



SZENT ISTVÁN UNIVERSITY  
DOCTORAL SCHOOL OF ENVIRONMENTAL SCIENCES

**Adsorption of the cations of nutrients and  
toxic elements on soils**

THESES OF PH.D. DISSERTATION

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## Background of the research, objectives

The role of soils in the adsorption of elements and compounds is essential, both from the point of view of potentially toxic elements (essential microelements), and the toxic elements, since they regulate their mobility and bioavailability in the soil. This is one of the most important ecosystem services offered by soils (Alloway, 2013).

The sorptional behavior of essential microelements (e.g. Cu, Zn) and toxic elements (e.g. Cd, Pb) greatly differ in soils, it is a well-studied research phenomenon. They differ physiologically greatly from each other, thus it is essential to understand their mobility in soils. In order to understand their mobility, research carried out in real environmental situations raises ethical questions concerning financial and other environmental issues. Thus, our knowledge is mainly based on environmental pollutions, catastrophes and laboratory experimental studies.

The adsorption of the above mentioned cations can be strongly influenced by the soil organic matter content. Biochars applied to amend soil organic matter content and to improve soil condition, are nowadays in the focus of research. These biochars are basically pyrolyzed biomass with very high organic matter content. Long-term experimental data (about 100 years) are not available for science regarding their life-time and effectivity, thus, the research is based on examining the sites of historically documented forest fires.

Models used for describing the movement of elements are usually based on boundary conditions that are far away from real environmental circumstances, thus their justification are strongly doubted in scientific literature. The question arises, however, whether we need to insist on the existence of boundary conditions, or we should accept the empirical models that describe their movement in the soil. It was justified in several studies throughout the years, that by these empirical models sufficient results can be obtained about the sorptional behavior of a given element, even in a complicated, multiple-phased system, like the soil.

*My objectives were the following:*

- to examine the sorptional behavior of the cations of essential microelements (*Cu, Zn, Co*), and toxic elements (*Cd, Pb*) in different soils as many cases as possible. Furthermore, to find the relationship among the presence of amendments (*glycerol as biodiesel by-product, biochar, bonechar*) that has significant effect on soil properties (*pH, preliminary load*) and the change of adsorptional properties caused by them.
- I also want to examine the fitting of the most frequently used models and isotherms (*distribution coefficient, Freundlich isotherm, Langmuir isotherm, Sips isotherm*) and their applicability on the above mentioned sorption processes.

## Materials and Methods

Soils with pH(H<sub>2</sub>O) less than 7.0 were used for my experiences as model soils where there was no detectable CaCO<sub>3</sub>. The top 20 cm of the following *brown forest soils* were sampled:

**Trizs:** soil samples under wood burning piles with different ages (80, 35 and 25 years old) were collected under forest vegetation. Based on the data available about the sites the area is undisturbed since the end of the wood burning activity (these sites will be referred to as: control; 80; 35; and 25 year-old piles)

**Gödöllő-Szárítópuszta:** the topsoil (0-20 cm) was taken from Szent István University Experimental Farm. The vegetation was acacia.

**Putnok:** there are no GPS data available about the site, however, I determined the physical and chemical parameters of the soil.

The following soil amendments were given to the soil samples during incubation:

**Glycerol produced as a by-product during biodiesel production:** there are no available data about the technological background of the material, however, its main components are known (83% glycerol, pH about 10).

**Solid pirolyzed end-products:** biochar and bonechar that were produced in the frame of the EU FP7 REFERTIL 289785 Project. The main components of these materials are known.

During soil incubation, model soil samples were prepared (< 2mm) for laboratory experiments. Different amendments were given: freshly pirolyzed organic matter (biochar, bonechar) and glycerol by-product were added to the soil samples with different concentrations of Zn [in the form of HCl and Zn<sup>2+</sup> Zn(NO<sub>3</sub>)<sub>2</sub>]. The mixtures were incubated at moisture level set at field capacity and at 20±2°C temperature. After finishing the incubation, the samples were dried and sieved (2mm). The treatments of the experiment can be seen in *Table 1*.

**Table 1.** Treatments set for the incubation

<b>Change in pH and the effect of pre-treatment on the Zn adsorption capacity of soil</b>										
<i>Soil: Putnok; Amendments: HCl (pH); Zn(NO<sub>3</sub>)<sub>2</sub> (0; 500; 2500 mgZn/kg); Incubation time: 2 weeks</i>										
pH4/0Zn	pH4/500Zn	pH4/2500Zn	pH5/0Zn	pH5/500Zn	pH5/2500Zn	pH6/0Zn	pH6/500Zn	pH6/2500Zn		
<b>Short-term effect of biochar and bonechar on the Cu and Zn adsorption ability of the soil</b>										
<i>Soil: Gödöllő-Szárítópuszta; Amendment: biochar and bonechar (1; 2,5; 5; 10%); Incubation time: 4 weeks</i>										
Control	biochar	F1%	F2,5%	F5%	F10%	bonechar	Cs1%	Cs2,5%	Cs5%	Cs10%
<b>Effect of glycerol by-product on the Zn adsorption activity of soil</b>										
<i>Soil: Gödöllő-Szárítópuszta; Amendment: glycerol by-product (1%); glycerol compound (VSZ) a.r. (1%); Zn(NO<sub>3</sub>)<sub>2</sub> (500mgZn/kg); Incubation time: 4 weeks; 8 weeks*</i>										
Control	gly							Zn4		gly <sub>vsz</sub>

The **adsorption experiments** were carried out in all cases by batch technique (2 g soil : 20 mL shaking solution, 24 hours of shaking). For the preparation of the initial solutions (shaking solutions) in all cases, the nitrate salts of the given cations (Zn<sup>2+</sup>, Cu<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>) were used in a concentration range of 0-1000 mg/dm<sup>3</sup>.

By knowing the concentration of the shaking solution (c<sub>r</sub>) and the equilibrium solution (c<sub>e</sub>), applying the ratio of adsorbent weight to solution (1g:10cm<sup>3</sup>), the adsorbed amount (q) was calculated by the following equation:

$$q = \frac{V}{m} (c_r - c_e)$$

The concentration of the equilibrium solutions were determined by Perkin Elmer 303 AA atom adsorption spectrophotometer and Shimadzu ICPE-9000 ICP-OES equipment. Freundlich-, Langmuir- and Sips isotherms were fitted onto the experimental points.

During the sorption experiment, the change in the pH and the acidity of the solution was determined potentiometrically, and by the titration with NaOH of the equilibrium solutions.

For the **desorption experiments** the solid phase obtained by the adsorption experiment was used. The solid phase was shaken with 20 cm<sup>3</sup> background solution (0,01M NaNO<sub>3</sub>) for 24 hours at 22±1°C temperature, then centrifuging and filtering the solution, the cation concentration was measured in the solution phase. This desorption step was repeated maximum six times on each sample. Langmuir isotherm was fitted onto the results obtained for the desorption experiment

During the **hot water extraction** method, 10 x 100 cm<sup>3</sup> amount was collected from the 30 g of samples by the hot water percolation (HWP) method (Füleky and Czinkota, 1993). The cation concentration of the fractions was determined by Perkin Elmer 303 AA Atom absorption Spectrophotometer. The elapsed time was also measured during the hot water extraction. First-order kinetic curve was fitted onto the experimental points.

$$y = A_d(1 - e^{-k_d t})$$

*y* = the amount of desorbed Zn (mg/kg)  
*A<sub>d</sub>* = maximum amount of Zn that can be extracted (mg/kg)  
*k<sub>d</sub>* = kinetic constant (1/s)  
*t* = time (s)

To describe the extraction, a modified version of the first-order kinetic equation was also used, in which the time factor was multiplied by the known constant flow velocity, and the volume of the extracted matter was also used as kinetic parameter (*h* = *v* · *t*) (Czinkota, 1994). In this case the equation can be written in the following form:

$$y = A_d(1 - e^{-k_d h})$$

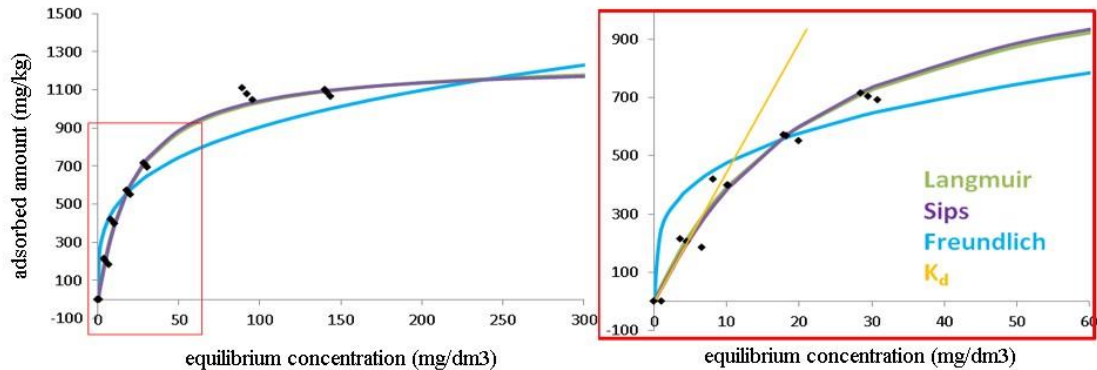
*y* = the amount of desorbed Zn (mg/kg)  
*A<sub>d</sub>* = maximum amount of Zn that can be desorbed (mg/kg)  
*k<sub>d</sub>* = kinetic constant (1/cm<sup>3</sup>)  
*h* = amount of liquid that flew through (cm<sup>3</sup>)

The soil examinations and the experiments were set minimum in three repetitions in all cases. The fitting of the isotherms and the kinetic curves were carried out by the least square method. My conclusions were drawn after the fitting and the **statistical analyses** (examination of the residuum of the measured values and the values calculated by the model, LSD<sub>5%</sub> and Tukey pair test) of the isotherm parameters. During drawing the conclusion, attention was paid to the confidence intervals when the fitting was carried out and the significance level (p<0,05).

In case of linear correlation, Pearson correlation was carried out, during which it can be proved at p < 0,05 level by using t-probe, whether the value of the correlation coefficient (R) is far away from zero.

## Results and Evaluations

The most frequently used models to describe the adsorption on soils are the Henry- (distribution coefficient) ( $K_d$ ), the Freundlich- and the Langmuir-isotherms (*Figure 1*). All these models can be applied, however, during drawing the conclusions attention must be paid to the physical and chemical processes in the background of the model.



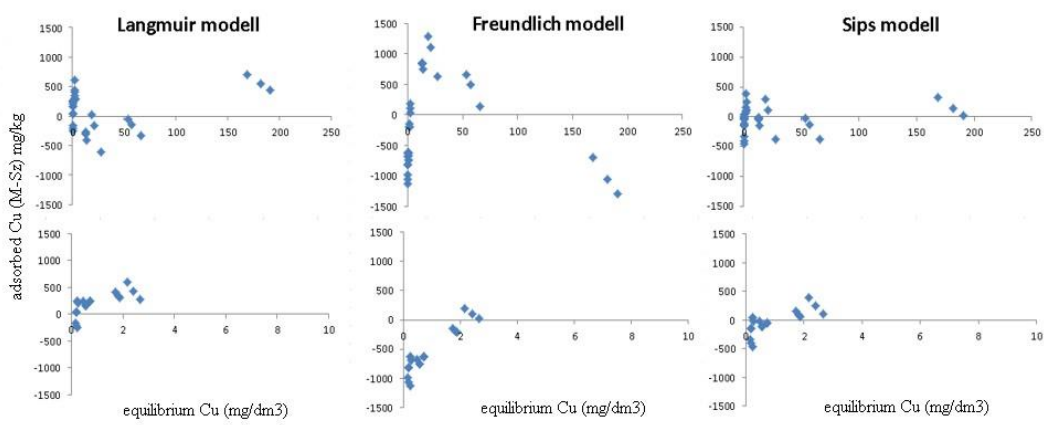
**Figure 1.** Fitting of the Henry ( $K_d$ ), Freundlich-, Langmuir- and the Sips-isotherms onto the experimental points at low and high equilibrium concentrations in case of brown forest soils. ( $OM_a < OM_b$ ).  
(Adsorption of Zn on control soil - Trizs)

The  $K_d$  values can give some information about the affinity of the soil or the adsorbent towards the adsorbate. In case of competitive adsorption, it makes it easier to set the order of adsorption at a certain point of the sorption process, thus, mistakes can be avoided during the fitting procedure. In case of the competitive sorption with five elements in the soil-biochar systems, the following order can be made based on the  $K_d$  values:  $Pb \gg Cu \gg Cd \geq Zn \geq Co$ .

The  $K_d$  values give opportunity to examine correlations, by which relationship can be shown between the sorption capacity of a soil for a certain element and some of its property. Strong correlation ( $R^2 > 0,88$ ) was found during the sorption experiment between the pH in the equilibrium system and the logarithm of the  $K_d$  value. The applicability of these correlations, however, need to be handled carefully since the logarithmic transformation causes significant distortions in the measured values, thus, their application can lead us to draw false conclusions. It does not give enough information whether the soil is saturated or unsaturated with a certain adsorbate. In order to draw conclusions regarding this, an adsorption series can be set, and by the application of **adsorption isotherms**, more exact and useful conclusions can be drawn.

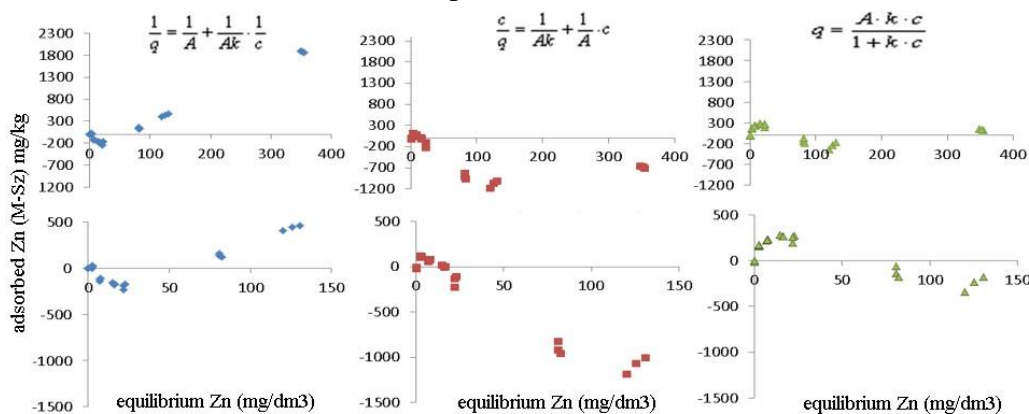
Regarding the fitting of the isotherm models, the  $R^2$  value is very informative, it characterizes the whole function, but it does not show the characteristics of the function at certain points of the whole concentration range. It is suggested to examine the retention properties of the soils in a wider range than the natural systems, in order to draw conclusions.

Based on the residuum examinations (*Figure 2*) of the applied models, it can be stated that in the case of the applied adsorbates, the Freundlich-isotherm did not show better fitting than the Langmuir-isotherm throughout the whole concentration range of the sorption experiment. The smallest difference between the measured and calculated values could be observed in all cases in the middle part of the saturation curve, however, the Freundlich-isotherm overestimates; the Langmuir-isotherm underestimates the capacity for the adsorbent in low concentrations. This statement is probably true even if we do not ignore the Gaussian error propagation, which causes problems when we calculate the adsorbed amount.



**Figure 2.** The observed differences between the measured (M) and calculated (Sz) amount of adsorbed Cu in case of the 25 year-old soil-biochar system, as a function of the Cu concentration (mg/dm<sup>3</sup>).

The best fit was obtained by the Sips (Langmuir-Freundlich)-isotherm for my experimental data. In low concentration range, it is closer to Freundlich-isotherm, based on the shape of the curve, the heterogeneity between the adsorption sites can be more observed. However, after the saturation of the adsorption sites which have larger energy, the adsorption sites are energetically closer to each other, thus the curve reaches a saturation value similar to the Langmuir-isotherm, which more or less equals to the maximum amount of adsorbed quantity ( $q_{max}$ ). In almost all cases, the Sips-isotherm showed the best  $R^2$  values, and the smallest residuum values in the extended concentration range of the sorption process. It can be concluded from the better fit of the Sips-model that by its application it is easier to estimate the buffering capacity of the adsorbate during the adsorption process, which is an informative parameter of the well-fitting model. It is important to note, however, that the Langmuir-isotherm, which is easier to handle and has less parameters, it's fitting is still quite close to Sips-isotherm, thus, with careful application, it can give important information when the sorption behavior of different adsorbents are compared.



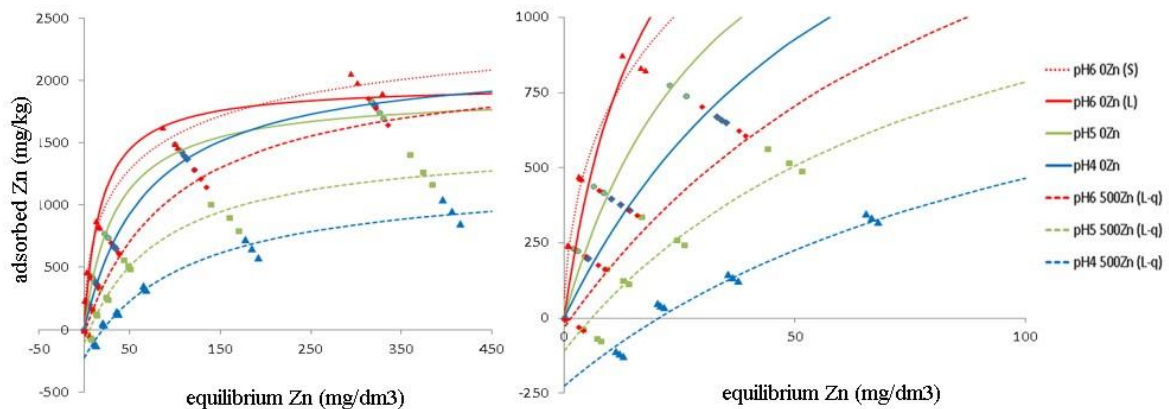
**Figure 3.** Residuums (the difference between the amount of adsorbed Zn in case of the measured /“M”/ and the calculated values /“Sz”/ by the linear, and non-linear Langmuir-model) in case of the 35 year-old soil-biochar system as a function of Zn concentration

Based on the examination of the different shapes of the **linearized Langmuir-isotherm** (Figure 3), that is frequently used in scientific literature, we can state that the distortion of the non-linear form is generally smaller. The parameters of function obtained from the linear fitting in some cases extremely overestimate the adsorption capacity of the adsorbent, and furthermore, they differ from each other. This phenomenon is even more pronounced, if we have greater adsorption capacity (e.g. soils with high organic matter content). In case of real environmental problem, this can mean very high risk.



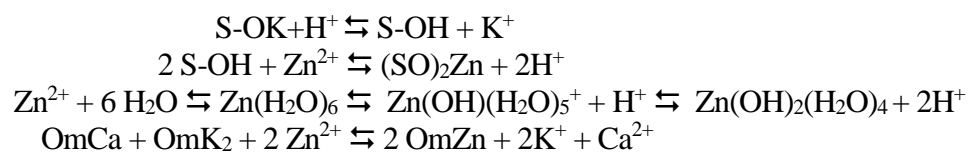
The sorption properties of soils can be influenced by several other circumstances. Based on the artificial influence of **pH** (pH6→pH5 and pH6→pH4) and **preliminary Zn load** (500 and 2500 mg/kg Zn) we can state the following about a brown forest soil (*Figure 4*):

- the change caused in soil pH and the preliminary Zn load affected the sorption properties of the soil,
- the process can be well described within the examined concentration range by the help of Langmuir, and Sips-isotherms ( $R^2 > 0,9342$ ),
- based on the fitted isotherms, we can state that the Zn adsorption ability of the examined brown forest soil (Putnok, Hungary) was not influenced significantly by the pH decrease from pH 6 to pH 4, which means that the soil can buffer such degree of soil acidification,
- the decrease of soil pH only changed the buffering capacity of soil, i.e. it decreased it.
- the effect of the preliminary Zn load on the sorption capacity of soils is stronger than the effect of pH change. If we do not change the soil pH on purpose, there is no significant decrease in the sorption capacity, and with minor preliminary Zn load (500 mg/kg), the same amount of Zn can be adsorbed on the soil as in case of the control. This is probably due to the fact that during the incubation time the Zn diffuses into the inner pores of the soil particles and gives more opportunity for further cation adsorption. The soil cannot buffer the above mentioned way the load that exceeds (2500mg/kg) the adsorption capacity of soils (~2000 mg/kg), thus, further Zn adsorption cannot be observed after the incubation time and the desorption of Zn will be dominant.
- the amount of hot water extracted Zn can be significant, it can even reach 50% of the adsorbed amount. In case the load is greater than the maximum adsorption capacity of the soil, the portion above the adsorption maximum can be easily mobilized.

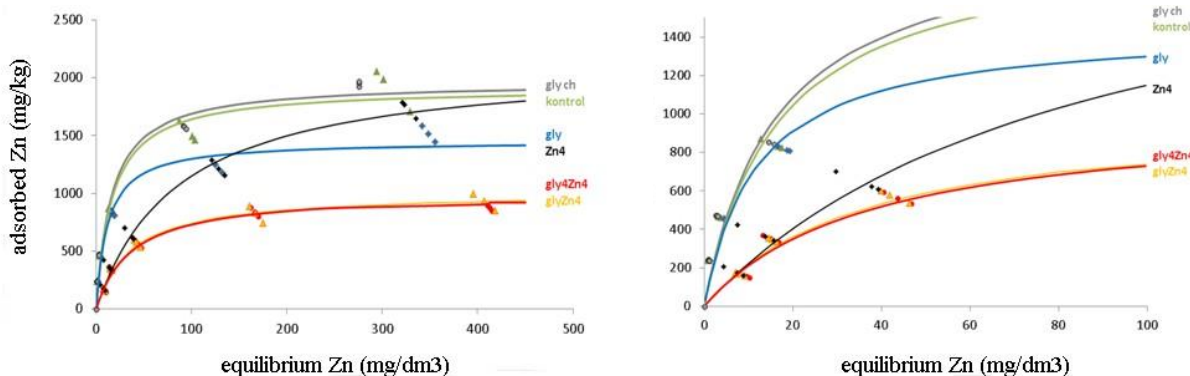


**Figure 4.** The effect of pH and the preliminary Zn load on the Zn adsorption capacity of soil

Under the circumstances of the experiment, the following processes can possibly take place on the active surfaces of the mineral (S) and organic macromolecules (Om) that are important for sorption:



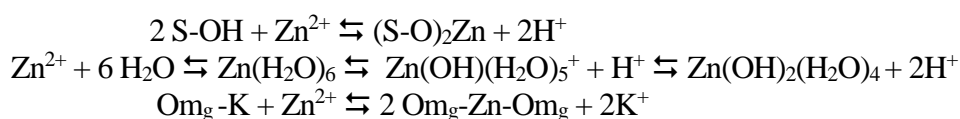
**Glycerol** is a valuable **by-product** of the biodiesel production with high macro-, and micronutrients, thus, it might be used for improving soil fertility. Due to its high water holding capacity, it can increase the water infiltration and water retention capacity of soils (Czinkota, 2007). It is an easily available carbon source for soil microorganisms, thus, it can increase the soil organic matter content in the long run when it is incorporated into the soil. When added to the soil (1%, 4/8 weeks of incubation), it influences the sorption properties of the soil by its alkaline pH (pH~10) and its high macro-, and microelement content (*Figure 5*).



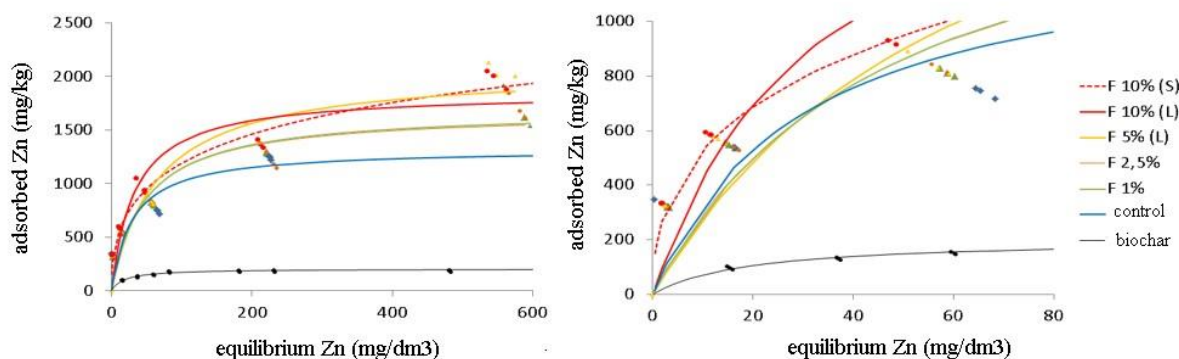
**Figure 5.** The effect of glycerol by-product on the Zn adsorption capacity of a brown forest soil (Gödöllő-Szárítópuszta) applying Langmuir- (L) isotherm model

- The glycerol by-product slightly decreased the Zn adsorption capacity of soil. The explanation for the slight decrease in the affinity of the soil towards Zn, can be explained by the significant amount of cations in glycerol. These cations are, on one hand, in competition with Zn during adsorption, on the other hand, the Zn ions and the anions in the by-product form complexes, which can overshadow the positive charge of Zn and thus decrease its adsorption.
- The effect of the preliminary Zn load on the adsorption capacity of the soil is more pronounced than the effect of the by-product.
- The glycerol by-product had an effect on the water infiltration capacity, it decreased it.
- The hot water extractable Zn concentration of the samples that had preliminary Zn load did not have significant effect of the incubation by the glycerol by-product. We can further state that the amount of hot water extractable Zn (<40 mg/kg) was a lot smaller than the preliminary Zn load (500 mg/kg).
- The glycerol by-product with its alkaline pH does not cause significant change in soil pH when it is added to the soil at 1%, however, it has positive effect on the soil buffering capacity. Based on these, it can be stated that it has positive effect on acidic soils.
- Based on further examinations (e.g. on arable land), glycerol applied in small amount (maximum 1%) can be very good soil improver due to its high macro-, and microelement, and its organic matter content.

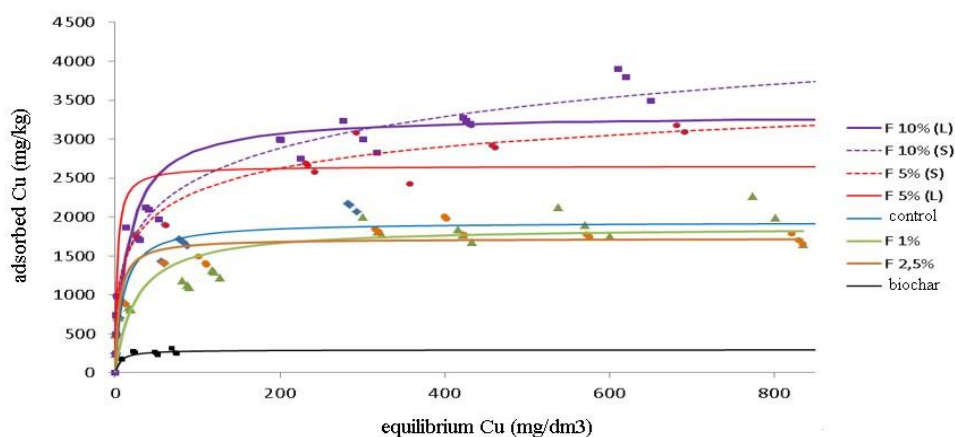
The following processes can be behind the Zn adsorption experiment on samples incubated with glycerol by-product (S-OH) that has significant amount of cations ( $K_g^+$ ,  $Ca_g^{2+}$ ,  $Na_g^+$ ,  $Mg_g^{2+}$ ) and organic molecules ( $Om_g^-$ ).



The effect of **freshly produced biochar** (Figures 6 and 7) and **bonechar** (Figures 8 and 9) mixed into the soil in 1; 2,5; 5; 10% (four weeks of incubation) on the Zn and Cu sorption properties of soils can be concluded the following way:



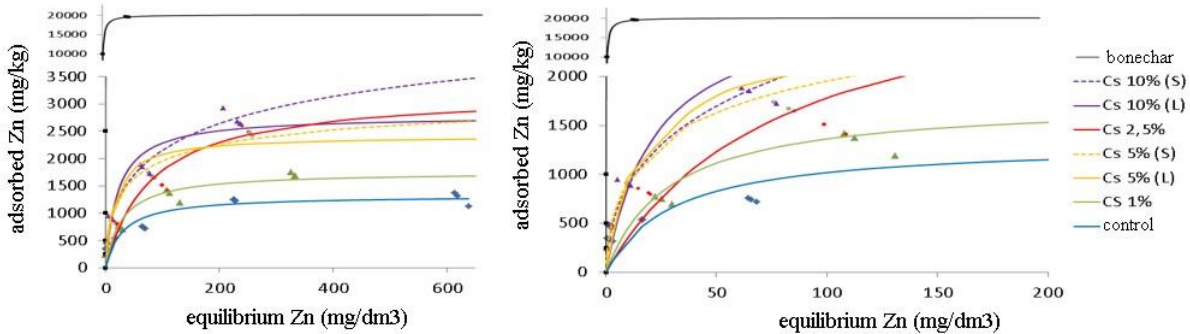
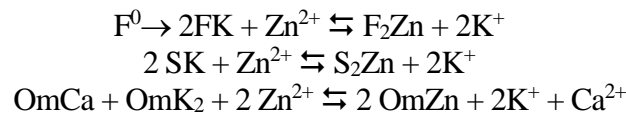
**Figure 6.** The effect of biochar on the Zn adsorption of soil (Gödöllő-Szárítópuszta) applying Langmuir- (L) and Sips- (S) isotherm models



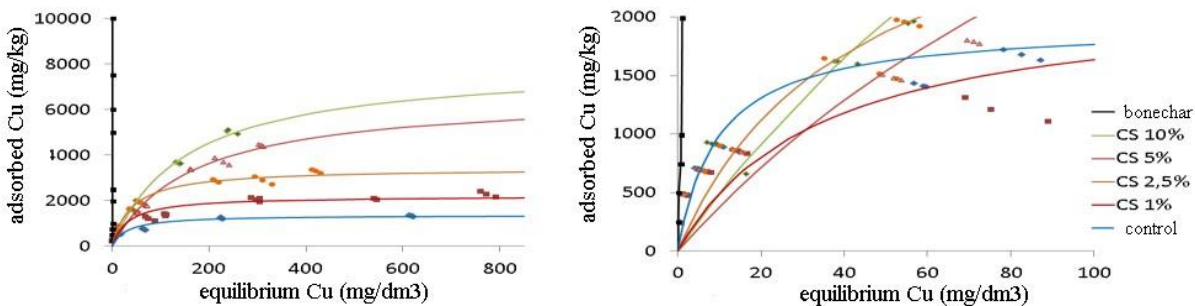
**Figure 7.** The effect of biochar on the Cu adsorption of soil (Gödöllő-Szárítópuszta) applying Langmuir- (L) and Sips- (S) isotherm models

- The applied isotherm models (Freundlich, Langmuir, Sips) made the understanding of the phenomenon possible together.
- More Cu was adsorbed on the samples than Zn in all cases. Copper is one of the easiest adsorbing “heavy metal” in soils (Chen et al. 1992, Stevenson, 1982), it forms stabile complex with the humus components (Schnitzer 1969, Harter 1979), and also with the mineral parts (i.e. vermiculite) of the soil (Covelo et al. 2007).
- When biochar was mixed into the soil in 1 and 2,5%, due to the effect of incubation in the soil, it did not increase (or just slightly increased) the Cu and Zn adsorption of the soil. However, when biochar was mixed into the soil in 5 or 10%, they significantly ( $p < 0,05$ ) increased it. In case of Zn adsorption, there was no significant difference between the 5 and 10% dose, however, for Cu, it was significantly different. The reason for this might be that the chemical structure of the freshly produced biochar changed in the soil. Regarding the chemical structure of biochar, it mainly depends on the circumstances of pyrolysis and also the applied raw materials. The surface area of the freshly produced biochar is great, however, in case of cation exchange capacity, the amount of specific exchange sites is more significant than the surface area (Leyva-Ramos et al., 2002). A good example for this is the active carbon, which is produced by the activation and oxidation of the surface of the pyrolyzed organic matter (Ioannidou and Zabaniotou, 2007; Xiao and Thomas, 2004). Microorganisms carry out these surface oxidation processes in the soil, and as a result, the number of specific exchange sites increase, thus the adsorption capacity of carbon increases as well (Lehman 2009, Ladigina 2013).

The following ion exchange processes are probably behind the cation adsorption of soils with biochar amendments ( $F^0/F^-$ ) ( $S^-$  - mineral colloid;  $Om^{2-}$  - organic colloid):



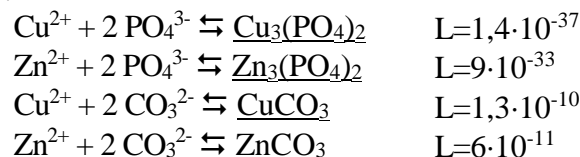
**Figure 8.** The effect of bonechar on the Zn adsorption capacity of soil (Gödöllő-Szárítópuszta) applying Langmuir- (L) and Sips- (S) isotherm models



**Figure 9.** The effect of bonechar on the Cu adsorption capacity of soil (Gödöllő-Szárítópuszta) applying Langmuir- (L) isotherm model

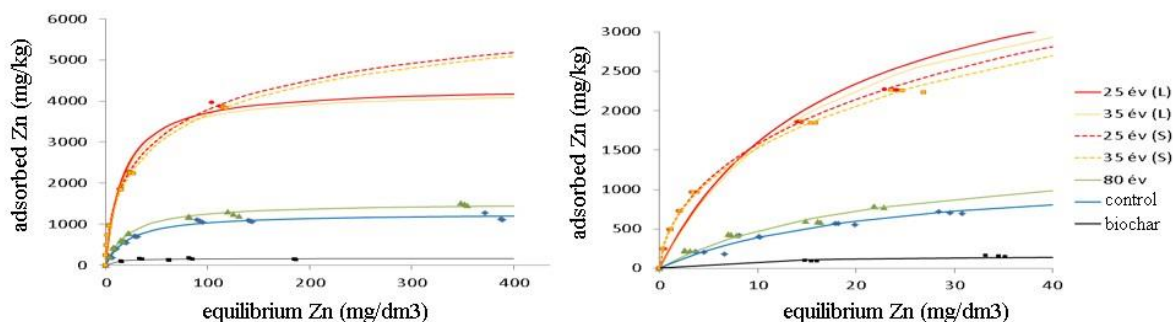
- The amount of adsorbed Cu and Zn (>10 000 mg/kg) by bonechar is significantly greater than the adsorption by biochar (200-300 mg/kg). The formed bond in case of the bonechar is probably an inner sphere, specific bond, due to its large phosphate and carbonate content. Attention must be paid to this phenomenon in case of nutrients (e.g. essential microelements), since these cations can go into solution in a more difficult way, than if they were electrostatically bond in an exchangeable form.
- The soil containing 2,5% bonechar can bond twice as much Zn and Cu than the control, acidic, brown forest soil. In case of 10% mixture, Zn adsorption does not change significantly, but Cu adsorption increases three-fold as compared to the control soil.
- It is important to point out that the steepness and the saturation values of the adsorption isotherms of soil samples that contain bonechar (even in case of sample Cs10%) are significantly lower compared to the clear bonechar. The reason for this might be that the cations that are originally in the soil can saturate the adsorption surfaces of the bonechar.

The following presumed precipitation processes are behind the cation adsorption of the soil with bonechar amendments, due to ion exchange processes, and also to the phosphates and carbonates present in the bonechar.

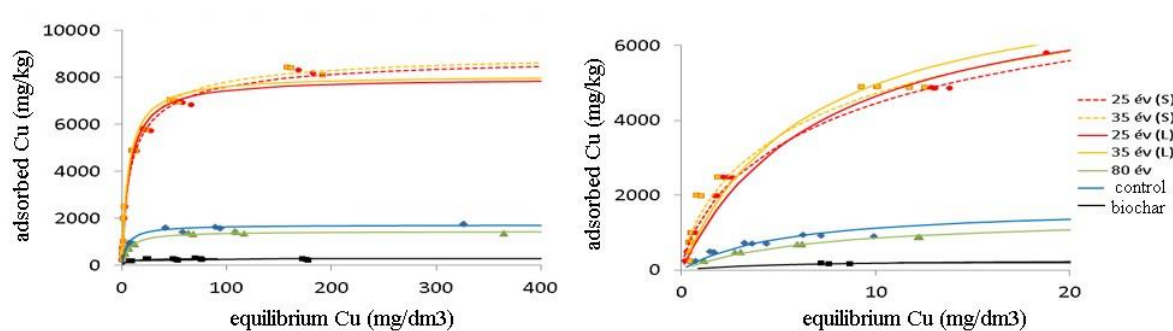




My results regarding the **soil-biochar systems** on wood burning sites (Trizs), where burning was officially carried out 25, 35 and 80 years ago. The sites have not been disturbed since then. The Zn (Figure 10) and Cu sorption (Figure 11) of these soils are presented below.

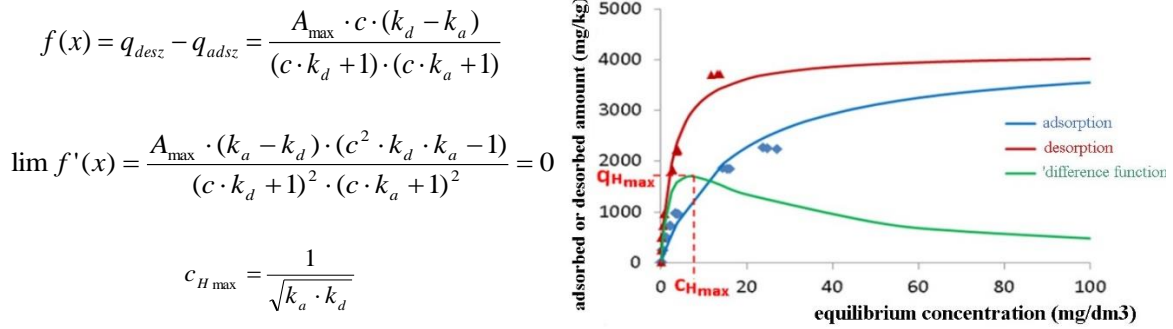


**Figure 10.** The long-term effect of biochar on the Zn adsorption capacity of a brown forest soil (Trizs) applying Langmuir- (L) and Sips- (S) isotherm models



**Figure 11.** The long-term effect of biochar on the Cu adsorption capacity of a brown forest soil (Trizs) applying Langmuir- (L) and Sips- (S) isotherm models

- The long-term presence of biochar in soil (25 and 35 years) significantly increased its Cu (four fold) and Zn (three fold) adsorption capacity.
- Based on the parameters of the applied sorption models ( $A_L$ ,  $A_S$  and  $k_F$ ), it can be stated that more Cu was adsorbed on the soil than Zn. Furthermore, the greater the difference between the adsorption of Zn and Cu, the greater the oxidizable organic matter content in soils (Karathanasis, 1999; Arias et al. 2006, Covelo et al., 2007, Sipos et al., 2008).
- After 80 years, there is no significant difference in the soil organic matter content, the Cu and Zn adsorption capacity of soils, compared to the control sites. However, the amount of the desorbed cations (mainly Cu) is significantly less. This phenomenon is probably due to the more developed soil organic matter (lower  $E_4/E_6$  ratio, higher HI and OI). The organic matter in the 80 year-old site probably has more developed structure, thus, it can provide stronger bonds for Cu by complex, and chelate bonds, as compared to the sites with organic matter that has lower molecular weight and less complex structure in the control soil.
- The correlation between the adsorption capacity and age of these different biochar sites was strong ( $R^2 > 0,9599$ ;  $p < 0,05$ ). Based on this correlation the calculated exhaustion time is less than 100 years. Thus, the pyrolyzed organic matter is not necessarily applicable to store  $CO_2$  in the soil for several years (Knicker, 2011).
- The positive effect of biochar on the structure, chemical and physical properties of soils is still detectable after 80 years.
- Thus, biochar, and also different pyrolyzed organic matter and carbon products are suitable in short-, and long-term to increase the Cu and Zn adsorption capacity of soils. Thus, these can be applied well in agricultural areas.

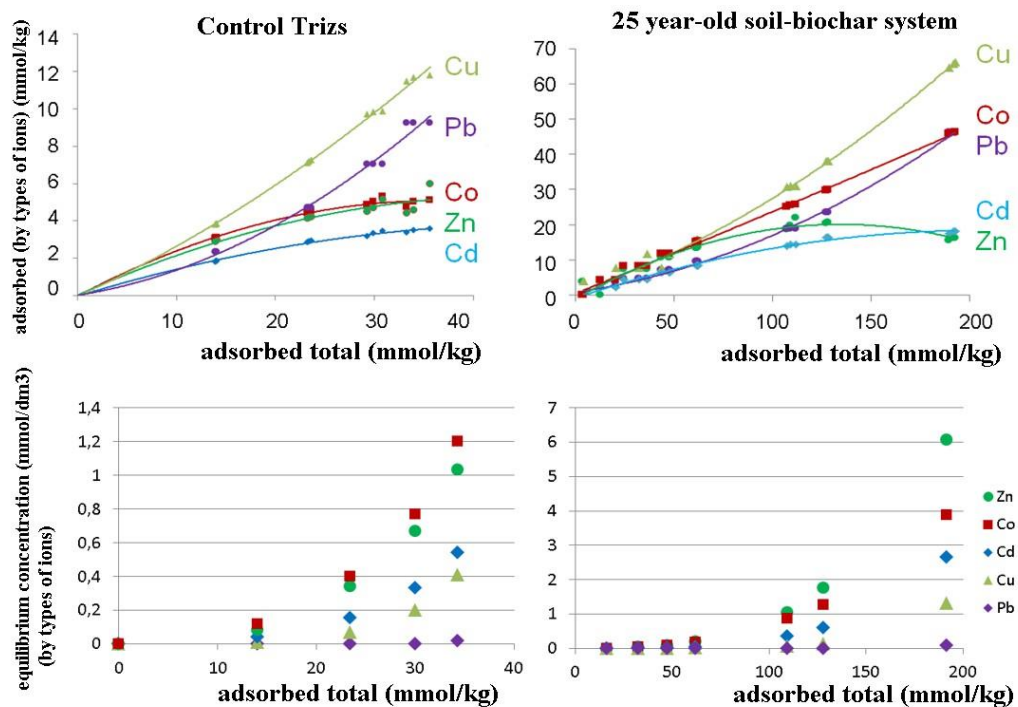


**Figure 12.** „Pseudo hysteresis” and parameters for its characterization

The „pseudo hysteresis” between adsorption and desorption processes can be seen and evaluated after fitting with common „ $A_L$ ” value (Figure 12). The hysteresis distance can be characterized by the help of the limit values of the difference of functions (adsorption and desorption curves). The maximum hysteresis distance ( $q_{H_{\max}}$ ) of the Cu adsorption in case of the 25 and 35 year-old soil-biochar system is twice as much as the calculated value in case of the Zn. The equilibrium concentrations ( $c_{H_{\max}}$ ) that belong to the maximum hysteresis distance are lower in case of the Cu. The above mentioned points support the fact that soil organic matter has greater affinity to adsorb Cu than Zn.

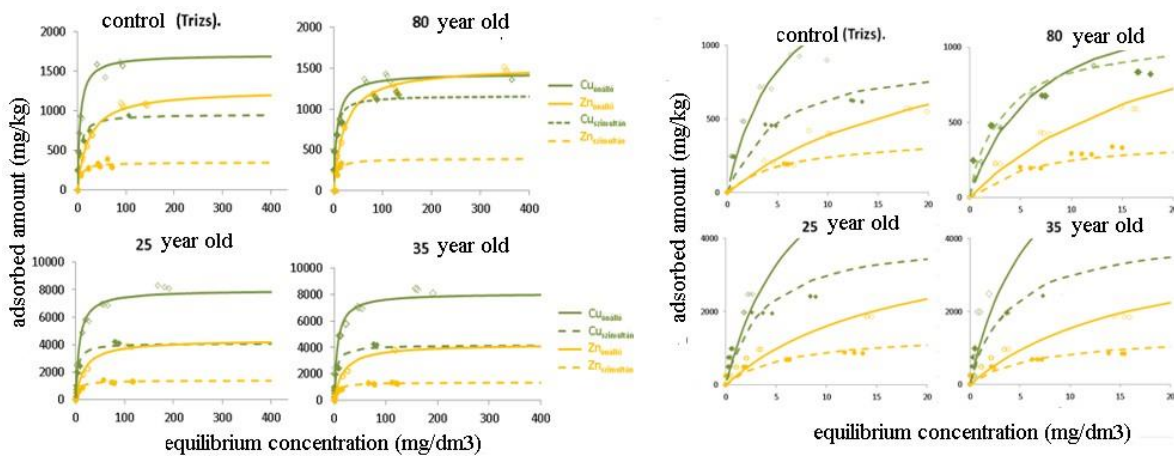
The conclusions drawn from the **competitive adsorption experiment with five elements (Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>)** on the differently aged soil-biochar system (25, 35 and 80 years old) (Figure 13):

- The R<sup>2</sup> value of the Langmuir model fitted to the experimental points was only slightly smaller than the R<sup>2</sup> value of the Sips-isotherm model.
- The Freundlich model only showed the best fit to the experimental points of the adsorption of Pb, due to the high affinity of Pb to soils.
- The adsorption order based on the A<sub>L</sub> values (mmol/kg) is the following: Pb ≥ Cu > Zn ≥ Co > Cd. This order is the same as the order set by the K<sub>d</sub> value except for the place of Cd. The K<sub>d</sub> value does not calculate with the maximum adsorption capacity.
- In such a complex system, like soils, we do not obtain more information (neither A<sub>L</sub> nor K<sub>L</sub> values) compared to the traditional Langmuir-isotherm, if we consider the other ions in the competition (competitive isotherm). Further question arises, that beside the adsorbate ions, which ions – that are already present in the soil – should we consider when the model is applied?
- The competitive isotherm is mathematically not commutative, i.e. the obtained results depend on whether in the case of the two competing ions which one is present in the 1. and 2. place of the isotherm.
- In case of several adsorbate cations that are present at the same time, the competition is more and more intensive as the potential exchange sites saturate, and its effect is even stronger in higher concentration range (Saha et al. 2002; Antoniadis and Tsadilas, 2007).



**Figure 13.** The adsorption rate of certain elements in different concentration ranges of the competitive adsorption with five elements, and the equilibrium concentrations belonging to the certain stages (Trizis) (The curve fitted onto the points only serves better visibility.)

I drew the following conclusions when I compared the results of the **one-element Cu and Zn adsorption** with the **five-element competitive adsorption of Cu and Zn** (Figure 14):



**Figure 14.** Comparison of the Cu and Zn mono-element and the five-element competitive adsorption in differently aged soil-biochar systems ( $Cu_{itself}$  —;  $Cu_{simultaneous}$  ---;  $Zn_{itself}$  —;  $Zn_{simultaneous}$  ---)

- We can state in cases both the Cu and Zn, that the fit of the isotherm function is better if only one element is present in the solution. This is in line with the results of Vega et al. (2008).
- The soil samples with well-developed soil organic matter (based on  $E_4/E_6$  ratio) adsorbed approximately the same amount of Cu during both one-element, and five-element adsorption. It proves that the soil probably has specific bounding sites for Cu (Bradl, 2004, Adriano, 2001).



## New Scientific Findings

1. I justified that the pH change (pH6→pH5→pH4) in soil, and the preliminary Zn load (500 mg/kg) have similarly negative effect on the sorption properties of soils. While the artificial decrease of pH results only in the decrease of buffering capacity, the preliminary Zn load significantly decreases the sorption capacity of soil.
2. I demonstrated that glycerol, as a chemical compound, does not have significant effect on the Zn adsorption capacity of soils. The decrease in the Zn adsorption capacity is probably due to the competition of other ions that are in the by-product, in case 1% glycerol by-product was applied to the soil as treatment.
3. I demonstrated that the application of the *freshly pyrolyzed bonechar* (1-10%) can cause significant increase in the Cu and Zn sorption capacity of soils. While the *freshly produced biochar* (1-10% mixture) does not have significant effect on the Cu and Zn adsorption of the soil, contrarily, the biochar that has been present in the soil for several decades can increase the Cu and Zn sorption capacity of soils. The effect of biochar on the sorption capacity of soil can be characterized by a curve with a maximum value as a function of time.
4. I stated that the effect of biochar on the sorption capacity of soil can be characterized by a curve with a maximum value as a function of time. The lifetime of biochar is probably less than 100 years, based on my experiments.
5. I applied mathematical method in order to characterize the sorption hysteresis. By the help of the limit value of the difference function of the “adsorption” and “desorption” curve, the maximal hysteresis distance became detectable, and also the equilibrium adsorbent concentration which belongs to it.
6. I stated and based on the large number of experiments, I proved (residuum examination), that during the adsorption of heavy metal cations on the soil, among the most frequently applied isotherms (distribution coefficient, Freundlich, Langmuir, Sips/Langmuir-Freundlich isotherms), the Sips-isotherm shows the best fit in extended concentration range. Around saturation concentrations, the Langmuir-isotherm shows similar shape to Sips-isotherm. The Freundlich-isotherm does not show enough information in connection with the saturation capacity. In low concentration range, the Freundlich-isotherm overestimates, while the Langmuir-isotherm underestimates the amount of adsorbed ions.
7. Based on the comparison of the one-element and five-element sorption experiments, I stated that in such a complex system, like soils, we do not obtain more information (neither  $A_L$  nor  $K_L$  values) compared to the traditional Langmuir-isotherm, if we consider the other ions in the competition (competitive isotherm). My results show, that the competitive isotherm is mathematically not commutative, i.e. the obtained results depend on whether in the case of the two competing ions which one is present in the first and second place of the isotherm.

## Conclusions and Suggestions

We can apply different models to describe the adsorption of “heavy metal cations” on soils, by which we can characterize the sorption processes. The most frequently applied models ( $K_d$ , Freundlich-, Langmuir-isotherm) are all well applicable, however, in all cases, we need to pay attention to the physical and chemical boundary conditions when we draw the conclusions.

I suggest to use the Sips-isotherm, in case we want to know the exact distribution of the adsorbent between the solid and the liquid phase around it, based on an isotherm which fit onto a sorption experiment. Since the Sips model have a better fit compared to the others, thus the buffering capacity of the adsorbent can be better estimated, that is a really important parameter of a well-fitting model.

The distortion effect of the linearized form of these above mentioned adsorption isotherms can be significant in some cases, thus, I suggest to use the non-linear forms of these isotherms.

The sorption behavior of soils is sensible to the outside effect (pH, preliminary cation load), thus, attention needs to be paid when amendments (biochars, pyrolyzed organic matter, etc.) are applied to the soil, both from environmental and plant nutrition aspects.

During the adsorption of essential and toxic “heavy metals”, the sorption capacity and the buffering capacity of soils are important parameters. By knowing these parameters, the soils will be comparable about a certain adsorbate. The sorption behavior of soils can be well characterized by the special points / parameters of the function that describes hysteresis. By examining these, we can state that the organic amendments with different raw materials can result in opposite effect on the cation adsorption capacity, but at the same time, they improve several soil physical, chemical and biological parameters.

## Publications related to the research topic

### 1. Scientific publication (accepted in scientific journal), peer reviewed, full text

#### 1.1. In foreign language, in a journal with impact factor (according to WEB OF SCIENCE):

##### 1.1.1. Hungarian edition

Vargha, V., Rétháti, G., Heffner, T., Pogácsás, K., Korecz, L., László, Zs., Czinkota, I., Tolner, L., Kelemen, O.  
Behavior of Polyethylene Films in Soil.  
PERIODICA POLYTECHNICA-CHEMICAL ENGINEERING 60: (1) pp. 60-68.  
(2016) (IF=0,557) **(18 pont)**

#### 1.2. In foreign language, in a journal without impact factor

##### 1.2.1. Hungarian edition

Labancz V., Rétháti G., Makó A., Szegi T. (2017): The examination of humic substances in soils and composts with high organic content with different methods. Review on Agriculture and Rural Development 6: 71-76. ISSN 2063-4803 **(7 pont)**

Czinkota, I., Issa, I., Rétháti, G., Kovács, B.  
Determination of the Behaviour and the Transport Parameters of Chromium in Soil-Water Systems.  
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Lévay, N., Füleky, Gy., Rétháti, G.  
Zinc sorption of some European volcanic soils.  
BULLETIN OF THE SZENT ISTVÁN UNIVERSITY (GÖDÖLLŐ) 2006: pp. 90-96. **(7 pont)**

##### 1.2.2. Foreign edition

Rétháti, G., Yadav, R.N., Füleky, Gy.  
Effect of acidification and preliminary Zn load on sorption of soil.  
CARPATHIAN JOURNAL of EARTH and ENVIRONMENTAL SCIENCES 13:(1) pp 267-275; DOI:10.26471/cjees/2018/013/023 (2018) **(7 pont)**

Rétháti, G., Vejzer, A., Simon, B., Benjared, R., Füleky, Gy.  
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pp. 33-38. (2014) **(7 pont)**

Rétháti, G., Pogácsás, K., Heffner, T., Simon, B., Czinkota, I., Tolner, L., Kelemen, O., Vargha, V.  
Monitoring the degradation of partly decomposable plastic foils. ACTA UNIVERSITATIS SAPIENTIAE AGRICULTURE AND ENVIRONMENT 6: (1) pp. 39-44. (2014) **(7 pont)**

1.3. In Hungarian, in a Hungarian journal without impact factor

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Issa, I., Rétháti, G., Czanik, P., Czinkota, I.  
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AGROKÉMIA ÉS TALAJTAN 56:(1) pp. 39-48. (2007) (5 pont)

Lévay, N., Füleky, Gy., Rétháti, G.  
Vulkáni eredetű talajok Zn megkötő képességének vizsgálata.  
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**4. Publications on conference proceedings (printed or electronic version – only with ISBN, ISSN)**

4.1. Publication with full text, non-periodic conference edition, in foreign language, peer reviewed:

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Tolner, L., Ziegler, I., Füleky, Gy., Gulyás, M., Rétháti, G. (2016): Stimulant and toxic effect of biomass ash dosage in pot experiment. XV. Alps-Adria Scientific Workshop Mali Lošinj, Croatia (2016.04.25-30.), NÖVÉNYTERMELES / CROP PRODUCTION 65 (Suppl.) pp.43-46. (5 pont)

Czinkota, I., Kocsis, I., Rétháti, G., Vágó, I., Aleksza, L. Investigation of oxidative decomposition of different compost samples. XIV. Alps-Adria Scientific Workshop. Neum, Bosnia-Hercegovina: (2015.05.11-16.) NÖVÉNYTERMELES/CROP PRODUCTION 64 (Suppl.) pp. 91-94. (2015) (5 pont)

Rétháti, G., Benjared, R., Füleky, Gy. Zn sorption of solid pyrolysis products. 14th Alps-Adria Scientific Workshop. Neum, Bosnia-Hercegovina (2015.05.11 -16.) NÖVÉNYTERMELES / CROP PRODUCTION 64 (Suppl) pp. 79-82. (2015) (5 pont)

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#### 4.2. Full text publication, non periodic conference edition, in Hungarian, peer reviewed

Simon, B., Rétháti, G., Láng, V., Pintér, O., Michéli, E., Kiss, J. Féltermészetes élőhelyek talajtermékenységi paramétereinek vizsgálata a Quessa projekt keretében. In: Csicsek Gábor, Kiss Ibolya (szerk.) XI. Kárpát-medencei Környezettudományi Konferencia tanulmánykötete. Pécs, Magyarország, (2015.05.06-09.) (2015) pp. 146-151. (ISBN:978-963-642-873-0) **(3 pont)**

Simon, B., Treutz, Zs., Veréb, M., Rétháti, G., Kampfl, Gy., Szegi, T., Láng, V. A talajtermékenység, mint ökoszisztéma szolgáltatás kvantitatív vizsgálata. In: Hernádi H, Sisák I, Szabóné Kele G (szerk.) A talajok térbeli változatossága - elméleti és gyakorlati vonatkozások: Talajtani Vándorgyűlés, Keszthely. Magyarország, (2014.09.04-06.) Keszthely: (2015) pp. 327-335. (ISBN:978-963-9639-80-5) **(3 pont)**

Tolner, I. T., Gál, A., Simon, B., Tolner, L., Czinkota, I., Rétháti, G. Különböző korú talajba keveredett faszénmaradványok hatásának vizsgálata a talaj kémiai és optikai tulajdonságaira. In: Hernádi H, Sisák I, Szabóné Kele G (szerk.) A talajok térbeli változatossága - elméleti és gyakorlati vonatkozások: Talajtani Vándorgyűlés, Keszthely, Magyarország, (2014.09.04-06.) (2015) pp. 337-347. (ISBN:978-963-9639-80-5) **(3 pont)**

Rétháti, G., Pogácsás, K., Heffner, T., Simon, B., Czinkota, I., Tolner, L., Kelemen, O., Vargha, V. Környezetben részlegesen lebomló műanyag fóliák degradációjának nyomon követése. Monitoring the degradation of partly decomposable plastic foils. In: Zsigmond AR, Szigyártó IL, Szikszai A (szerk.) X. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, Románia, (2014.03.27-29.) pp. 181-185. **(3 pont)**

Rétháti, G., Vejzer, A., Simon, B., Benjared, R., Füleky, Gy. Különböző pirolízis termékkel kezelt talajok cinkmegkötő képességének vizsgálata. In: Zsigmond AR, Szigyártó I.L., Szikszai, A. (szerk.) X. Kárpát-medencei Környezettudományi Konferencia. Kolozsvár, Románia, (2014.03.27-29.) pp. 33-37. **(3 pont)**

Tolner, L., Czinkota, I., Vadkerti, Zs., Kovács, A., Rétháti, G. Glicerín hatása az angolperje csírázására és kezdeti növekedésére. MAGYAR EPIDEMIOLOGIA 10:(Suppl.) p. 46. 1 p. (2013) **(3 pont)**

Rétháti, G., Vejzer, A., Czinkota, I., Füleky, Gy. A kukorica növény egyedfejlődésének és nehézfém felvételének vizsgálata glicerín melléktermék hatására. In: Sándor Zsolt, Szabó András (szerk.) Újabb kutatási eredmények a növénytudományokban. Debrecen, Magyarország, (2013.05.05.) (2013) pp. 41-46. (ISBN:978-615-518340-9) **(3 pont)**

Rétháti, G., Vejzer, A., Czinkota, I. Glicerín melléktermék hatása a talaj Zn megkötő képességére. In: Dobos Endre, Bertóti Réka Diana, Szabóné Kele Gabriella (szerk.) Talajtan a mezőgazdaság, a vidékfejlesztés és a környezetgazdálkodás szolgálatában: Talajtani Vándorgyűlés. Miskolc, Magyarország, (2012.08.23-25.) (2013) pp. 409-418. (ISBN: 978-963-08-6322-3) **(3pont)**

## **5. Publications in conference proceeding (printed or electronic – without certification)**

5.1. Full text, foreign language

5.2. Full text, in Hungarian

5.3. One page summary in Hungarian or in foreign language

Czinkota, I., Rétháti, G., Tolner, L., Dálnoki, A.B., Sebők, A. Széles körben használatos adszorptívum csere izoterma levezetése és használati lehetőségei. In: MTA Analitikai és Környezeti Kémiai Tudományos Bizottság Környezeti Kémiai Munkabizottsága (szerk.) Hatodik Környezatkémiai Szimpózium. Bakonybél, Magyarország, 2017.10.12-13. p. 31. **(1 pont)**

Fekete, Gy., Rétháti, G., Kovács, A., Dálnoki, A.B., Grósz, J., Tóth, P.P.: Mikroalgák szervesanyag-tartalmának vizsgálata In: MTA Analitikai és Környezeti Kémiai Tudományos Bizottság Környezeti Kémiai Munkabizottsága (szerk.) Hatodik Környezatkémiai Szimpózium. Bakonybél, Magyarország, 2017.10.12-13. p. 15. **(1 pont)**

Rétháti, G., Czinkota, I., Sebők, A., Tolner, L., Kationok ( $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ) talajon történő szimultán megkötődésének jellemzése. In: MTA Analitikai és Környezeti Kémiai Tudományos Bizottság Környezeti Kémiai Munkabizottsága (szerk.) Ötödik Környezatkémiai Szimpózium. Tihany, Magyarország, 2016.10.06-07. p. 23. **(1 pont)**

Tolner, L., Rétháti, G., Kovács, A., Dálnoki, A. B., Fekete, Gy., Czinkota, I. Biodízelgyártás melléktermék (glicerín) hatása a talaj nitrogén formáira és az angolperje kezdeti fejlődésére. In: MTA Analitikai és Környezeti Kémiai Tudományos Bizottság Környezeti Kémiai Munkabizottsága (szerk.) Ötödik Környezatkémiai Szimpózium. Tihany, Magyarország, 2016.10.06-07. p. 21. **(1 pont)**

Rétháti, G., Varga, D., Sebők, A., Füleky, Gy., Tolner, L., Czinkota, I. Talajok rézmegkötő képességének vizsgálata oszlopkísérletek segítségével. In: Salma Imre, Zsigrainé Vasánits Anikó, Németh Zoltán (szerk.) Negyedik Környezetkémiai Szimpózium. Tata, Magyarország, 2015.10.08-09. p. 27. **(1 pont)**

Tolner, L., Rétháti, G., Füleky, Gy. Tönkretesszük-e vegyszerekkel a talajainkat? In: Salma Imre, Zsigrainé Vasánits Anikó, Németh Zoltán (szerk.) Negyedik Környezetkémiai Szimpózium. Tata, Magyarország, 2015.10.08-09. p. 27. **(1 pont)**

Rétháti, G., Czinkota, I., Tolner, L., Füleky, Gy. Különböző korú talaj-faszén rendszerek Cu és Zn megkötő képességének összehasonlítása. In: MTA Analitikai és Környezeti Kémiai Tudományos Bizottság Környezeti Kémiai Munkabizottsága (szerk.) Harmadik Környezetkémiai Szimpózium. Lajosmizse, Magyarország, 2014.10.09-10. p. 34. **(1 pont)**

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Rétháti, G., Vejzer, A., Gál, A., Simon, B., Füleky, Gy. Examination of zinc adsorption capacity of soils treated with different pyrolysis products. In: ORBIT 2014 Scientific Conference: 9th Conference on Organic Resources and Biological Treatment. Konferencia helye, ideje: Gödöllő, Magyarország, 2014.06.26-28. p. 42. **(2pont)**

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