

Study on the interaction of heavy metals on farmland in Petrópolis, Rio de Janeiro, Brazil.

RAPHAEL PIETZSCH¹, HELENA POLIVANOV², ANTONIO SOARES DA SILVA², RENATA DE CARVALHO JIMENEZ ALAMINO² & TÁCIO MAURO P. DE CAMPOS³

¹ Universidade Federal do Rio de Janeiro / Universidade Federal Fluminense. (e-mail: pietzschamora@com)

² Universidade Federal do Rio de Janeiro. (e-mail: helena@acd.ufrj.br),
(e-mail: antoniossoares@yahoo.com.br), (e-mail: r_alamino@yahoo.com.br)

³ Pontifícia Universidade Católica do Rio de Janeiro. (e-mail: tacio@civ.puc-rio.br)

Abstract: The contamination of soil and groundwater as a result of the mobility of elements used in farming is of major concern. This paper will present and analyze results of a study aiming to evaluate the mobility of Zn, Cu and Cd contained in NPK fertilizers and simple super phosphate, used on a toposequence formed by a latosol and a podzolic soil. The A and B horizons were analyzed in four different locations of the toposequence. The studied area consists of latosols and podzolic soil profiles (A and B horizons) located on the Marambaia Farm, Petrópolis, Rio de Janeiro, Brazil. A tropical climate prevails in this mountainous area, with heavy rains being mostly concentrated within the months of November and March. Undisturbed samples of the soils were collected in the field and submitted, in laboratory column experiments, to infiltration by solutions of Zn, Cu and Cd, under concentrations representing the amount of these elements in fertilizers sprayed on the site. This procedure allowed the evaluation of transport parameters that describe the migration of chemical species through porous media under controlled conditions in the laboratory. The leachate collected from each experiment was analyzed by flame atomic absorption spectrometry to determine their metal concentration. The results showed that metals were retained in the superficial horizons of the soils. Due to superficial erosive processes that occur in the area, it can also be concluded that the metals could be leached from the soil and dispersed by nearby rivers.

Résumé: La contamination du sol et des eaux souterraines est raison de la mobilité des éléments utilisés dans l'affermage est concernée principal. Cet article présentera et analysera des résultats d'une étude visant à évaluer la mobilité du Zn, du Cu et du Cd contenus en engrais de NPK et phosphate superbe simple, utilisés sur un toposequence constitué par un sol ferralitique et un sol argileux. Les horizons A et B ont été analysés dans quatre endroits différents du toposequence. Le secteur étudié se compose des sols ferralitiques et des profils de sol argileux plus rouge (les horizons A et B) situé dans le Ferme Marambaia, Petrópolis, Rio de Janeiro, Brésil. Un climat tropical règne dans ce secteur montagneux, avec la forte pluie étant la plupart du temps concentrée dans les mois de novembre et de mars. Des échantillons non remaniés des sols ont été rassemblés dans le domaine et soumis, dans des essai de colonne de laboratoire, à l'infiltration par des solut ions du Zn, du Cu et du Cd, sous des concentrations représentant la quantité de ces éléments sur des fertilisant pulvérisés sur l'emplacement. Ce procédé a permis l'évaluation des paramètres de transport qui décrit la migration des espèces chimiques par des milieu poreux dans des conditions commandées dans le laboratoire. Le matériau lessivée rassemblé le long du temps de chaque expérience a été analysé par la spectrophotométrie d'absorption atomique en utilisant le système d'atomisation de flamme à déterminé l'occurrence des métaux dans eux. Les résultats ont prouvé que les métaux étaient subsistance retenue aux horizons superficiels des sols. En raison des processus érosifs superficiels qui se produisent dans le secteur qu'il pert également conclure que des métaux pourraient être transporter avec le sol, disséminant sa présence à d'autres endroits et réalisant les fleuves voisins.

Keywords: contaminated land, soils, environmental geology, laboratory tests, models, erosion.

INTRODUCTION

Soils represent an important element to ecosystems as they represent an interface between the lithosphere and biosphere. They provide a nutritious environment to vegetables and are of the utmost importance to the degradation and transference of biomass. The dispersion of pollutants in this environment consequently represents a serious ecological issue. The study of soil contamination, often as a result of anthropogenic activities, is therefore important.

The sources of contaminating materials or pollutants may be diverse, for example: the disposal of industrial and mining residuals, use of fertilizers and pesticides in farmland, sanitary landfills, domestic and hospital waste, among others. As well as several sources, there are many types of contaminants; organics, inorganics and biological.

The application of phosphated fertilizers is an important way to contribute Cd and other heavy metal contaminants to a soil. These heavy metals may come from phosphatic rocks, and many of these elements remain on the phosphate during the improvement process (USEPA, 1999). Other inorganic fertilizers, like the NPK, can also contain heavy metals in different proportions (Nicholson *et al.*, 2003; USEPA, 1999).

Among these, the heavy metals in particular, are a threat not only to plants and animals, but also to human beings, due to their toxicity and because they are not biodegradable (Martin-Garin *et al.*, 2002).

Even though the levels of heavy metals in the soil do not reach alarming levels, it should be considered that these elements can remain in the environment, in a potentially available form for a long time.

The aim of this study was to evaluate the possibility of heavy metal contamination on a toposequence, through application of fertilizers at Fazenda Marambaia, Petrópolis, Rio de Janeiro, as well as evaluate the metal mobility throughout the soil.

METHODOLOGY

The study was carried out on A and B soil horizons at four locations along a toposequence at Fazenda Marambaia, Petrópolis, Rio de Janeiro (P1, P2, P3, and P4 on Figure 1). Undisturbed samples (Figure 2) were collected from each location and their chemical, physical and mineralogical characteristics determined. Later, laboratory column tests were carried out using percolating solutions containing the previously detected metals from the applied fertilizers in the study area. Metal concentrations were similar to those found in the applied fertilizers and the behaviour of their migration in the different horizons (A and B) was analyzed.



Figure 1. Location of samples collection



Figure 2. Collection of the undisturbed samples

Pedologic, granulometric and mineralogical characterizations

The pedologic, granulometric and mineralogical characterization of the clay fraction of the sampled soils were presented by Silva (1997). To determine the granulometry, sieving and pipette methods were used (Embrapa 1997), and the soils classified using the American Triangle of Textural Classes of Soils, proposed by the Soil Survey Manual and modified by the Brazilian Society of Soil Science (Embrapa, 1997).

Pedologically, the first location (P1), close to the summit, is characterized by a red-yellow latossol with a medium texture. The lower second location (P2), is also represented by a red-yellow latossol, but differed from the first location by its yellowish color and structure of sub angular blocks, that break into small granules. The third location (P3) is characterized by a podzolic soil with medium to clayish texture. On the lower slope (P4), there is a lateral change to a red-yellow latossol with medium to clayish texture.

The methodology adopted for the analysis of the clay fraction mineralogy firstly consisted of the separation of that fraction by the pipette method (Embrapa, 1997). The soil was dispersed using sodium hydroxide (NaOH, 1N) before separating the sand fraction from the clay and silt fractions. The mineralogy of the clay fraction was then determined using X-ray diffraction (XRD) analysis.

The studied toposequence is essentially kaolinitic, this clay mineral appears in the whole sequence with well defined XRD peaks. Besides the kaolinite, goethite and gibbsite were also identified. Chlorite was detected at locations P3 and P4 (Silva, 1997).

Chemical characterization

The determination of the physico-chemical characteristics of the collected soil, as well as the determination of the metals Cd, Cu and Zn present prior to the application of fertilizer, was accomplished by following the analytical methods proposed by Embrapa (1997). The pH, T value (sum of the sorptive complex), organic carbon (C), and organic material (OM) were determined. The results are shown in Table 1.

Table 1. Physico-chemical characteristics of the studied soils.

Horizon	pH	H ⁺ +Al ⁺³	H ⁺	Al ⁺³	Ca ⁺²	Mg ⁺²	K ⁺	T value	C	OM
Location 1										
A	5.1	4	4	ALD	1	0.8	0.4	6.2	20	3.4
B	4.8	2.8	2.6	0.2	0.2	0.1	0.13	3.23	7	1.2
Location 2										
A	4.8	4.2	3.9	0.3	0.9	0.5	0.24	5.84	16	2.8
B	5	2.5	2.4	0.1	0.5	0.2	0.09	3.29	7	1.2
Location 3										
A	5	4.2	4.1	0.1	1.4	0.7	0.23	6.53	20	3.4
B	5.4	2.4	2.4	ALD	1	0.3	0.08	1.38	7	1.2
Location 4										
A	5	1.6	1.6	ALD	4	1.2	0.42	7.22	16	2.8
B	5.3	1.7	1.7	ALD	1.4	0.5	0.23	3.83	6	1

Column tests

The equipment used to accomplish the tests is formed by two marriotte flasks, that allow the maintenance of a constant flow of the influent, each one supplying two acrylic cylinders with the contaminant solution (Figure 3), totaling four simultaneous tests. A low uniform gradient ($i = 4$) was established with the intention of preventing an accelerated outflow.



Figure 3. The column apparatus

Each acrylic cylinder contained one soil sample. In order to better distribute the liquid through the columns, drilled acrylic discs with filter papers were placed on top and on the base of the samples. The acrylic cylinders have, on average, an internal diameter of 6,9cm and a height of 10cm and consequently, an internal volume of about 373cm³.

The concentration of the applied solutions was matched with that found in the fertilizers applied on the studied area. The amount, manually distributed, was about 137,94g of NPK fertilizer and 50,55g of superphosphate fertilizer on the areas represented by locations P1, P2 and P3, while at location P4, half this amount was applied (Silva, 2005).

To determine the concentrations of these metals present in these fertilizers (Table 2), a total chemical analysis was carried out using inductively coupled plasma optical emission spectrophotometry (ICP-OES).

Table 2. Concentration of the metals contained in the fertilizers sprayed over the studied area

ELEMENT	Simple super phosphate	NPK
	(mg/kg)	
Cu	38.3	1.46
Cd	0.66	0.63
Zn	43.1	1.07

From this data and knowing the proportion of the fertilizer usually applied on the investigated area, two contaminating solutions were prepared, one with Cu and another with Zn, having concentrations similar to those in the fertilizers (Table 3). The solutions were prepared from a penta-hydrated copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 8/3-hydrated cadmium sulfate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) and hepta-hydrated zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$).

Table 3. Initial characteristics of the applied solutions

Element	P1	P2	P3	P4	solution pH
	(mg/L)				
Cd initial conc.	0.12	0.12	0.12	0.09	5.07
Cu initial conc.	2.14	2.14	2.14	1.17	5.07
Zn initial conc.	2.33	2.33	2.33	1.24	5.07

After establishing the initial parameters, the column tests were carried out, in eight experiments, corresponding to the A and B horizons of the P1, P2, P3 and P4 locations. The samples were initially saturated in distilled water, inducing an ascendant flux, in order to expel all the air from the soil pore-spaces. Full saturation was indicated when percolating distilled water was detected in the outflow results.

Following soil saturation, the distilled water was replaced by the contaminated solutions and the flux flow was inverted, simulating the field conditions. The solutions percolated fifteen times through each sample, collecting 80ml of the contaminant in each stage which was analyzed by flame atomic absorption spectrometry (FAAS).

RESULTS AND DISCUSSIONS

To evaluate the migration behaviour of the contaminants, models of sorption isotherms were used. The best adjustment of interaction among the studied soil and the percolant solutions was determined. The experimental results were fitted using the simple linear regression method and the linear, Freundlich and Langmuir sorption models.

The Langmuir isotherms showed the best fit. In two unique situations the linear model proved better than the Langmuir isotherm and was adopted. The Freundlich model did not show any satisfactory results, so it was not used. The data referring to the adjustment of the models can be seen in Table 4.

Table 4. Coefficient of determination of the isotherm models for Cd, Cu and Zn.

Sample	Horizon	Cation	Linear	Freund	Lang	Sample	Horizon	Cation	Linear	Freund	Lang
P1	A	Cu	0.521	0.477	0.825	P3	A	Cu	0.002	0.006	0.79
		Cd	0.317	0.208	0.918			Cd	0.457	0.653	0.903
		Zn	0.002	0.003	0.837			Zn	0.051	1.000	0.911
	B	Cu	0.363	0.338	0.824		B	Cu	0.026	0.012	0.927
		Cd	0.953	0.516	0.025			Cd	0.192	0.424	0.607
		Zn	0.249	0.35	0.636			Zn	0.045	0.842	1.000
P2	A	Cu	0.112	0.167	0.852	P4	A	Cu	0.053	0.37	0.874
		Cd	0.071	0.436	0.999			Cd	0.422	0.554	0.678
		Zn	0.013	0.034	0.963			Zn	0.312	--	1.000
	B	Cu	0.2	0.178	0.842		B	Cu	0.002	0.596	0.841
		Cd	--	--	--			Cd	0.72	0.517	0.18
		Zn	0.261	0.325	0.537			Zn	0.113	--	1.000

With regard to the contaminating Cu solution, all the soils demonstrated that their sorption capacity for this metal is visibly reduced over the timescale of the experiment (Figure 4). Comparing the different locations on Figure 4, it is also noticeable that the P4 and P2 samples absorbed more of this metal than the others referring to the two locations further up the slope, related to the horizons A and B together. The comparison can also be seen in Table 5.

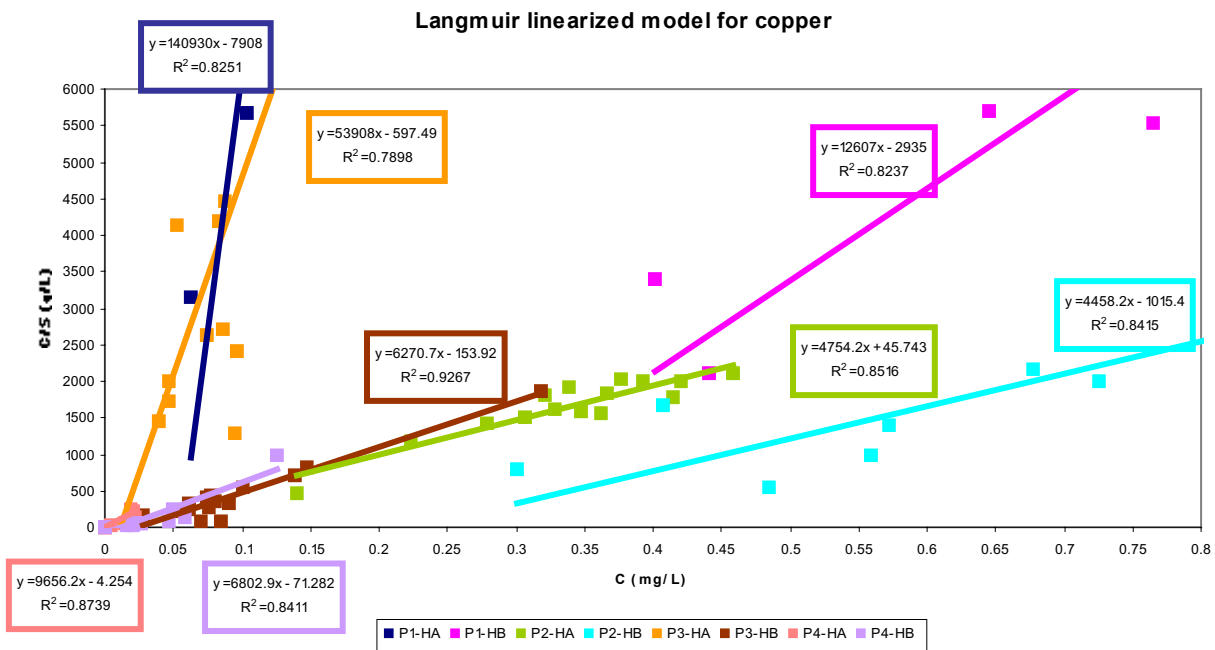


Figure 4. Experimental data for Cu, adjusted by means of the linearization of the Langmuir model. All samples.

In the A horizon of location P2, Cd was only detected in three effluents, while none was detected in B horizon at the same location. Due to this fact, it would not be possible to fit the data from this sample into any model, as with only three datapoints, it would not represent the behaviour of this metal. In the same way, it was impossible to apply any model to sample P2-HB, as indicated in Table 4.

To represent the Cd concentration in the amount of fertilizer applied on the area, both solutions had a concentration of less than 1 (one) ppm Cd. It is therefore difficult to comment on the fact that Cd was not detected in the A or B horizons at location P2. In the other cases, the Langmuir model fitted relatively well for samples P1-HA, P3-HA, and not so well to the samples P3-HB, P4-HA (Figure 5).

Table 5. Total (A+B) detained in soils (mg/kg).

	P1	P2	P3	P4
Cu	1.917	8.731	5.072	6.732
Cd	0.008	0.695	0.158	0.193
Zn	3.270	12.410	5.758	7.953

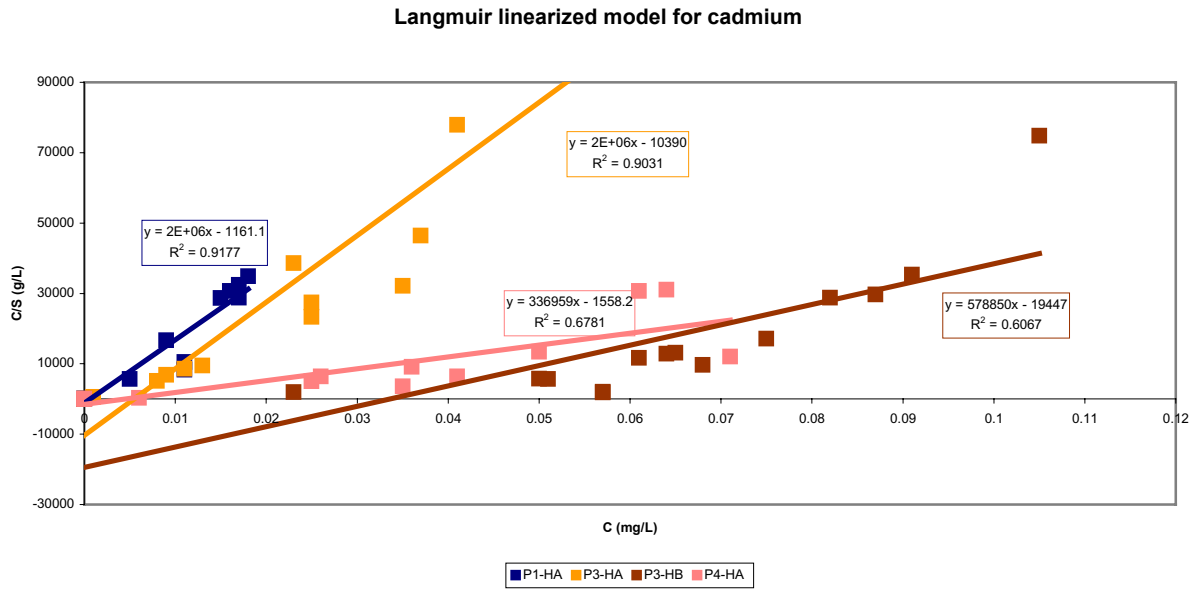


Figure 5. Experimental data for Cd, adjusted by means of the linearization of the Langmuir model. Samples P1-HA, P3-HA, P3-HB and P4-HA.

For the samples P1-HB, P4-HB, the best fit occurred with the linear isotherm model (Figure 5 and Table 4) as can often be the case for low concentrations. In both cases, however, the interpretation of the obtained data and graphic, leads to the conclusion that these specific horizons have a very limited capacity to retain Cd in comparison to the other samples. However, it is noticeable that the sorption decreases throughout the test with a corresponding increase in concentration in the effluent.

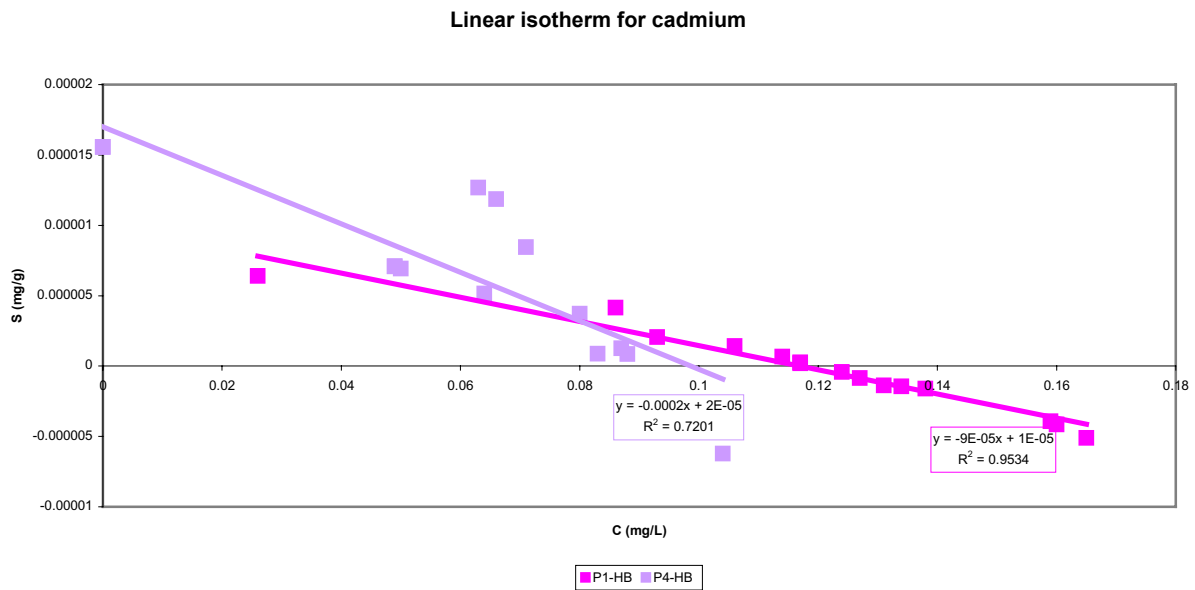


Figure 5. Experimental data for Cd, adjusted by means of the linearization of the Langmuir model. Samples P1-HB and P4-HB.

In the case of Zn, it was only detected in the samples from locations P1 and P2, in both horizons. Zn was not detected in the effluent from the A and B horizon samples from locations P3 and P4. Any attempt to apply one of the models to these results would not be justifiable. For locations P1 and P2, the Langmuir model again provided the best fit, as can be seen in Figure 6, although the fit to the B horizon samples was not as satisfactory as that for the A horizon samples.

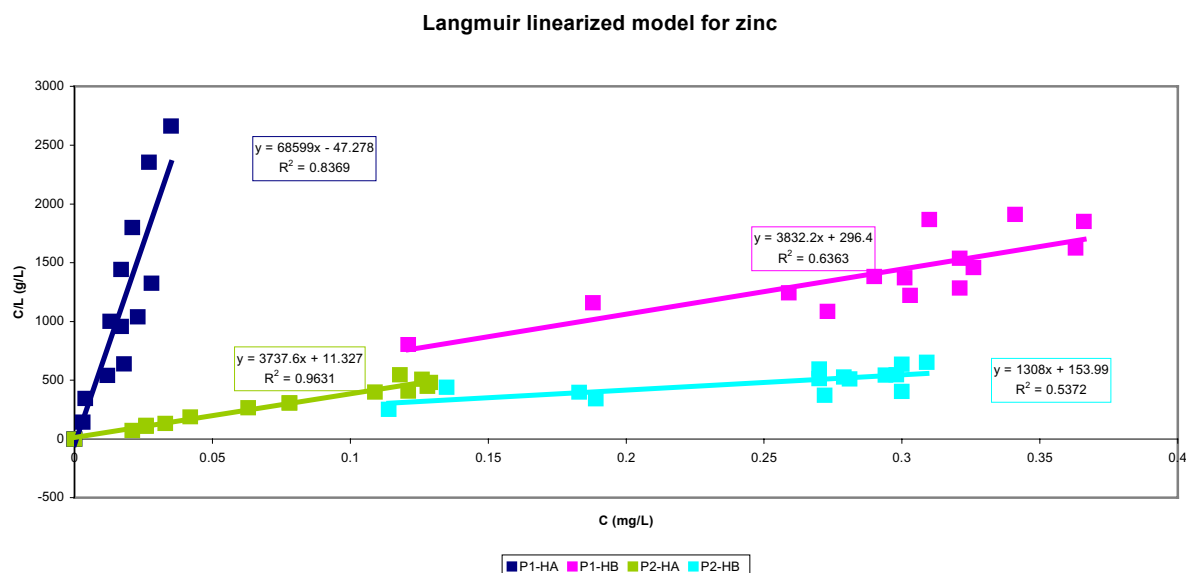


Figure 6. Experimental data for Zn, adjusted by means of the linearization of the Langmuir model. Samples P1-HA, P1-HB, P2-HA and P2-HB.

CONCLUSIONS

The analysis results of the column tests in this study allow us to conclude that, due to the low concentration of metal in solutions, these elements are essentially retained in the observed soils. On the other hand, considering that the soils have a finite capacity of sorption, and with successive fertilizer applications, the studied soil can diminish or even lose its retention capacity, leading to its dispersion through the area. Garcia (2005) related precipitation and erosion on the same study area, from the year 1997 to 2000, and showed a loss of soil of 32,2t/ha, 25,8t/ha, 14,6t/ha and 14,2t/ha a year respectively. These values are high and lead us to believe that the permanence of the metals in the superficial horizons allow them to be carried along with the soil. In consequence, there is a great possibility of this group being captured by rivers and distributed in the superficial waters of the region.

Acknowledgements: The authors are grateful to Mr Leandro Victor dos Santos and Miss Carolina da Silva Carpio, for their assistance on chemical analysis. They are also grateful to PETROBRAS, CNPq and PRONEX for financial incentive.

Corresponding author: Mr Raphael Pietzsch, Universidade Federal Fluminense, Departamento de Geoquímica, Outeiro São João Batista s/n, Morro do Valonguinho - Centro, Niterói, RJ, 24020007, Brazil. Tel: +55 21 2629-2215 Email: pietzschamora@aol.com

REFERENCES

- EMBRAPA – CNPS. 1997. *Manual of soil analysis methods*. 2nd ed. Rio de Janeiro. (in Portuguese).
- GARCIA, S. F. 2005. *Soil erosion and alteration of the microstructure of a Vermelho-Amarelo Latossol subjected to different treatments in an experimental station (Petrópolis – RJ)*. Thesis. PPGG/UFRJ. (in Portuguese).
- MARTIN-GARIN, A., GAUDET, J. P., CHARLET, L. & VITART, X. 2002. A dynamic study of the sorption and the transport process of cadmium in calcareous sandy soils. *Waste Management*, **22**(2). 201-207.
- NICHOLSON, F. A., SMITH, S. R., ALLOWAY, B. J., CARLTON-SMITH, C. & CHAMBERS, B. J. 2003. An inventory of heavy metal inputs to agricultural soils in England and Wales. *The Science of the Total Environment*, **311**(1-3). 205-219.
- SILVA, A. S. 2005. *The Mobility of heavy metals on a toposequence in Petrópolis – RJ*. Doctorate Thesis, PPGI/UFRJ. (in Portuguese).
- SILVA, A. S. 1997. *Physical behavior and soils erosion on a toposequence in Correias (Petrópolis-RJ)*. Thesis, PPGG/UFRJ. (in Portuguese).
- USEPA – United States Environmental Protection Agency. 1999. *Estimating risk from contaminants contained in agricultural fertilizers*, Draft Report. EPA 68-W-98-0085.