http://dx.doi.org/10.5935/0103-5053.20130265

J. Braz. Chem. Soc., Vol. 25, No. 1, 36-49, 2014.
Printed in Brazil - ©2014 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Enrichment of Tropical Peat with Micronutrients for Agricultural Applications: Evaluation of Adsorption and Desorption Processes

Camila de A. Melo,*[*,a,b] *Lilian K. de Oliveira,*[a,b] *Danielle Goveia,*[b]
***Leonardo F. Fraceto*[a] *and André H. Rosa*[*,a]**

[a]*Environmental Engineering Department, São Paulo State University (UNESP),*
Av. Três de Março 511, 18087-180 Sorocaba-SP, Brazil

[b]*Institute of Chemistry, São Paulo State University (UNESP),*
Rua Prof. Francisco Degni 55, 18087-180 Araraquara-SP, Brazil

O objetivo deste trabalho foi avaliar os processos de adsorção e dessorção de micronutrientes em amostras de turfas tropicais visando uma possível aplicação em solos. Para isso, experimentos de adsorção foram estudados em diferentes valores de pH e a partir de solução metálica multielementar e elementar. As capacidades de adsorção máximas ocorreram em pH 6,0 e a ordem de afinidade observada em geral foi: Cu > Fe > Co > Ni > Zn = Mn. A liberação dos micronutrientes foi avaliada sob diferentes valores de pH em meio aquoso, e posteriormente, em solo e planta. Os experimentos de liberação mostraram que os micronutrientes são liberados preferencialmente em pH 6,0 e na seguinte ordem: Fe > Zn > Mn > Co = Ni > Cu. A liberação dos micronutrientes para o solo é acompanhada pela sorção dos mesmos pela planta. Desta maneira, a aplicação de turfas tropicais enriquecidas com micronutrientes pode contribuir para uma maior produtividade agrícola uma vez que a liberação dos micronutrientes mostrou-se eficiente no desenvolvimento das plantas.

The objective of this work was to evaluate the adsorption and desorption of micronutrients in tropical peats, from the perspective of potential agricultural applications. Adsorption experiments were performed at different pH values, using solutions containing individual and multiple metal ions. Maximum adsorption capacity occurred at pH 6.0, and the order of affinity was Cu > Fe > Co > Ni > Zn = Mn. Release of the micronutrients was evaluated at different pH values, using an aqueous medium as well as soil and plants. Release of the micronutrients was most efficient at pH 6.0, and followed the order: Fe > Zn > Mn > Co = Ni > Cu. Micronutrient release to the soil was accompanied by uptake by the plant. The use of tropical peat enriched with micronutrients could contribute to improved agricultural productivity, since the release profile of the micronutrients can effectively stimulate plant growth.

Keywords: adsorption, desorption, micronutrients, peat, plant growth

Introduction

There are ongoing concerns in relation to human population growth and the need to produce greater quantities of food at lower cost. Assuming forward population growth, the development of new techniques will be needed to improve the fertility of existing agricultural soils in a sustainable way. Greater agricultural productivity is often limited by the maximum achievable rates of utilization of macro- and micronutrients by plants, as well as the content of organic matter in soils.[1]

Peats are formed by the decomposition of plant residues under conditions of high humidity and absence of oxygen. They are distinguished by their high organic matter contents (60-80%), which enable them to be used in a variety of different applications. These include their use to adsorb metal species (including macro- and micronutrients), and as organic fertilizers to improve the physico-chemical properties of soils and incorporate nutrients.[2-7] It has been shown that the application of humic substances (organic material extracted from soils and peat) can affect plant growth and nutrient release. Verlinden *et al.*[8,9] reported that the application of humic substances together with mineral fertilizers in plantations of maize, grass, potatoes,

---

*e-mail: ahrosa@sorocaba.unesp.br

and spinach improved crop yields. It was found that there was a gradual increase of macronutrients such as nitrogen and phosphorus in the soil, while there was no influence on other elements such as sodium and calcium. It is therefore clear that the use of peat can help to improve agricultural productivity. However, a factor that has limited the widespread use of peat in agriculture is a lack of studies that have investigated the capacity of peats to adsorb micronutrients under different conditions, although there have been a number of studies of peats from temperate regions and their interaction with different metals, notably copper.[10-12]

The mechanisms of adsorption of micronutrients by soils include ion exchange, physical adsorption, and chemical bonding with phenolic or carboxylic groups of the organic matter.[13] The adsorption reactions determine the availability of micronutrients to the plants and their mobility in the soils.[14] In many studies, adsorption isotherm models are employed in order to better understand the phenomena involved.[15] Adsorption is also influenced by factors including regional climate, topography, and vegetation, which give to different peats their individual characteristics.

The availability of micronutrients to plants is determined not only by processes of adsorption, but also by the desorption processes that are responsible for the release of micronutrients in forms that can be absorbed by the plant. The mechanism of uptake of nutrients by plants involves the production of organic acids by the roots, which together with water eventually solubilizes the nutrients and makes them available.[16] For this reason, the evaluation of desorption processes is performed using extractants such as acids, complexation agents, and saline solutions, which simulate the possible physico-chemical processes that occur in the environment. However, the use of extractants such as EDTA and DTPA can accelerate desorption, leading to overestimation of the concentrations of nutrients likely to be released in soils.[17]

There have been few studies concerning characterization of the mechanisms of adsorption and desorption of multiple micronutrients in peats from tropical regions. Brazil possesses peat reserves of around 15000 km^2, which is equivalent to around 129 million tons of this material.[18] The use of these peats as natural organic fertilizers in agricultural soils could provide benefits including water retention, pH buffering, and the retention of cations, due to the high organic matter content of peat.[19] However, the successful application of these materials requires consideration of the type of soil, the plant species under cultivation, and the physico-chemical characteristics of the peat.[20]

The objective of the present work was to investigate the mechanisms that influence the capacity of tropical peats to adsorb and desorb the micronutrients copper, cobalt, iron, manganese, nickel, and zinc. The peat samples were first characterized using elemental and spectroscopic techniques. Different pH conditions and micronutrient concentrations were employed, and the Langmuir and Freundlich isotherms were applied to the results. The desorption processes were evaluated using aqueous solutions and agricultural soils.

Experimental

Materials and chemicals

All reagents used were of high purity grade. High purity deionized water was used in all the experiments (resistivity of 18.2 MΩ cm at 25 °C, Milli-Q system, Millipore). Dilute acid and alkaline solutions were prepared by dilution of concentrated HCl and dissolution of NaOH in deionized water. Working solutions of the micronutrients (Cu, Co, Fe, Mn, Ni, and Zn) were prepared daily by dilution of 1000 mg L^{-1} stock solutions.

Sampling and characterization of peat samples

The peat samples were collected from two peatlands located in Sergipe State, Brazil. The sample collected in Santo Amaro das Brotas (36º58'52"W; 10º49'3"S) was named TSA and the sample collected in Serra de Itabaiana (37º20'25"W; 10º45'29"S) was named TSI (Figure 1). The sampling was undertaken in February 2011, with five samples collected at a depth of 20 cm from the surface (n = 5). The samples were transported to the laboratory in polyethylene bags, then dried at 30 °C to constant weight,

Figure 1. Map of the sampling locations in Sergipe State, Brazil.

homogenized in a porcelain mortar, and sieved to a particle size of 2 mm.

The pH of the samples was determined according to the EPA 9045 protocol.[21] The organic matter and ash contents were measured by gravimetry, with calcination of around 5.0 g of the peat samples for 4 h at 750 °C.[22] Granulometry was performed according to the pipette technique of Suguio,[23] after treatment of the peat samples with H_2O_2 due to the high contents of organic matter. The samples were decomposed using concentrated HNO_3 and H_2O_2, with heating at 95 ºC for 4 h on a hotplate,[24] after calcination for 4 h at 400 ºC to assist the decomposition of organic matter. The residual mineral fraction was removed by filtering through a 0.45 µm pore size membrane (Millipore). The concentrations of the micronutrients (Cu, Co, Fe, Mn, Ni, and Zn) were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES), as described below.

The samples were characterized by ^{13}C nuclear magnetic resonance (^{13}C NMR), with cross-polarization (CP) and magic angle spinning (MAS), using a Bruker Avance III 400 MHz spectrometer, with 5 kHz rotation, a contact time of 2 ms, a relaxation time of 5 s, and a scan number of 11000. The carbon, hydrogen, and nitrogen contents of the samples were measured using a Thermo Finnigan Flash EA 1112 elemental analyzer, and the oxygen contents were determined by difference.

Adsorption of micronutrients by the peats: time to equilibrium and influence of pH

The batch adsorption experiments employed 2.0 g of peat sample and 100 mL of deionized water, which were transferred to an Erlenmeyer flask placed in an orbital shaker. The micronutrients were added to the solution to give concentrations of 10 mg L^{-1} of each element. The pH was adjusted to different values (3.0, 4.5, and 6.0) using solutions of 1.0 mol L^{-1} HCl or 1.0 mol L^{-1} NaOH, and 5 mL aliquots were withdrawn for analysis at predetermined time intervals (0, 10, 30, 60, 120, 240, 1440, 2880, and 4380 min). The aliquots were centrifuged at 3500 rpm, and the concentrations of micronutrients in the supernatants were determined by ICP-OES. The pH was measured at the end of each experiment to monitor any changes. The concentrations of the adsorbed micronutrients were then calculated as the difference between the initial concentration and the concentration measured in the supernatant. The adsorptive capacity (q_{eq} in units of mg g^{-1}) was calculated using:

$$q_{eq} = \frac{(Ci - Cf)V}{m} \tag{1}$$

where, Ci and Cf are the initial and final micronutrient concentrations, respectively, *V* is the volume used, and *m* is the mass of peat used.

Micronutrient adsorption isotherms

The adsorption experiments were performed using the two peat samples (TSA and TSI) and the six micronutrients. The adsorption isotherms were evaluated in two different ways. Firstly, the micronutrients were added to the peats using multi-metal solutions, with the concentrations of the metals ranging from 5.0 to 100.0 mg L^{-1}. Secondly, the micronutrients were added using solutions containing the individual metals at concentrations ranging from 5.0 to 40.0 mg L^{-1}. A 2 mL aliquot was removed from each flask prior to addition of the peat samples, for subsequent determination of the initial micronutrient concentrations. Approximately 2.0 g of each peat was added to Erlenmeyer flasks containing 100 mL of the multiple or individual metal solutions, and the pH was adjusted to 6.0 with 1.0 mol L^{-1} HCl or NaOH. The flasks were kept under shaking, and the experiments were performed in triplicate. After addition of the peat, the flasks were shaken every 2 h during the day, and after 24 h, another 2 mL aliquot was removed from each flask for subsequent determination of the final micronutrient concentrations.

The Langmuir and Freundlich mathematical models were used to elucidate the mechanisms of adsorption of the micronutrients by the peat samples. The Langmuir isotherm describes the formation of a monolayer on surfaces where there are a finite number of available sites. The Freundlich model is an exponential equation that predicts the formation of a multilayer on an adsorbent whose surface is heterogeneous, with different types of sites, and the concentration of solute at the surface increases according to the concentration in solution.[25] The Langmuir isotherm can be described by:

$$q_{eq} = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}} \tag{2}$$

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{q_m K_L} + \frac{C_{eq}}{q_m} \tag{3}$$

where q_{eq} is the adsorptive capacity at equilibrium (mg g^{-1}), C_{eq} is the micronutrient concentration at equilibrium (mg g^{-1}), and q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and the adsorption energy, respectively. These parameters can be obtained by linearization of the model (equation 3) and construction of a graph of C_{eq}/q_{eq} *vs.* C_{eq}. The Freundlich isotherm can be described by:

$$q_{eq} = k_F C_{eq} \frac{1}{n} \quad (4)$$

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \quad (5)$$

where K_F (L g^{-1}) and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively. The constants can be obtained after linearization, by plotting a graph of log C_{eq} *vs.* log q_{eq} (equation 5).

Once the maximum adsorption capacity had been obtained from the adsorption isotherms, new adsorption experiments were designed to evaluate the release of the micronutrients. The experiments were performed using multiple and individual metal solutions, with the micronutrients being added to final concentrations of 5.0 mg L^{-1} in 100 mL Erlenmeyer flasks. The peat mass used was 2.0 g, and the pH was adjusted to 6.0 with 1.0 mol L^{-1} HCl or NaOH. The adsorption capacity was calculated for each new experiment. After centrifuging the flasks, aliquots of supernatant were collected, and the remaining supernatant solution was decanted and discarded appropriately. The separated mass of peat containing the adsorbed micronutrients was then dried to constant weight in an oven at 30 °C.

Release of the nutrients from the peat samples

The release of the micronutrients that had been previously adsorbed by the peat samples was evaluated in two different sets of experiments, using either water or soil. The release experiments using water were performed at two pH values: 4.5 and 6.0. Portions (0.25 g) of the peat samples enriched with either individual or multiple micronutrients were added to Erlenmeyer flasks containing 50 mL of deionized water with pH previously adjusted using 1.0 mol L^{-1} HCl or NaOH. The flasks were kept under constant mechanical agitation at a controlled temperature of 25 ± 2 ºC. The experiments were performed in triplicate. 1 mL aliquots were withdrawn at predetermined times (0, 30, 60, 120, and 240 min, then 1, 2, 3, 4, and 5 days) for determination of the micronutrient concentrations. The release experiments were also performed using peat samples without adsorbed micronutrients (*in natura* samples). In this case, about 1.0 g of each sample was added to a 100 mL Erlenmeyer flask containing deionized water, and the pH was adjusted to 4.5 or 6.0 with 1.0 mol L^{-1} HCl or NaOH. The experiments were performed in triplicate. 1 mL aliquots were withdrawn at predetermined times (0, 30, 60, 120, 240, and 1440 min), and the concentrations of the micronutrients were determined by ICP-OES.

The release experiments with soil were performed using pots containing maize plants. Evaluations were made of the release of the micronutrients into the soil, the presence of the metals in the leaves, and the development of the plants in terms of height. Eighteen pots were filled with approximately 1.5 kg of regional soil (Latossol Red-Yellow). Six pots were used as controls, and only contained the soil, while six pots contained soil plus about 20.0 g of *in natura* peat (TSA or TSI), and another six pots contained soil plus about 20.0 g of peat (TSA or TSI) that had been previously enriched with the micronutrients. In all experiments, three pots each were used for the TSA and TSI peats. The pots were irrigated with water on a daily basis, and the experiment lasted 30 days.

Soil samples were collected from each pot on the first day for subsequent determination of the concentrations of the micronutrients, and after 15 and 30 days collections were made of soil samples from each pot, as well as leaf samples from at least one plant in each pot. At the same time, plant development was evaluated by measuring the maximum leaf height. The leaf and soil samples were then properly stored in labeled plastic bags, and subsequently decomposed using concentrated HNO_3 and H_2O_2, with heating at 95 °C for about 4 h on a hotplate. The concentrations of the metals were then determined by ICP-OES.

Determination of micronutrients

The metal concentrations were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), using an Agilent Model 720 instrument fitted with a "seaspray" nebulizer. The instrumental conditions were an RF power of 1.10 kW, an argon flow of 15.0 L min^{-1}, and a spray pressure of 200 kPa. The standard solutions used for calibration were prepared from a 100.0 mg L^{-1} multi-element stock solution. The limits of detection (LOD) and quantification (LOQ) were calculated from the standard deviation of the readings of ten analytical blanks. The LOD, LOQ, and wavelength used for each element are summarized in Table 1.

Results and Discussion

Peat sample characterization

The physico-chemical characteristics of the two peats are provided in Table 2. The organic matter (OM) content of TSA exceeded 80%, indicative of a high degree of chemical and biological activity in the peatland. This level of organic matter is higher than values reported in the literature for

Table 1. Limits of detection (LOD) and quantification (LOQ), and wavelengths used for analysis of Cu, Co, Fe, Mn, Ni, and Zn by ICP-OES

	Wavelength / nm	LOD / (μg L^{-1})	LOQ / (μg L^{-1})
Cu	324.754	3.2	10.7
Co	238.892	2.4	8.1
Fe	238.204	2.3	7.8
Mn	257.610	3.0	10.1
Ni	231.604	1.4	4.5
Zn	206.200	2.5	8.2

peats from temperate and tropical regions,[26,27] and is in agreement with the measured pH values, since greater decomposition of organic matter lowers the pH due to conversion of plant materials to carboxylic acids, esters, ketones, and alcohols. The organic matter content of the TSI sample was below 60%, which is characteristic of a peat derived from decomposition that was more recent. This was supported by a slightly higher pH, also indicative of an earlier stage of decomposition.

The granulometric measurements revealed a higher clay content of sample TSA and a higher sand content of sample TSI. Clay directly influences the micronutrient adsorption capacity by increasing the surface area of active sites due to the formation of clay-humus complexes.[1]

The micronutrient contents of the peats were higher than found in other studies (Table 2), which could be due to geological factors as well as anthropogenic activity.[26,27] Concentrations of micronutrients are normally low in areas where anthropogenic activities are absent.[28,29] Here, the peat samples were collected in environmental reserves in regions with generally low levels of anthropogenic activity, but which were nevertheless close to roads. The peats combined high organic matter contents with low concentrations of the micronutrients essential for plant growth, suggesting that they might be suitable for agricultural purposes following micronutrient enrichment.

The elemental compositions and atomic ratios of the peat samples are provided in Table 3. Smaller H/C and O/C ratios were obtained for sample TSA. The H/C atomic ratio provides information on the degree of saturation of carbon in an organic molecule, with low values being indicative of greater aromaticity. The O/C ratio reflects the carbohydrate content, which diminishes as the ratio decreases. The results therefore showed that sample TSA was more aromatic, in agreement with its higher organic matter content. Other studies have found similar H/C and O/C ratios.[30,31] The C/N ratio can provide information on the origin of the organic matter in natural environments, with values lower than 20 indicating greater microbial humification, and values higher than 20 reflecting a greater contribution from vascular plants.[32] In the present case, there had therefore been extensive humification by microbial activity in both types of peat.

Table 2. Physico-chemical characteristics of peat samples TSA and TSI, and values reported in the literature for peat samples from temperate and tropical regions

	TSA	TSI	Campsie	Sarawak
	This work	This work	Tipping *et al.*[26]	Abat *et al.*[27]
OM[a] / %	83.1	55.2	86.0	63.0
Ash / %	16.9	44.8	b	b
pH	3.8	4.3	4.8	3.3
Sand / %	56.3	57.9	b	6.3
Silt / %	1.0	4.0	b	29.0
Clay / %	42.6	37.6	b	3.1
Cu / (μg g^{-1})	15.0	3.5	0.5	ND
Co / (μg g^{-1})	LOD	LOD	b	b
Fe / (μg g^{-1})	88.5	35.5	ND	0.3
Mn / (μg g^{-1})	181.7	51.1	b	0.1
Ni / (μg g^{-1})	17.5	5.4	0.3	b
Zn / (μg g^{-1})	45.2	9.7	1.5	0.1

LOD: 2.24 μg g^{-1}; ND: not detectable; [a]OM: organic matter; [b]data not available.

The ^{13}C NMR technique enables estimates to be made of the relative amounts of different types of carbon present in the peat organic matter, by integrating the peaks generated in specific regions of the spectra.[33] The relative percentages of different carbon-containing groups in the peat samples are presented in Table 3. The 0-65 ppm region contains shifts associated with alkyl carbons, and was more pronounced for sample TSI. The regions associated with the shifts of other chemical groups are as follows: 65-110 ppm (carbohydrates); 110-140 ppm (aromatic groups); 140-160 ppm (phenolic groups); 160-190 ppm (carboxylic groups); 190-220 ppm (carbonyl groups).[34] The percentages obtained (Table 3) show that aromatic, phenolic, and carboxylic carbons were favored in sample TSA, reflecting a more aromatic structure compared to sample TSI.

Equilibrium time and influence of pH

The knowledge of the equilibrium time (the minimum time required for adequate adsorption of the micronutrients by the peat) is essential to ensure that the processes of adsorption/desorption have stabilized. The equilibrium time varies according to the type of adsorbent material as well as the metal species.[35] In this work, for both types of peat there were no further significant changes

Table 3. Elemental composition (%) and atomic ratios for peat samples TSA and TSI, and percentages assigned to different carbon groups

	Elemental analysis							^{13}C NMR					
								Chemical shift δ assignments / %					
	C	H	O	N	H/C	O/C	C/N	C aliphatic 0-65 ppm	Ethers, –OH, sugars 65-110 ppm	C aromatic 110-140 ppm	Phenols 140-160 ppm	–COOH 160-190 ppm	–CO 190-220 ppm
TSA	36.6	2.5	28.2	3.1	0.81	0.58	13.8	33.2	20.7	28.5	7.1	8.7	1.8
TSI	24.3	1.9	20.2	2.0	0.95	0.63	14.4	54.1	14.3	19.4	4.7	2.7	4.8

in the concentrations of the micronutrients after 240 min (Figure 2). It is recognized that pH influences adsorption, since surface sites can be activated by both protonation and dissociation. Determination of the optimum pH for micronutrient adsorption is particularly important in the case of peat, due to its high content of organic matter. This includes acidic components (such as carboxylic and phenolic species) that influence the interaction with other compounds of varying acidity or alkalinity.[30] The adsorption capacities of both peats increased at higher pH (Figure 3), with greatest adsorption at pH 6.0. This behavior reflected the dissociation of acid groups capable of interacting with cationic species. It is important to note that the pH measured at the end of the experiments was always lower than the initial pH, with values between 3.0 and 4.0. These changes in the pH could help to explain the nature of the adsorption; previous studies have suggested that a drop in pH could be indicative of ion exchange during the adsorption process.[4,6]

Adsorption of micronutrients by the peat samples

Figure 4 shows the adsorption isotherms obtained for each micronutrient in the multiple and individual metal

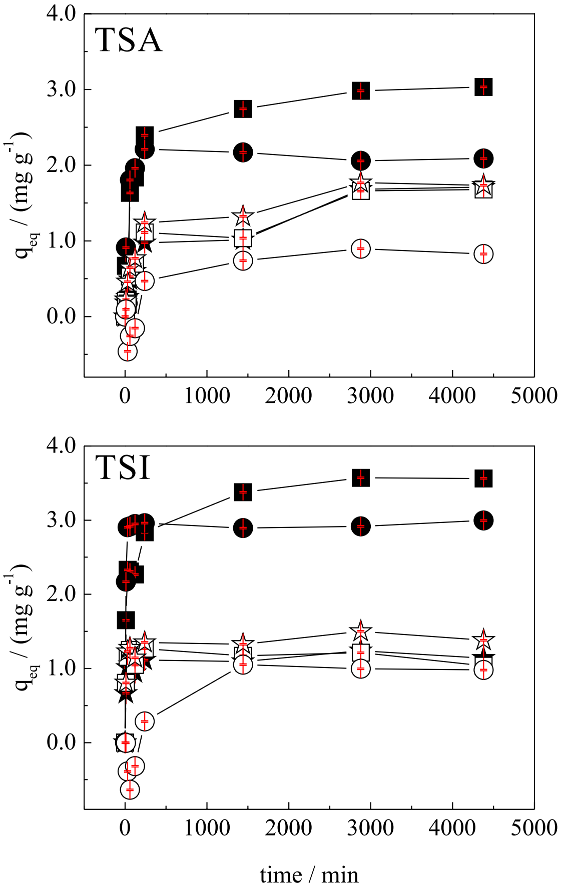

Figure 2. Equilibrium times for the adsorption of copper (■), cobalt (★), iron (●), manganese (□), nickel (☆), and zinc (○) by peat samples TSA and TSI.

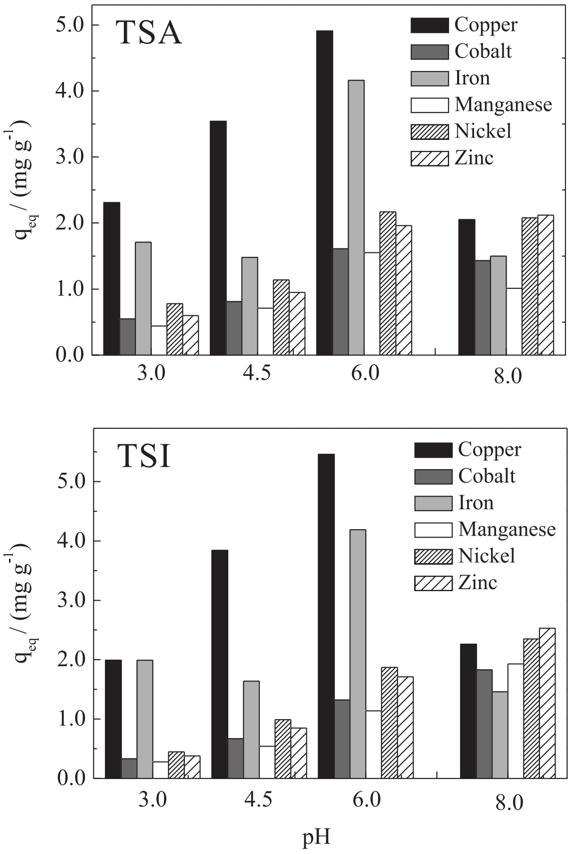

Figure 3. Adsorption capacities of the TSA and TSI peats for the micronutrients Cu, Co, Fe, Mn, Ni, and Zn, at different pH values (3.0, 4.5, and 6.0).

experiments using samples TSA and TSI. Most of the isotherms were type L, with the exception of that of iron, which was type C for both multiple and individual metal experiments. A type C isotherm indicates that the ratio between the amount of solute adsorbed and the amount remaining in solution at equilibrium is constant at any concentration.[35] A type L (Langmuir) isotherm is indicative of the progressive saturation of adsorption sites.[35] It therefore appeared that the Langmuir mathematical model provided the best fit to the data.

The Langmuir and Freundlich models were applied to the results obtained. Table 4 provides the calculated values of the Langmuir constants q_m and K_L, the Freundlich constants K_F and n, and the linear regression coefficients. Adsorption by the TSA peat was best described by the Langmuir model ($0.94 < R^2 < 0.99$), indicative of the

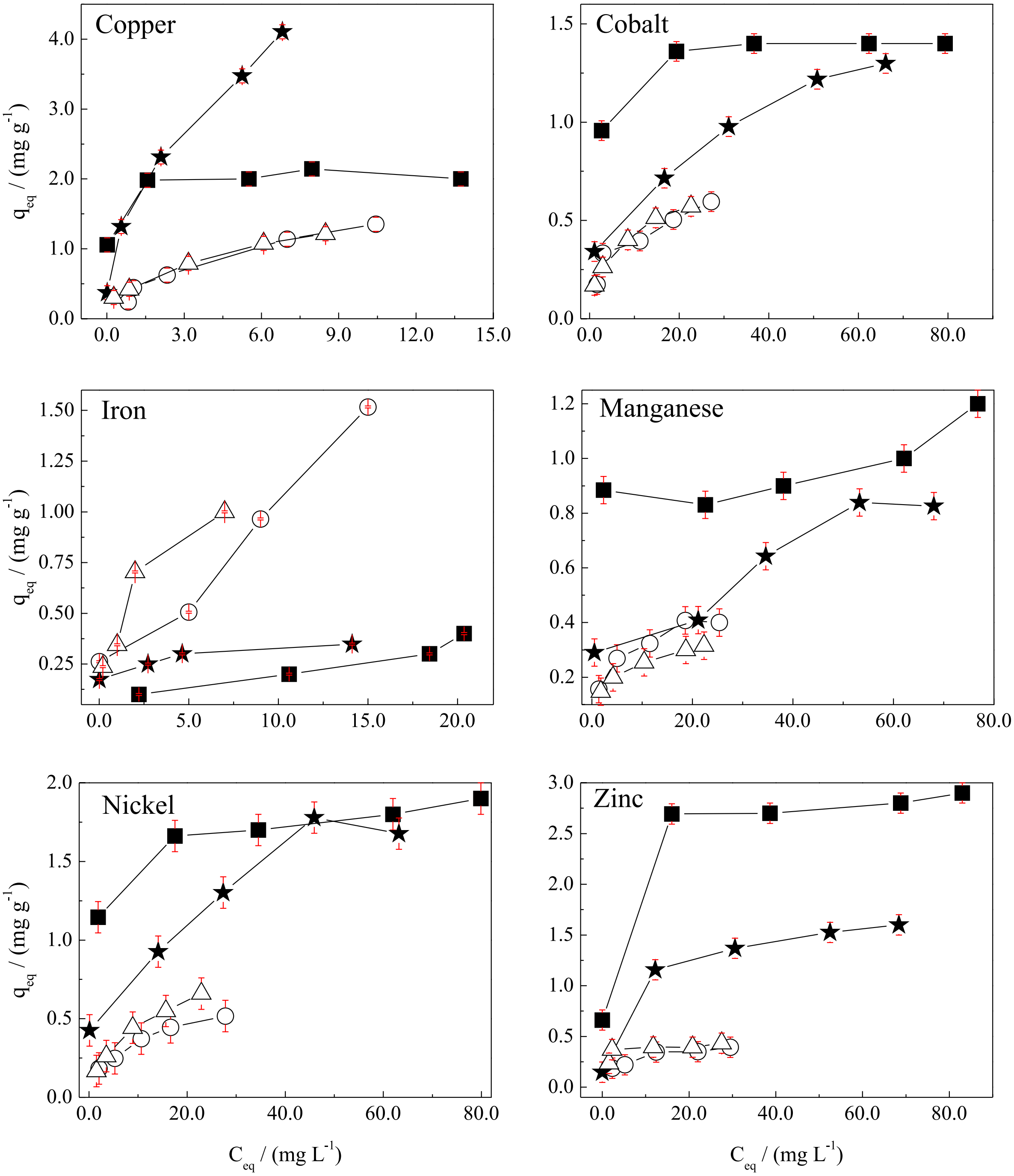

Figure 4. Adsorption isotherms for copper, cobalt, iron, manganese, nickel and zinc, using peat sample TSA in multiple (■) and individual (○) metal experiments, and peat sample TSI in multiple (★) and individual (△) metal experiments. Contact time: 24 hours; pH: 6.0.

presence of a monolayer associated with a limited number of identical binding sites.[36] For the TSI peat, good coefficients were obtained using both the Langmuir model and the Freundlich model. The Freundlich isotherm assumes the existence of an infinite multiple-layer adsorbent surface that never becomes saturated.[25] In other recent work, good correlation coefficients have been obtained for the adsorption of different metals by peat, using both the Langmuir model ($0.992 < R^2 < 0.967$) and the Freundlich model ($0.995 < R^2 < 0.962$).[28] In general, the Langmuir model provided a better fit to the data obtained here. However, in the case of Fe, the R^2 value for the TSA peat was low, compared to the other micronutrients, indicating that neither the Langmuir model nor the Freundlich model could explain the behavior of this element. It is possible that other isotherm models could provide better fits and therefore help to understand the adsorption process of Fe.

According to the values of q_m obtained, the order of affinity of the micronutrients adsorbed by the peat samples was Cu > Ni = Zn > Co > Fe = Mn for TSA, and Co = Cu > Zn > Fe > Ni > Mn for TSI, in the experiments where there was competition between the elements (multiple metal experiments). In the experiments without competition (using individual metals), the order of affinity was Cu > Fe > Co > Ni > Zn = Mn for TSA, and Cu > Fe > Ni > Co > Zn > Mn for TSI. The adsorption process occurs between the solutes in the liquid phase, which are typically in the form of ions, and the solid phase adsorbent, which has a permanent or variable surface charge, depending on the structure of the solid material.[14] The affinity of the ions for the solid phase mainly depends on the electrostatic interactions between the materials involved. Knowledge of the structure of the adsorbent is therefore extremely important for a better understanding of the results of adsorption experiments. The samples of peat contained high levels of organic matter, including carboxylic acids and phenolic compounds, as well as clay minerals. These two structural features are responsible for the surface

Table 4. Parameters of the Langmuir and Freundlich models for adsorption of Cu, Co, Fe, Mn, Ni, and Zn by peat samples TSA and TSI, at pH 6.0

TSA multiple	Langmuir			Freundlich		
	K_L / (L mg^{-1})	q_m / (mg g^{-1})	R^2	K_F / (mg g^{-1})	n	R^2
Co	0.66	1.02	0.98	0.95	16.80	0.43
Cu	5.14	1.39	0.99	1.52	14.51	0.73
Fe	0.07	0.57	0.58	1.00	21.65	0.32
Mn	0.36	0.58	0.97	1.00	8.77	0.74
Ni	1.11	1.35	0.99	1.13	12.16	0.67
Zn	0.17	1.35	0.99	1.43	6.13	0.97
TSI multiple	Langmuir			Freundlich		
	K_L / (L mg^{-1})	q_m / (mg g^{-1})	R^2	K_F / (mg g^{-1})	n	R^2
Co	10.68	3.6	0.99	0.32	0.14	0.97
Cu	1.02	2.76	0.99	1.86	4.29	0.97
Fe	0.34	1.56	0.99	0.31	13.24	0.25
Mn	12.58	0.08	0.93	0.21	4.85	0.89
Ni	7.24	0.26	0.97	0.65	4.53	0.96
Zn	0.66	1.92	0.99	0.52	3.76	0.99
TSA individual	Langmuir			Freundlich		
	K_L / (L mg^{-1})	q_m / (mg g^{-1})	R^2	K_F / (mg g^{-1})	n	R^2
Co	0.21	0.67	0.95	5.78	2.70	0.85
Cu	1.97	1.96	0.94	2.86	1.65	0.90
Fe	0.19	1.72	0.38	2.31	6.80	-0.30
Mn	0.45	0.41	0.97	6.69	3.22	0.90
Ni	0.15	0.63	0.98	7.60	2.38	0.98
Zn	0.27	0.41	0.93	6.79	3.58	0.84
TSI individual	Langmuir			Freundlich		
	K_L / (L mg^{-1})	q_m / (mg g^{-1})	R^2	K_F / (mg g^{-1})	n	R^2
Co	0.24	0.67	0.99	5.97	2.46	0.98
Cu	0.57	2.39	0.98	2.03	1.41	0.96
Fe	0.64	1.21	0.93	4.36	3.23	0.38
Mn	0.63	0.26	0.71	7.10	5.16	0.30
Ni	0.14	0.85	0.99	7.26	1.96	0.98
Zn	0.94	0.44	0.99	3.76	6.80	0.52

charge of the peat: organic acids influence solution pH, protonating or deprotonating the active adsorption sites, and clay minerals act as soft bases (donor atoms with high polarizability) that preferentially bind soft acids. According to Schwarzanbach and Pearson,[37,38] the micronutrient metals are classified as transition cations and transition acids. The adsorption is therefore determined by the charge, size, and ionization potential of each cation. The Irving-Williams series can also help understand the order of affinity for adsorption of the micronutrients by the peat samples. The series describes the stability of complexes in the following order: Mn < Fe < Co < Ni < Cu > Zn. The order of affinity found from application of the Langmuir model (Table 4) indicated that adsorption followed the Irving-Williams series order, where Cu is the first element (greater affinity) and Mn is the last element (lower affinity). The fact that Cu was the first element in both individual and multiple metal experiments was indicative of a more specific retention mechanism involving covalent bonds between the elements and the minerals in the sample. In the specific adsorption process, the adsorbed species form inner-sphere complexes on the surface, with reactions that are more selective and less reversible. Other work has also reported the higher affinity of Cu for a variety of different soils.[39] It should be noted that in the multiple metal experiments, the affinity of Fe was close to that of Mn, and was therefore weaker than the affinities of the other micronutrients. However, in the individual metal experiments, the affinity of Fe was close to that of Cu (strong affinity).

The maximum adsorptive capacities for Co, Mn, Ni, and Zn were slightly higher in the multiple metal experiments, despite competition between the elements in solution for adsorption sites, while those for Cu and Fe were higher in the individual metal experiments. These findings are in agreement with the order of affinity, since Cu and Fe showed the highest adsorption by peat samples TSA and TSI in the individual metal experiments. The results help to explain the types of interactions likely to have occurred during the adsorption processes. When there was competition between the elements in solution, there was a specific interaction of Cu with the active sites on the surface of peat, involving covalent bonds, while competition between the other elements resulted in non-specific interactions due to weak electrostatic attractions. It is therefore apparent that in the absence of competition between the elements, Cu and Fe showed specific interactions, while the other elements showed no specific interactions. This is an important consideration for interpretation of the results of release experiments, because adsorption may or may not be reversible, depending on the type of interaction.

Once the maximum adsorption capacities had been established from the adsorption isotherms, further experiments were performed to obtain the real maximum adsorption capacities (Table 5). The same behavioral profile was obtained as shown in the adsorption isotherm results, with the same order of affinity. The two peats, TSA and TSI, showed significant differences in adsorption capacity in both the multiple and individual metal experiments. The Student *t*-test was used to evaluate differences between the two samples (with a confidence level of 95%). The differences observed between samples TSA and TSI were expected, due to their different compositions. A major difference was that the TSA peat had higher clay content, compared to the TSI peat, and showed strong evidence of the presence of aromatic compounds and phenolic acids. The clay content directly affects the average particle size of the material, since clay particles are small and increase the contact area available for interactions. The highly electronegative aromatic phenolic and carboxylic groups containing oxygen are responsible for the interaction with other components that possess positive charge, such as the micronutrients. It was therefore expected that the micronutrient adsorption capacity of sample TSA would be higher than that of sample TSI.

Table 5. Maximum micronutrient adsorption capacities of peat samples TSA and TSI obtained using multiple and individual metal solutions at pH 6.0

	Adsorption / (mg g^{-1})			
	Multiple metals		Individual metals	
	TSA	TSI	TSA	TSI
Cu	2.23 ± 0.3	1.96 ± 0.3	3.03 ± 0.3	2.42 ± 0.3
Co	1.59 ± 0.1	1.48 ± 0.1	1.70 ± 0.1	1.75 ± 0.1
Fe	1.87 ± 0.3	1.29 ± 0.3	2.37 ± 0.3	2.62 ± 0.3
Mn	1.39 ± 0.1	1.31 ± 0.1	1.48 ± 0.1	1.57 ± 0.1
Ni	1.89 ± 0.2	1.78 ± 0.2	1.67 ± 0.2	1.84 ± 0.2
Zn	1.53 ± 0.1	1.44 ± 0.1	2.36 ± 0.3	1.87 ± 0.3

Release of micronutrients from the peat samples into water

Since desorption is as important as adsorption, experiments were performed to evaluate the reversibility of the adsorption process. In line with general practice, these experiments first employed an aqueous medium to obtain information concerning the release mechanisms. In the case of the *in natura* peat samples, it was found that Fe and Zn were released from both peats, especially at pH 4.5. Figure 5 shows the results of the release experiments performed at two different pH values, using samples of TSA and TSI that had been previously enriched with micronutrients adsorbed from multiple metal solutions. In all cases, the micronutrients released in highest concentrations were Fe and Zn, and the release was greatest at pH 6.0. The other micronutrients were released in lower concentrations. The observed orders of release were Zn > Fe > Mn > Co = Ni > Cu for sample TSA and Fe > Zn > Mn > Co = Ni > Cu for sample TSI. As discussed previously, Cu showed specific interaction with the peat samples and was the most strongly adsorbed element. It was therefore expected that Cu would be the least readily released element, which was confirmed by the results. The elements Fe, Zn, and Mn were least efficiently adsorbed by the peat samples. They were not strongly bound to the molecular structures of the peats, and were therefore liable to be easily desorbed. Abat *et al.*[27] obtained similar results, with Zn being more efficiently desorbed into $Ca(NO_3)_2$ solution, compared to Cu, using tropical peat samples from Malaysia. This behavior was attributed to the strong adsorption of Cu by peat organic matter. Goveia *et al.*[40] found that Fe, followed by Cu, were the elements most easily released from humin that had been extracted from peat and enriched with micronutrients. This behavior was attributed to different chemical interactions with the humin.[40]

Figure 6 illustrates the behavior obtained in the release experiments using peat samples TSA and TSI containing the micronutrients previously adsorbed from individual metal solutions, at two different pH values. Fe showed the greatest release in all the experiments. In the case of sample TSA, the pH did not significantly affect the concentrations of micronutrients released, while for sample TSI, differences were only observed for some of the micronutrients, with Fe showing greatest release at pH 4.5. The release orders obtained in the experiments using the peats enriched with individual metal solutions were Fe = Co > Zn = Ni > Cu > Mn (TSA) and Zn > Fe > Mn > Ni > Co > Cu (TSI). Once again, Cu showed the lowest overall release, while Fe and Zn were most easily released.

Table 6 summarizes the results obtained in the release experiments, showing the percentages of each micronutrient released. The first observation is that for sample TSI, the concentrations of micronutrients released were higher than for sample TSA. Again, the differences in molecular structures help to understand the results. The TSI peat showed no significant evidence of the presence of aromatic and phenolic compounds, so that interaction with the

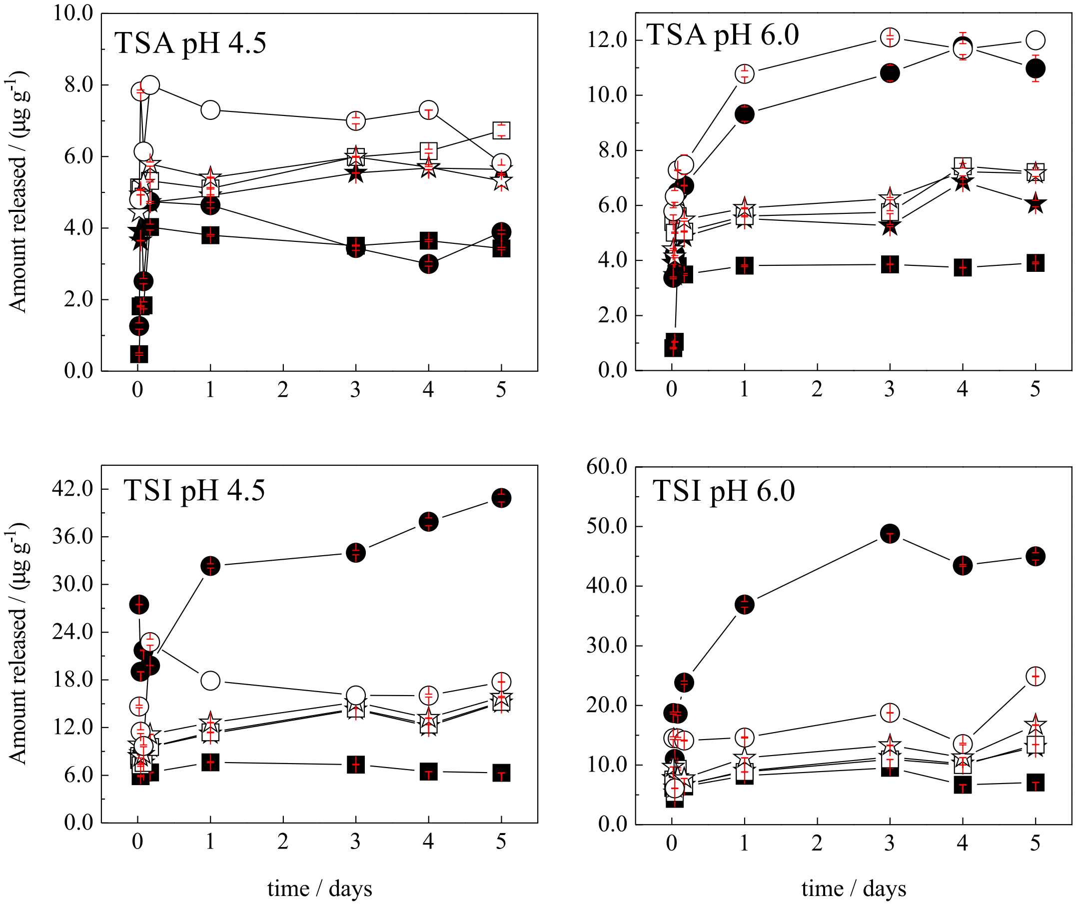

Figure 5. Release of the micronutrients copper (☐), cobalt (★), iron (●), manganese (☐), nickel (☆), and zinc (○), previously adsorbed onto peat samples TSA and TSI from a multiple metal solution, at different pH values.

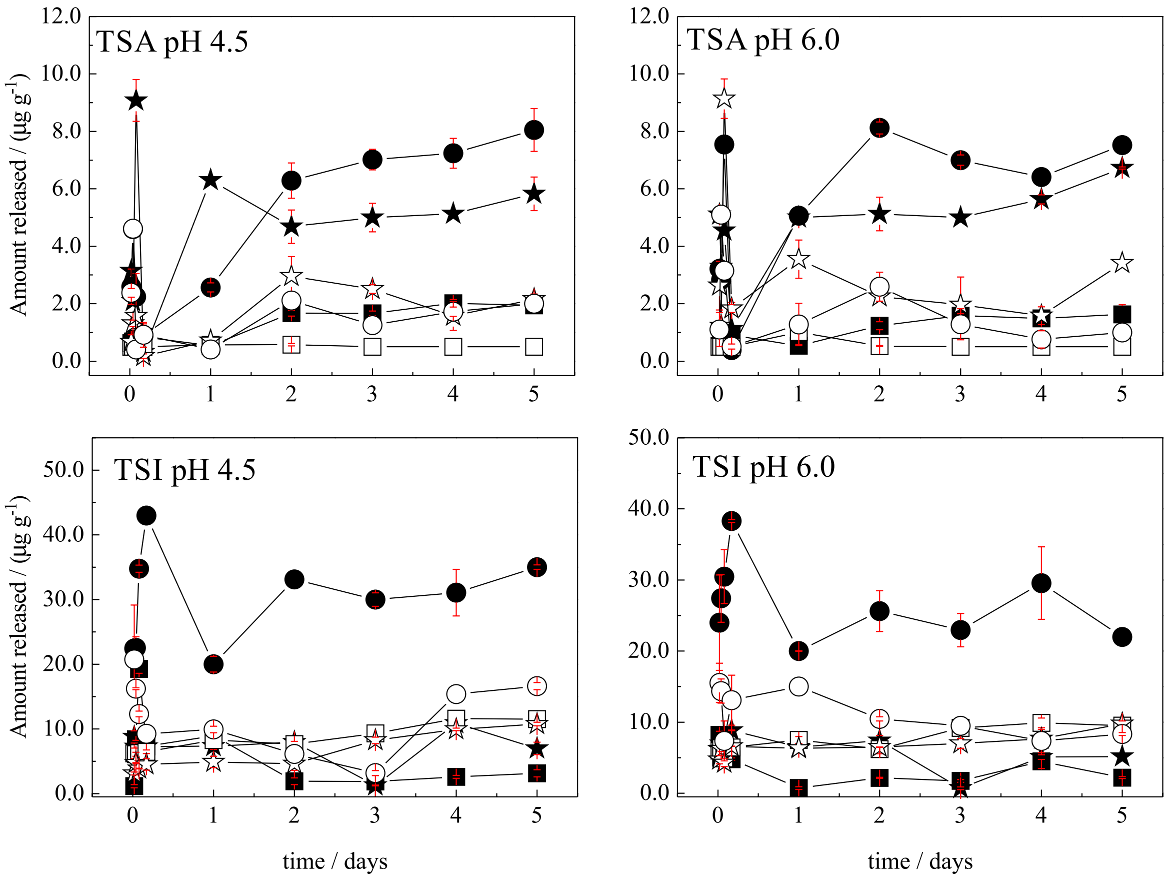

Figure 6. Release of the micronutrients copper (■), cobalt (★), iron (●), manganese (☐), nickel (☆), and zinc (○), previously adsorbed onto peat samples TSA and TSI from individual metal solutions, at different pH values.

micronutrients was weaker, resulting in desorption by a reversal of the adsorption process. Another observation was that the release percentages were higher for peat that had been enriched using multiple metal solutions. Due to the high competition between the micronutrients, the interactions established in the adsorption process were more easily reversed during desorption. From the point of view of possible agricultural applications, this could be advantageous, because the same material could be used to make different micronutrients available to plants. Although the release percentages may appear low (0.18 to 4.34%), these values are considered to be satisfactory, since the amounts of micronutrients required by plants are on the order of μg g^{-1}. High micronutrient concentrations can cause problems in plant development, or even death by poisoning.[41]

Table 6. Adsorption of micronutrients by peat samples TSA and TSI, and percentages released at different pH values

	Adsorption / (mg g^{-1})		Release / %			
Multiple	TSA	TSI	TSA pH 4.5	TSA pH 6.0	TSI pH 4.5	TSI pH 6.0
Cu	2.23	1.96	0.16	0.17	0.38	0.48
Co	1.59	1.48	0.35	0.43	0.82	0.88
Fe	1.87	1.29	0.32	0.63	3.16	4.34
Mn	1.39	1.31	0.48	0.53	0.95	1.02
Ni	1.89	1.78	0.31	0.38	0.88	0.93
Zn	1.53	1.44	0.72	0.79	1.23	1.72
Individual	TSA	TSI	TSA pH 4.5	TSA pH 6.0	TSI pH 4.5	TSI pH 6.0
Cu	3.03	2.42	0.06	0.05	0.13	0.18
Co	1.70	1.75	0.34	0.39	0.41	0.29
Fe	2.37	2.62	0.33	0.34	1.93	1.18
Mn	1.48	1.57	0.03	0.03	0.73	0.63
Ni	1.67	1.84	0.17	0.20	0.58	0.53
Zn	2.36	1.87	0.35	0.24	0.88	1.43

Release of micronutrients from the peat samples to the soil and plant

Release mechanisms can differ, depending on the environmental conditions. In soil, the release of nutrients is determined by various factors, including those associated with plant growth. One possible way of evaluating the availability of nutrients to the plants is to observe the growth of shoots, since the leaves tend to develop better when the plant receives more nutrients. The release experiments performed using soil in pots with maize plants showed that there were differences between the treatments using *in natura* peat and peat samples enriched with micronutrients (Figure 7). During the first 15 days of the experiment, no differences were observed in the leaf heights of the controls. However, when the *in natura* peat samples were used, a small difference was obtained between peats TSA and TSI at 15 days, with the TSA sample showing a better response in terms of leaf height. This could have been due to the higher organic matter and carbon and nitrogen contents (C: 36.6; N: 3.1) of the TSA peat, which assisted plant development. Greater leaf heights were obtained when the peat samples had been enriched with the micronutrients. This could also be seen after 30 days, with the enriched TSI peat resulting in greater leaf height, compared to the enriched TSA peat. This suggests that micronutrient release was higher from the TSI peat, in agreement with the results of the release experiments performed using water. Previous work has also demonstrated that the use of peat and other materials rich in humic substances can result in improvements in nutrient release and the height and mass of leaves.[8,9,42]

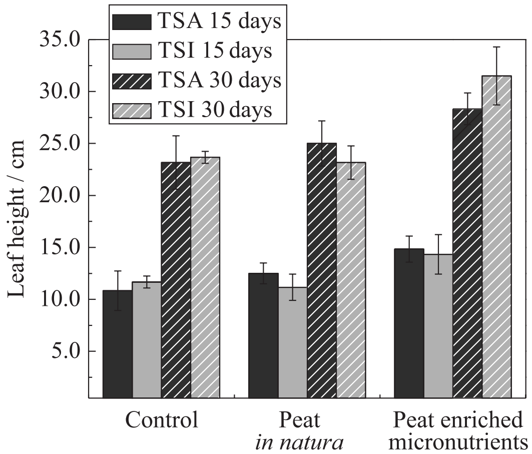

Figure 7. Leaf heights measured during release experiments using pots containing soil and maize plants: controls, treatment with *in natura* peats TSA and TSI, and treatment with micronutrient-enriched peats TSA and TSI.

The release of the micronutrients into the soil was measured (Figure 8, where the values obtained for the control have been deducted). The concentrations of Fe and Zn in the soil increased when the enriched peat samples were used, with Fe showing the greatest release for the TSA peat, and Zn for the TSI peat. Compared with the experiments using water, both micronutrients showed greater release from the TSI peat. The greater release of Fe into the soil using the TSA peat could have been due to the characteristics of the soil and/or the type of plant (in this case maize). Concentrations of Co and Mn were very low in all cases, while that of Cu either decreased with time (TSA) or remained fairly constant (TSI). The Ni concentration either remained stable (TSA) or tended to increase (TSI), as also observed in the release experiments using water.

Analysis of the plant leaves (Figure 8) showed that the concentration of Fe decreased with time (using both types of peat), while the concentrations of the other micronutrients remained fairly constant. In maize, the limiting nutrient is Zn, which acts as an enzyme activator and is fundamental for the development of plant tissues.[43] It has been reported that the use of mineral-based fertilizers to provide micronutrients such as Zn can increase lead contamination;[44] this problem could be avoided by using an organo-mineral fertilizer to provide micronutrients.[31]

Understanding the processes involved in the release of nutrients to the soil and their subsequent absorption by plants is not straightforward and requires research on various different scales. However, adsorption and release experiments performed in the laboratory can provide valuable initial information. In the present case, the use of peat enriched with micronutrients appears to offer a good potential alternative in agricultural applications. Peat is able to adsorb substantial amounts of micronutrients, which can then be released into the soil in suitable quantities to assist the development of crops.

Conclusions

The best adsorption of micronutrients by two different tropical peat samples was achieved by enrichment using a multi-metal solution. This procedure would facilitate the production of new fertilizers for use in agricultural applications, especially since the enriched peats are able to provide a simultaneous source of several different micronutrients at concentrations that are optimal for plant development. Differences in adsorption capacity were observed for the two peat samples assessed, with sample TSA showing a higher adsorption capacity, compared to sample TSI, due to its higher content of aromatic and phenolic groups.

The results of the release experiments demonstrated that essential plant micronutrients can be released from peat into both water and soil in amounts that can provide observable improvements in plant development. Peats enriched with micronutrients offer a good potential alternative for use in agricultural applications, since in addition to adding organic matter to the soil, they can also provide plants with nutrients in the amounts required.

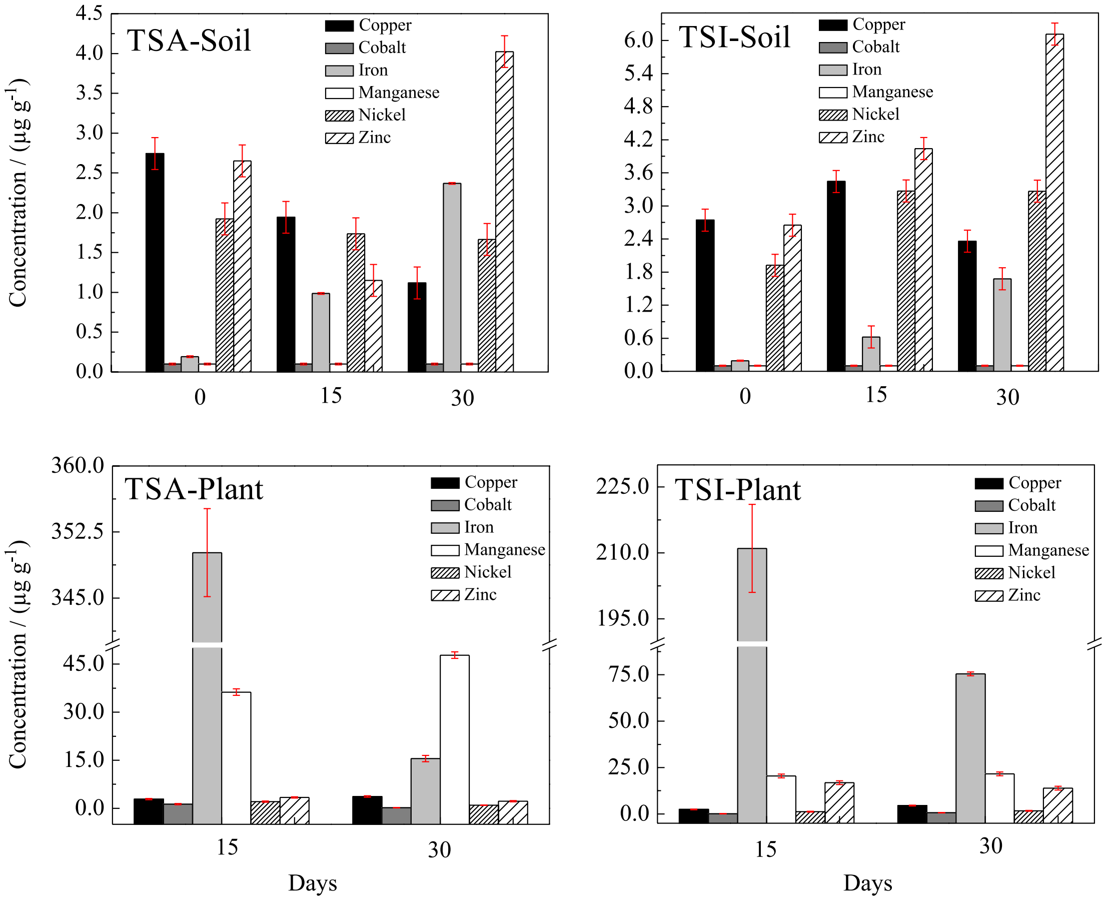

Figure 8. Concentrations of the micronutrients copper, cobalt, iron, manganese, nickel, and zinc released from the enriched peats TSA and TSI, measured in the soils and maize leaves after periods of 15 and 30 days.

Acknowledgements

This research was supported by the following agencies: Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, 2010/12210-1), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES). The authors would like to thank Dr. Tiago Venâncio of the Universidade Federal de São Carlos (UFSCar) for the ^{13}C NMR analysis and Bruno Barboza Cunha for help with the sampling of peat samples.

References

1. Kiehl, E. J.; *Fertilizantes Orgânicos*; Ceres: Piracicaba, 1985.
2. Spedding, P. J.; *Fuel* **1988**, *67,* 883.
3. Hytonen, J.; *Biomass Bioenergy* **1998**, *15*, 83.
4. Kalmykova, Y.; Stromvall, A.; Steenari, B.; *J. Hazard. Mater.* **2008**, *152*, 885.
5. Li, C.; Champagne, P.; *J. Hazard. Mater.* **2009**, *171*, 872.
6. Koivula, M. P.; Kujala, K.; Rönkkömäki, H.; Mäkelä, M.; *J. Hazard. Mater*. **2009**, *164*, 345.
7. Kechavarzi, C.; Dawson, Q.; Leeds-Harrison, P. B.; *Geoderma* **2010**, *154,* 196.
8. Verlinden, G.; Coussens, T.; De Vliegher, A.; Baert, G.; Haesaert, G.; *Grass Forage Sci.* **2010,** *65*, 133.
9. Verlinden, G.; Pycke, B.; Mertens, J.; Debersaques, F.; Verheyen, K.; Baert, G.; Bries, J.; Haesaert, G.; *J. Plant Nutr.* **2009,** *32*, 1407.
10. Karlsson, T.; Elgh-Dalgren, K.; Skyllberg, U.; *Soil Sci. Soc. Am. J.* **2008**, *72*, 1286.
11. López-Periago, J. E.; Arias-Estévez, M.; Nóvoa-Munoz, J. C.; Fernández-Calvino, D.; Soto, B.; Pérez-Novo, C.; Simal-Gándara, J.; *Soil Sci. Soc. Am. J.* **2008**, *72*, 63.
12. Elbana, T. A.; Selim, H. M.; *Soil Sci. Soc. Am. J.* **2011**, *75*, 2101.
13. Alloway, B. J.; *Heavy Metals in Soils*, 2nd ed.; Blackie Academic & Professional: London, 1995.
14. Ellis, B. G.; Knezek, B. D.; In *Micronutrients in Agriculture*; Mortvedt, J. J.; Giordano, C. M.; Lindsay, W. L., eds.; Soil Science Society of America: Madison, 1972.
15. Janetti, E. B.; Dror, I.; Guadagnini, M. R. A.; Berkowitz, B.; *Soil Sci. Soc. Am. J.* **2012**, *76*, 1229.
16. Sharma, C. P.; *Plant Micronutrients*; Science Publishers: Enfield, 2006.

17. McLaren, R. G.; Backes, C. A.; Rate, A. W.; Swift, R. S.; *Soil Sci. Soc. Am. J*. **1998**, *62*, 332.
18. http://www.peatsociety.org/peatlands-and-peat/global-peat-resources-country accessed in October 2011.
19. Moore, P. D.; *Int. J. Coal Geol*. **1989**, *12*, 89.
20. Niemi, R. M.; Vepsäläinen, M.; Wallenius, K.; Erkomaa, K.; Kukkonen, S.; Palojärvi, A.; Vestber, M.; *Eur. J. Soil Biol.* **2008**, *44,* 419.
21. http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9045d.pdf accessed in January 2012.
22. Batista, A. P. S.; Romão, L. P. C.; Arguello, M. L. P. M.; Garcia, C. A. B.; Alves, J. P. H.; Passos, E. A.; Rosa, A. H.; *J. Hazard. Mater.* **2009**, *163*, 517.
23. Suguio, K.; *Introdução à Sedimentologia*; EDUSP: São Paulo, 1973.
24. http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/3050b.pdf accessed in May 2012.
25. Liu, Y.; Wang, J.; *Fundamentals and Applications of Biosorption Isotherms, Kinetics and Thermodynamics*; Nova Science Publishers Inc.: New York, 2009.
26. Tipping, E.; Smith, E. J.; Lawlor, A. J.; Hughes, S.; Stevens, P. A.; *Environ. Pollut.* **2003**, *123*, 239.
27. Abat, M.; McLaughlin, M. J.; Kirby, J. K.; Stacey, S. P.; *Geoderma* **2012**, *175*, 58.
28. Al-Faqih, L.; Johnson, P. D.; Allen, S. J.; *Bioresource Technol.* **2008**, *99*, 1394.
29. Kyziol, J.; *Pol. J. Environ. Stud.* **2002**, *11*, 713.
30. Romao, L. P. C.; Lead, J. R.; Rocha, J. C.; Oliveira, L. C.; Rosa, A. H.; Mendonça, A. G. R.; Ribeiro, A. S.; *J. Brazil. Chem. Soc.* **2007**, *18*, 714.
31. Botero, W. G.; Oliveira, L. C.; Rocha, J. C.; Rosa, A. H.; Santos, A.; *J. Hazard. Mater.* **2010**, *177*, 307.
32. Sanches, S. M.; de Campos, S. X.; Vieira, E. M.; *Eclet. Quim.* **2007**, *32*, 49.
33. Fernandes, A. N.; Giovanela, M.; Esteves, V. I.; Sierra, M. M. S.; *J. Mol. Struct.* **2010**, *971*, 33.
34. Becker, E. D.; *High Resolution NMR: Theory and Chemical Applications*; Academic Press: San Diego, 2000.
35. Limousin, G.; Gaudet, J. P.; Charlet, L.; Szenknect, S.; Barthès, V.; Krimissa, M.; *Appl. Geochem*. **2007**, *22*, 249.
36. Weber Jr., W. J.; DiGiano, F. A.; *Process Dynamics in Environmental Systems*; Wiley Interscience: New York, 1996.
37. Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M.; *Environmental Organic Chemistry*; John Wiley & Sons: Hoboken, 2003.
38. Pearson, R. G.; *J. Am. Chem. Soc.* **1963**, *85*, 3533.
39. Sharma, S. K.; Sehkon, N. S.; Deswal, S.; John, S.; *Int. J. Civil Environ. Eng.* **2009**, *1*, 1.
40. Goveia, D.; Melo, C. A.; Oliveira, L. K.; Fraceto, L. F.; Rocha, J. C.; Dias Filho, N. L.; Rosa, A. H.; *J. Braz. Chem. Soc.* **2013**, *24*, 721.
41. Sisinno, C. L. S.; Oliveira-Filho, E. C.; *Princípios de Toxicologia Ambiental*; Interciência: Rio de Janeiro, 2013.
42. Tufenkci, S.; Turkmen, O.; Sonmez, F.; Erdinc, C.; Sensoy, S.; *Fresenius Environ. Bull.* **2006**, *15*, 295.
43. Floneragan, J.; Webb, M. J.; In *Zinc in Soils and Plants*; Robson, A. D., ed.; Kluwer: Dordrecht, 1993.
44. Nacke, H.; Goncalves, A. C.; Schwantes, D.; Nava, I. A.; Strey, L.; Coelho, G. F.; *Arch. Environ. Contam. Toxicol.* **2013,** *64*, 537.

Submitted: June 25, 2013

FAPESP has sponsored the publication of this article.