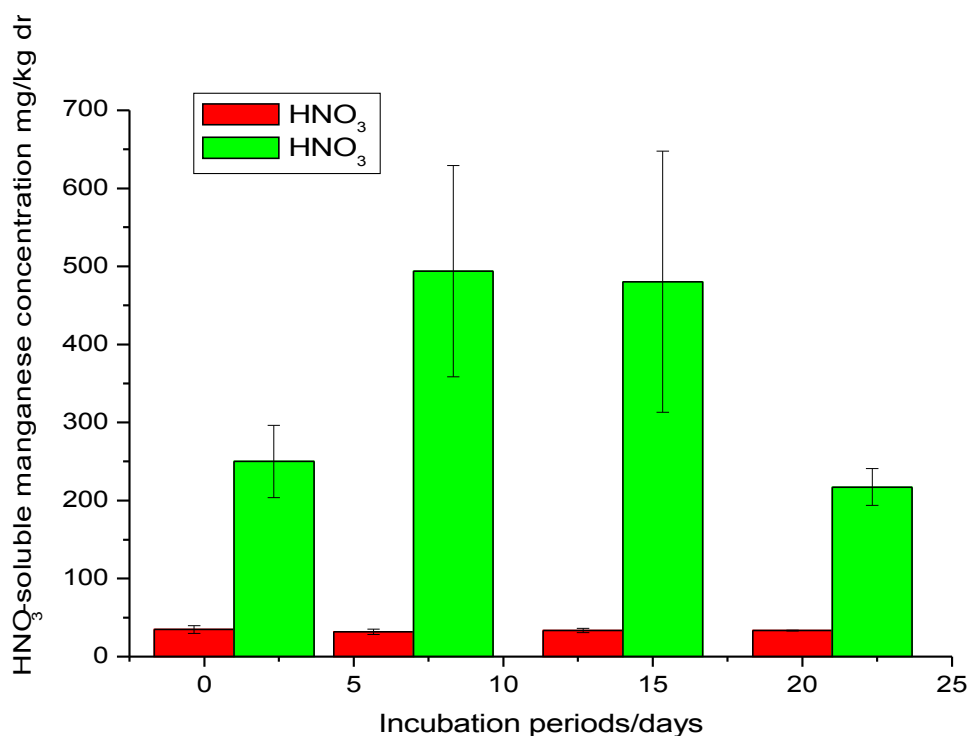


Figure 23. HNO<sub>3</sub>-soluble manganese concentration using HNO<sub>3</sub> solution (mg/kg dry soil) of Tivadar (T) and Gergelyiugornya (G) flood plain soil samples

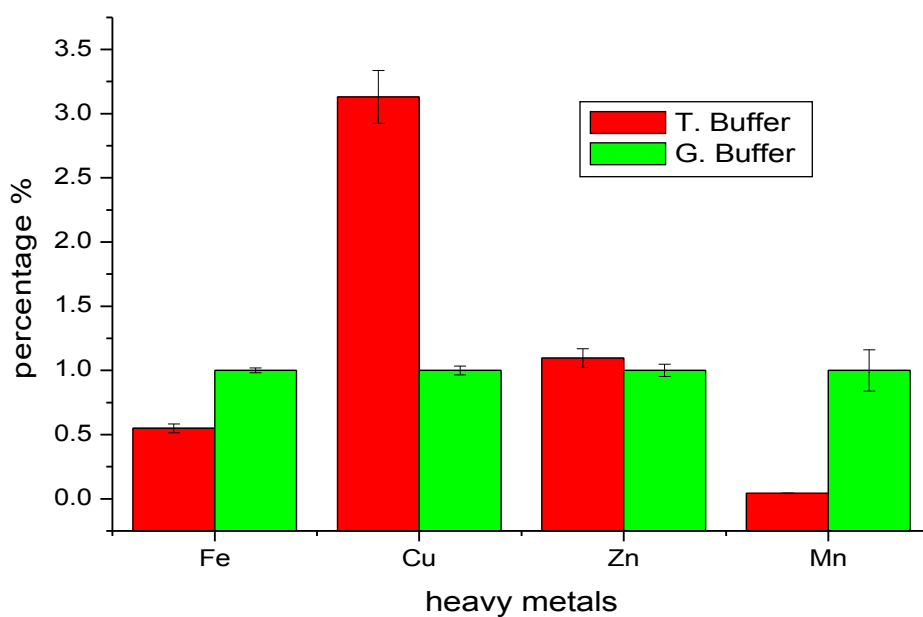


Figure 24. Buffer-soluble of heavy metal concentration in percentage of Tivadar (T) and Gergelyiugornya (G) flood plain soil samples

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.

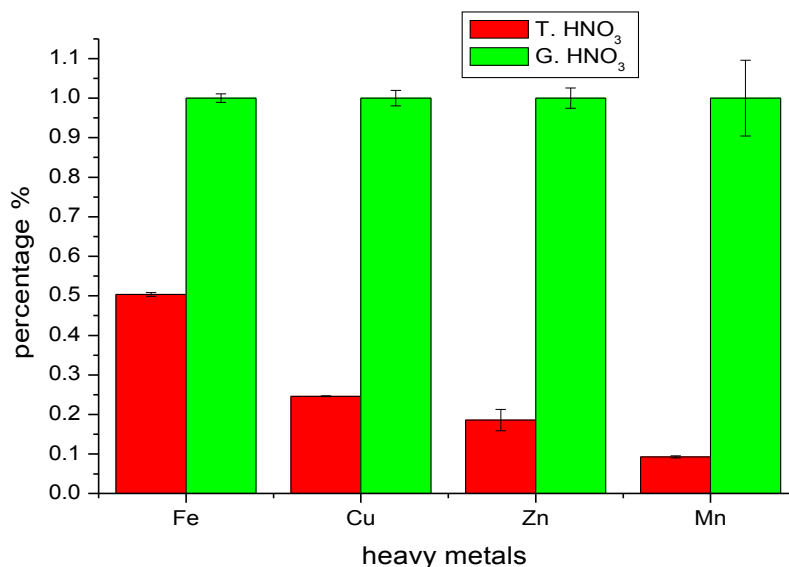


Figure 25. HNO<sub>3</sub>-soluble heavy metals concentrations in percentage of Tivadar (T) and Gergelyugornya (G) flood plain soil samples

#### 4.2.1. 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 Gergelyugornya 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<sub>3</sub>) all the measured heavy metal concentrations were an order of magnitude higher in Gergelyugornya 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.

### 4.3. Modelling of metals concentration

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

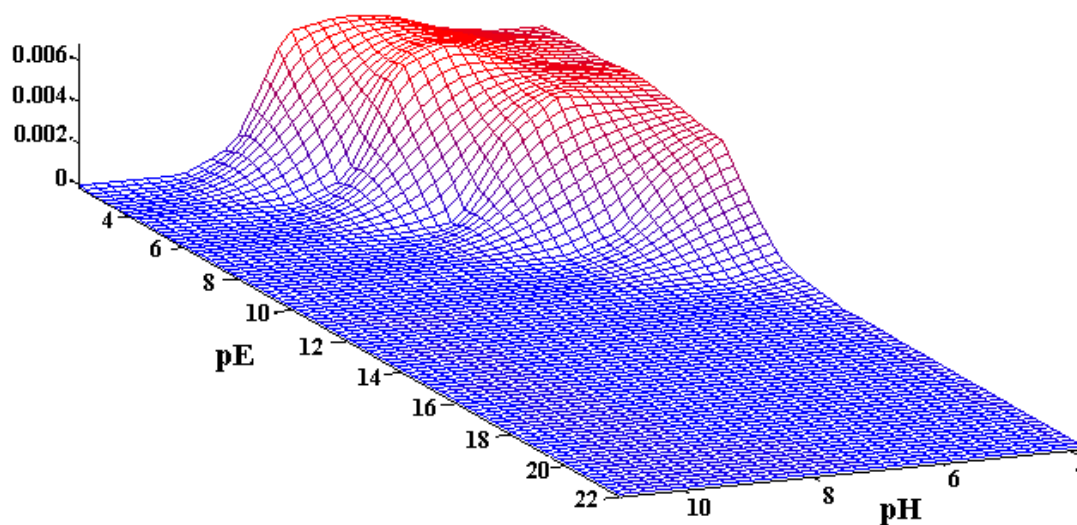


Figure 26. The model results of the basic running parameters of the Fe<sup>3+</sup>, where the X axis represents the pH and the Y axis represents the pE, while the Z axis represents Fe<sup>3+</sup> concentration (mol/dm<sup>3</sup>).

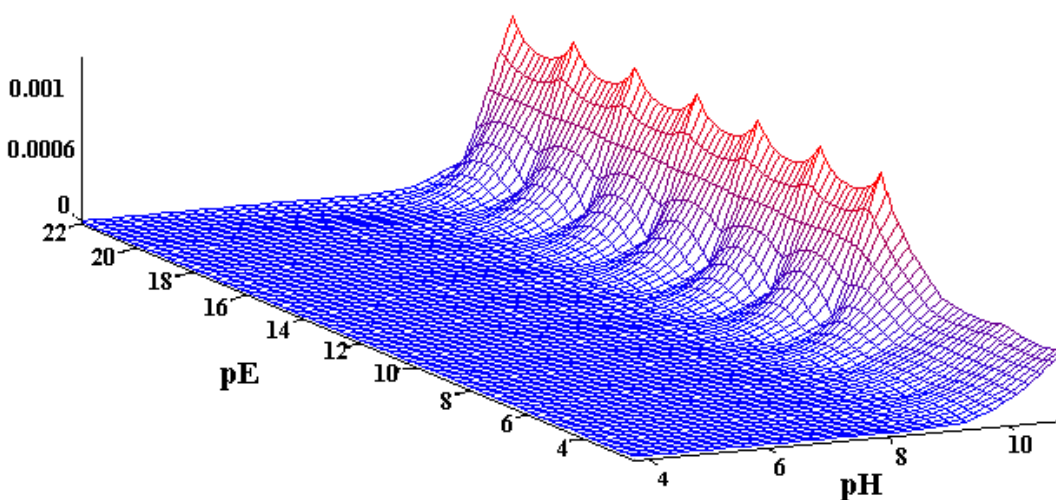


Figure 27. The model results of the basic running parameters of the Fe<sup>2+</sup>, where the X axis represents the pH and the Y axis represents the pE while the Z axis represents Fe<sup>2+</sup> concentration (mol/dm<sup>3</sup>).

The three-dimensional Figures (26-30) represent the concentrations of Fe, Cu, Mn and Zn as a function of pH and pE. It can be observed that Fe(III) (Figure 21) 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<sup>-8</sup> to 10<sup>-20</sup>M as pH increases from 4 to 8. The concentration of Fe(II) reached its peak at relatively higher pE and pH values (Figure 27). 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) (see Figure 26, Figure 27) 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 but the figure also shows that ferric iron concentration decreases with increasing pE. 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.

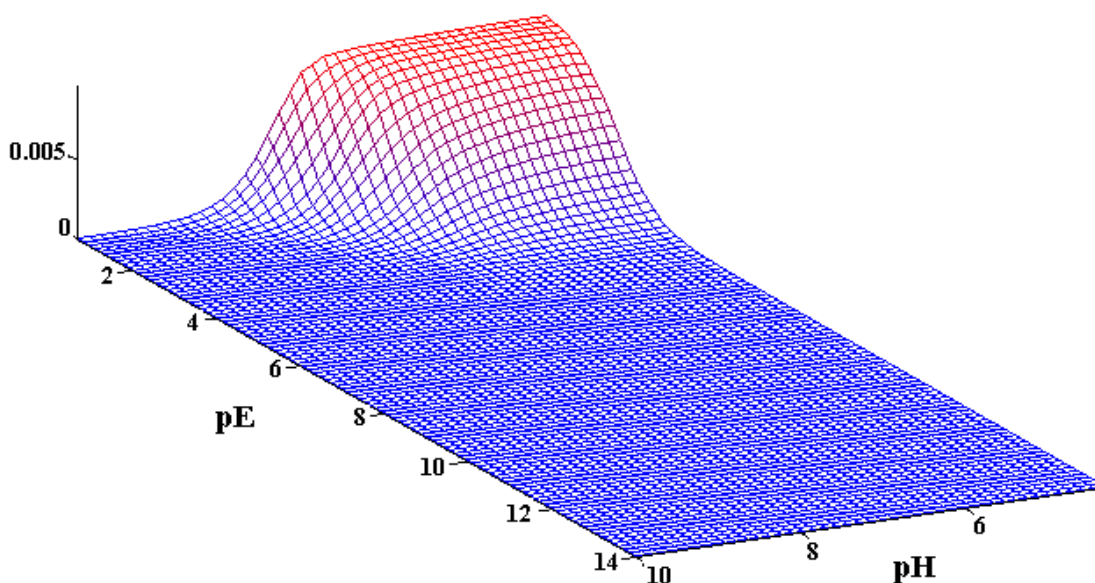


Figure 28. The model results of the basic running parameters of the  $\text{Cu}^{2+}$ , where the X axis represents the pH and the Y axis represents the pE while the Z axis represents  $\text{Cu}^{2+}$  concentration ( $\text{mol/dm}^3$ ).

In Figure 28 it can be seen that a decrease 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 behavior 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.

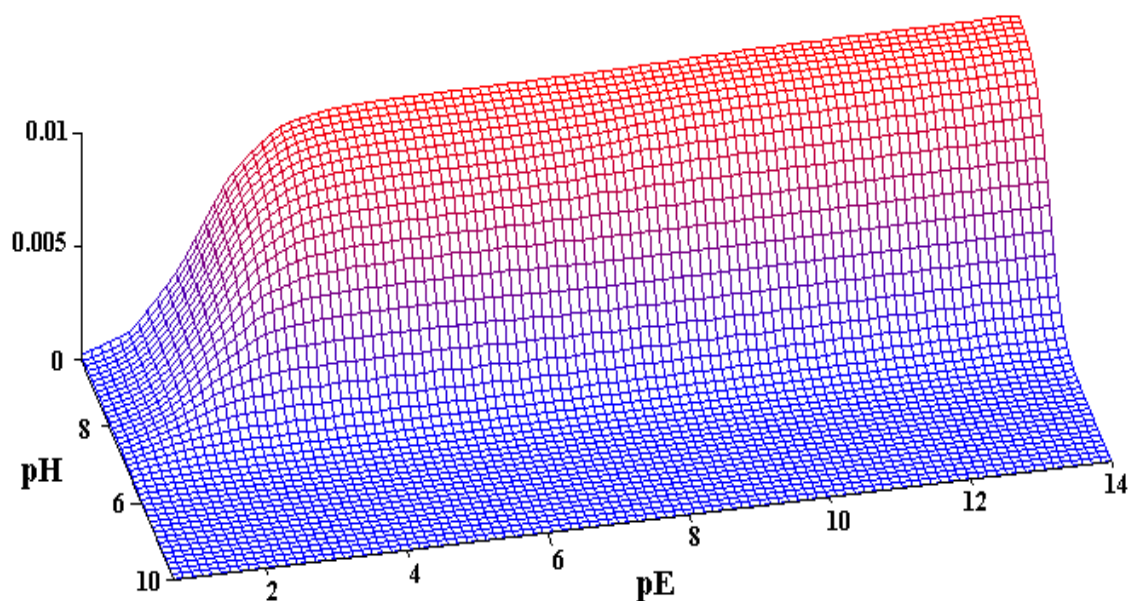


Figure 29. The model results of the basic running parameters of the  $Zn^{2+}$ , where the X axis represents the pE and the Y axis represents the pH while the Z axis represents  $Zn^{2+}$  concentration (mol/dm<sup>3</sup>).

The concentration of Zn is pE independent and increases at lower pH values (Figure 29). Our data is in agreement with GAO (2007) who 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.

As can be seen from Figure 30 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  $E_h$  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.

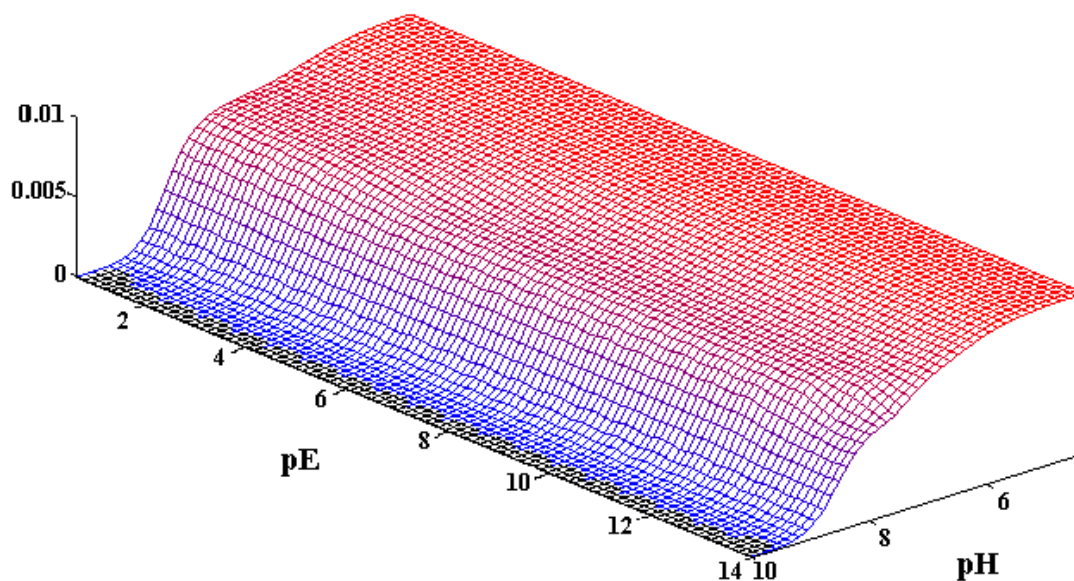


Figure 30. The model results of the basic running parameters of the Mn<sup>2+</sup>, where the X axis represents the pH and the Y axis represents the pE while the Z axis represents Mn<sup>2+</sup> concentration (mol/dm<sup>3</sup>).

#### 4.3.1.1. 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. It has already been shown (see Figure 26, Figure 27, Figure 28, Figure 29 and Figure 30) that both high pH and low pH values can increase the solubility of heavy metals. The model fit for Cu, Zn and Mn (see Figure 28, Figure 29 and Figure 30) was fairly good and this was in agreement with the literature. The poorer fits for FeIII, FeII (see Figure 26 and Figure 27) 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.

#### 4.3.2. Modelling in case of cyanide-affected system

In general the Figures (31-35) represent the different concentrations of metals with cyanide and without cyanide and show the effect of cyanide on heavy metal concentration as a function of pH and pE. According to Figure 31 we pointed out that 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 (Figure 31). MEEUSSEN et al. (1994, 1995) stated that iron–cyanide complexes are becoming more soluble with increasing soil pH and increasing redox potential.

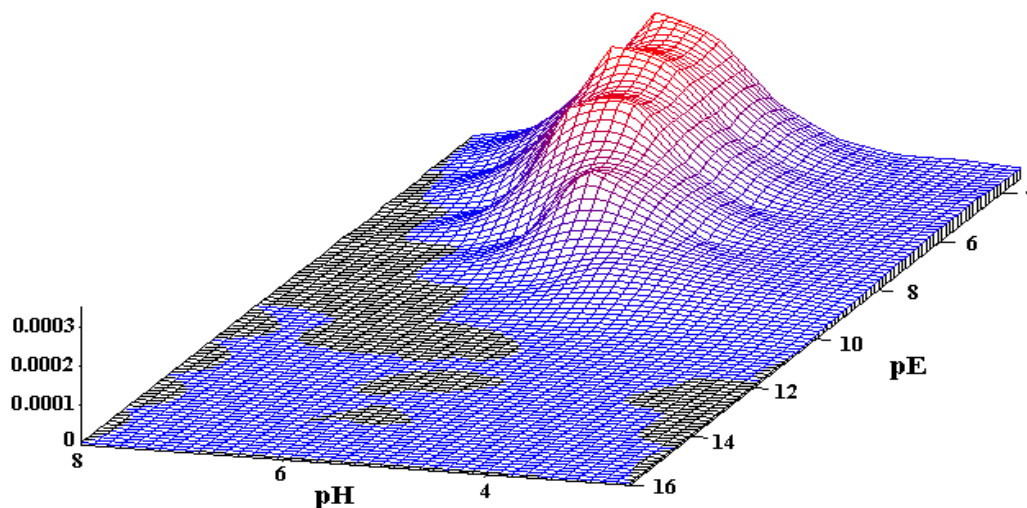


Figure 31. The cyanide effect - (variation between the  $\text{Fe}^{3+}$  concentrations of cyanide and non-cyanide polluted soils), where the X axis represents the pE and the Y axis represents the pH while the Z axis represents the different  $\text{Fe}^{3+}$  concentration (mol/dm<sup>3</sup>) between cyanide and non-cyanide

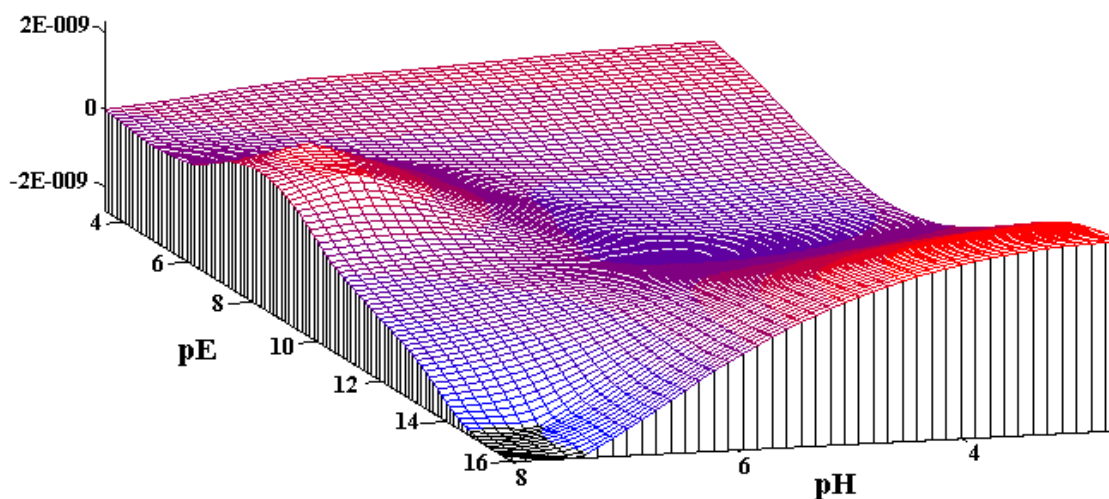


Figure 32. The cyanide effect - (variation between the  $\text{Fe}^{2+}$  concentrations of cyanide and non-cyanide polluted soils), where the X axis represents the pH and the Y axis represents the pE while the Z axis represents the difference in  $\text{Fe}^{2+}$  concentration (mol/dm<sup>3</sup>) between cyanide and non-cyanide

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 (see Figure 33) 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 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.

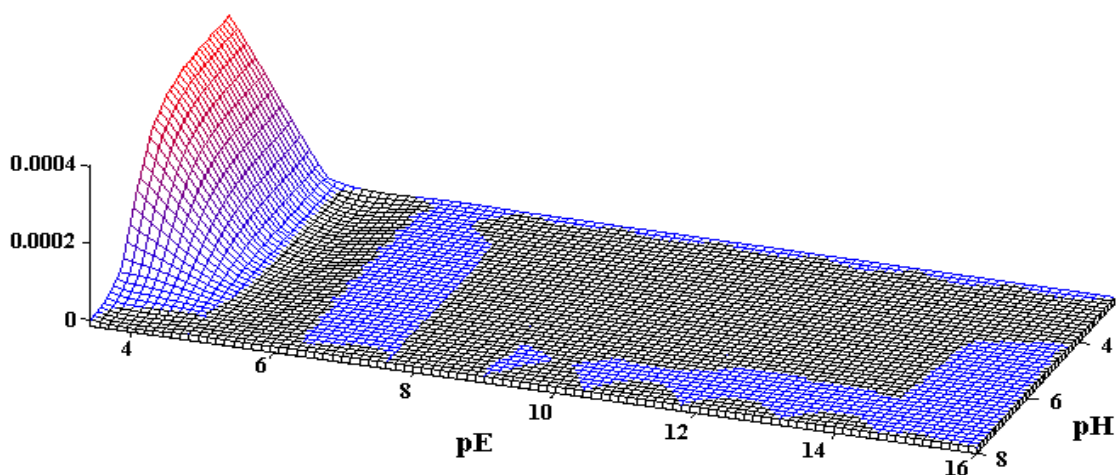


Figure 33. The cyanide effect - (variation between the  $\text{Cu}^{2+}$  concentrations of cyanide and non-cyanide polluted soils), where the X axis represents the pH and the Y axis represents the pE while the Z axis represents the difference in  $\text{Fe}^{2+}$  concentration ( $\text{mol}/\text{dm}^3$ ) between cyanide and non-cyanide

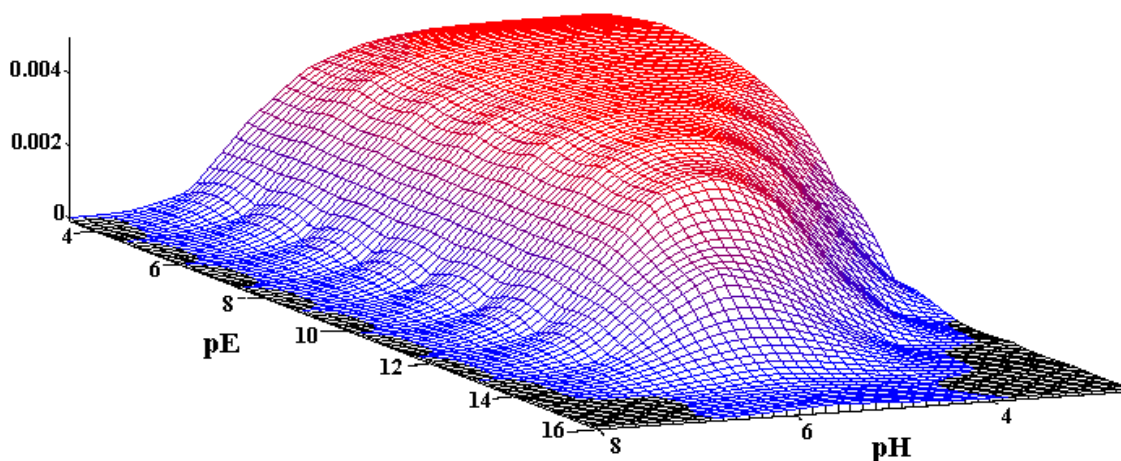


Figure 34. The cyanide effect - (variation between the  $\text{Zn}^{2+}$  concentrations of cyanide and non-cyanide polluted soils), where the X axis represents the pH and the Y axis represents the pE while the Z axis represents the variation of  $\text{Zn}^{2+}$  concentration ( $\text{mol}/\text{dm}^3$ ) between cyanide and non-cyanide.

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 (Figure 34). 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. Figure 35 shows high concentration at relatively high pH and high pE which 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.

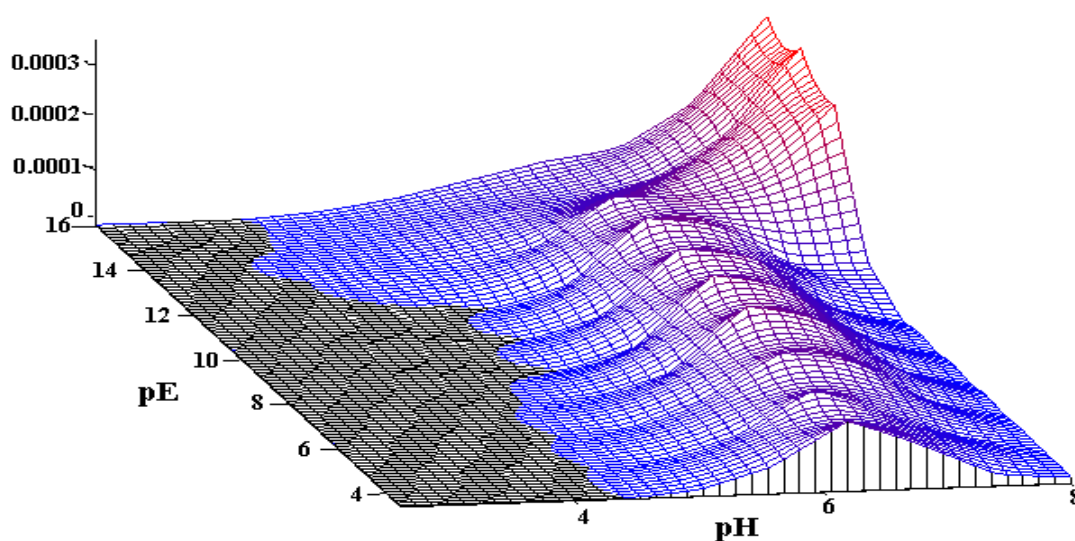


Figure 35. The cyanide effect - (variation between the  $Mn^{2+}$  concentrations of cyanide and non-cyanide polluted soils), where the X axis represents the pH and the Y axis represents the pE while the Z axis represents the variation of  $Mn^{2+}$  concentration ( $mol/dm^3$ ) between cyanide and non-cyanide

#### 4.3.2.1. 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 as shown in Figure 31 and Figure 33. The decreasing of pH when the pE is increasing causes a maximum concentration for ferrous iron as shown in Figure 32, while there is a decrease in the variation concentration by decreasing of the pH and pE for Zinc (Figure 34). It can be seen on Figure 35 that the variation in highest point at high pH and high pE values because of the complex solubility effect of cyanide ions. 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.

## 5. 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 (Gergelyugornya) and non-polluted (Tivadar) site. Aqua regia-extractable metals of both soils showed high and significant correlation for all examined metals compare to HNO<sub>3</sub> 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 Gergelyugornya 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.

## 6. 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<sub>3</sub> 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<sub>n</sub> 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 (Gergelyugornya) 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.

## 7. ÖSSZEFOGLALÁS

A Tisza partjáról származó különböző talajmintákat vizsgáltunk, az egyik minta a Szamos-torkolat felett Tivadarnál, míg a másik közvetlenül a torkolat alatt, Gergelyugornyánál lett véve. A legnagyobb eltérést a közvetlenül a meder széléből vett talajmintákban észleltük. A talajmintáknak megvizsgáltuk az oldható Fe, Mn, Cu és Zn tartalmát EDTA,  $\text{HNO}_3$  és királyvízes extrakcióval. A legnagyobb eltérést a közvetlenül a meder széléből vett talajmintákban észleltük kidolgoztunk egy változó idejű titrálásos módszert a talajminták redox pufferkapacitásának vizsgálatára, és ezzel mértük meg a talajmintáinkat.

A talajmintákkal érleléses kísérletet végeztünk annak kimutatására, hogy az esetleges hosszabb vízborítás hatására bekövetkező reduktív hatás hogyan befolyásolja az oldható nehézfém koncentrációkat. A kísérlet során a benedvesített talajmintákat hat héten keresztül levegőtől elzárva szobahőmérsékleten tároltuk, majd hetente mintát vettünk és mértük a nehézfém koncentrációkat. A cianid hatásának becslésére számítógépes modellezést végeztünk a MINTEQ programmal, mivel kísérleti adatok nagy mennyiségben nem állnak rendelkezésre különböző pH és pE értékeken kiszámítottuk az egyensúlyi nehézfém koncentrációkat cianid jelenlétében és anélkül.

A vizsgált talajminták redox pufferképességének vizsgálata során azt találtuk, hogy a minta redox potenciálja jelentős mértékben függ a mérés idejétől, vagyis a redox folyamatok kis reakciósebességei jelentős mértékben befolyásolták a mért eredményeket. A növekvő várakozási idők az adagolások között egyértelműen nagyobb értékeket adtak (vagyis növelték az oxidációs és csökkentették a redukációs pufferkapacitás értékeket). Matematikailag vizsgálva a kinetikai összefüggést az oxidációs esetben lineáris, míg a redukációs irányban exponenciális függvénnyel lehetett legjobban leírni a folyamatot. Az adagolások közötti kb öt perces adagolási várakozási időnél a két érték közel egyenlő volt. A két egymáshoz közeli szennyezett (5. minta) és szennyezetlen (3. minta) redox tulajdonságait összevetve, szignifikáns különbséget találtunk az oxidációs pufferkapacitás értékeiben. Ennek értéke a szennyezett mintában volt nagyobb, különösen a hosszabb idejű, egyensúlyi rendszerhez közelebbi vizsgálatoknál. A különböző sebességű redukációs pufferkapacitás értékek nagyon jól korrelálnak egymással, és a meredekség közel 1. Ez azt jelenti, hogy redukció szempontjából a két talajminta nem különbözik egymástól jelentősen. Ez annak lehet a következménye, hogy ebben a mintában nagyobb mennyiségű, redukált állapotú anyag, pl. nehézfém található. Ez a feltevés azzal is alátámasztható, hogy megvizsgálva az adott minták oldható vasII tartalmát, azok szintén szignifikánsan különböznek és a pufferkapacitással azonos tendenciákat mutatnak.

Különböző extrakciós módszerekkel kivont Fe, Mn, Cu és Zn koncentrációkat megmérve minden esetben szignifikánsan nagyobb koncentráció értékeket kaptunk a Szamos torkolata alatti, vagyis szennyezett mintákban, mint a torkolat feletti szennyezetlen mintákban. A réz és cink esetében a szennyezett minták koncentrációja a szennyezett mintában gyakorlatilag nem függött a kivonószertől, így feltételezhetjük, hogy itt nagyon lazán kötött, könnyen mobilizálható formában van a vizsgált nehézfém.

Levegőtől elzárt talajmintákkal inkubációs kísérleteket folytattunk annak eldöntésére, hogy a redukció hogyan hat a vizsgált nehézfémek oldhatóságára. Azonban a várt folyamatosan növekvő koncentráció értékek helyett, kb. 15 nap elteltével kaptunk maximális koncentrációt. Ezután újra csökkenés következett be az oldható nehézfémek koncentrációjában. Ezt az eredményt egyszerű kémiai jelenségekkel nem tudtuk megmagyarázni, valószínűleg mikrobiológiai folyamatok állnak a jelenség hátterében. Termodinamikai egyensúlyokon alapuló számítógépes modellezéssel és a kapott koncentrációértékek 3D ábrázolásával megvizsgáltuk a pH és pE hatását a vizsgált nehézfémek oldhatóságára a talajoldatban, illetve azt, hogy a feltételesen hozzáadott cianid ion miképpen befolyásolja ezeket az értékeket. A cianid nélkül futtatott modellek eredményei az irodalomban leírt értékekkel összhangban vannak, ezzel ellenőriztük a modell alkalmazhatóságát. A hozzáadott cianid ion hatására megfigyelve a koncentráció-változást, vagyis a két érték különbségét, már olyan új eredményt kaptunk, amely a szakirodalomban nem szerepel, és tájékoztató jelleggel mindenképpen használható a cianid szennyezés hatásának becslésére a talajoldat nehézfém koncentrációjára.

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