

# CHEMICAL FORMS AND SORPTION OF COPPER AND ZINC IN SOILS OF CENTRAL CHILE

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## ABSTRACT

Soil samples from a field irrigated with untreated industrial and municipal wastewater for several decades and from a field not receiving wastewater (control) were analyzed for total Cu and Zn and for the amount of these elements removed in sequential extractions with  $MgCl_2$ ;  $NaOAc$ ;  $NH_2OH.HCl$ ;  $6H_2O_2-HNO_3-NH_4OAc$ ; and  $HNO_3-HF-HCl$ .

Organically-bound Cu forms predominated in the wastewater-affected soil whereas in the control soil both residual and organic forms yielded the same proportion of Cu. Distribution of Zn was different in the diverse fractions, and in the polluted soil the reducible and the residual forms predominated while in the control soil the residual form accounted for the highest proportion of recovered Zn.

Sequential extraction of Cu from a copper sulfate-amended soil incubated for 32 days at constant temperature resulted in the same proportional distribution of Cu forms in the polluted soil. In the control soil the oxidizable form decreased and the residual one increased noticeably.

The two-surface Langmuir adsorption model was used to interpret Cu and Zn adsorption by soils excepting Cu sorption by the polluted topsoil, where the one-surface model was applied.

## INTRODUCTION

Not all fractions of a chemical element in the soil are equally active chemically or biologically. The transfer of metals through soils seems governed by their chemical forms and it is therefore important to measure the distribution of metals according to their affinity to the soil components and the strength with which they are bound by them (Keller and Vedy, 1994). Several procedures have been proposed to determine chemical forms of metals in soils, sequential extraction or fractionation of metals from soils being a useful technique for this purpose. Information gathered by these procedures can be valuable in predicting the pollution potential of a given metal in the environment, its bioavailability and its mobility in the soil.

Several procedures have been proposed for the selective extraction of heavy metals from specific soil phases including iron and manganese oxides, organic material, carbonate, sulfide, clay minerals (McLaren and Crawford, 1973; Tessier et al. 1979; Hickey and Kittrich, 1984; Shuman, 1985; Chang et al., 1992; Keller and Vedy, 1994; Chlopecka et al., 1996; Luo and Christie, 1996; Zhang et al., 1997).

The accumulation of heavy metals in soils irrigated with untreated wastewaters has received some attention by the present authors as in the case of soils irrigated exclusively, and for more than 50 years, with the untreated municipal and industrial sewage waters of the city of Santiago, Chile (Schalscha et al., 1980; Mattigod et al., 1985; Schirado et al., 1986). These untreated sewage waters contain variable amounts of heavy metals (Garlaschi et al., 1985; Ahumada et al., 1997) and their fate in soils irrigated with them is the subject of the present study where the sequential extraction method proposed by Tessier et al. (1979) was used to evaluate the distribution of Cu and Zn chemical forms in two Inceptisols, one irrigated with untreated sewage water

and the other with non-sewage water, and to monitor the chemical forms and amounts of easily and potentially bio-available Cu and their change in time when a copper salt was added to these soils. This study was complemented with an evaluation of the sorption capacity of these soils for Cu and Zn.

## MATERIALS AND METHODS

Samples of two Inceptisols (clayey, mixed, thermo Xerochrepts) were taken from the surface (0-10 cm) and subsurface (10-40 cm) using a spade and a screw-type soil auger. Soil N° 1 is irrigated exclusively with untreated sewage water from the Zanjón de la Aguada canal (Schalscha et al., 1980) which crosses the city of Santiago, Chile from east to west, collecting about 80% of the city industrial and domestic wastewater and sewage. Soil N° 2 is not irrigated with wastewaters.

After being air-dried, the soils were sieved through a non-metallic sieve with 2mm openings. Soil pH was measured as the pH of a 1:1 soil-water paste. Organic Carbon was determined by the Walkley-Black procedure, and cation exchange capacity (CIC) by saturation with sodium at pH 8.2 (Jackson, 1970).

Total metals in each soil sample were determined using a Milestone MLS 1200 MEGA Microwave Oven, treating 200 mg of soil with a HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HF mixture. After this treatment, the samples were reduced to near dryness, made up to volume with 1 M HCl, filtered, and Cu and Zn then determined by Atomic Absorption Spectrometry (AAS).

The reagents used and soil weight ratio and extraction are: 1 g dry weight of soil was first extracted with 8 mL of pH 7 unbuffered 1 M MgCl<sub>2</sub> in a centrifuge tube for 1 hour at room temperature with continual agitation. This step would account for the Exchangeable fraction. After centrifuging and separating phases, the residue was extracted with 8 mL of pH 5 1 M sodium acetate for 5 hours with continuous agitation, thus the Carbonate fraction was obtained. After separating the phases, the Reducible fraction was obtained by extracting the solid residue with 20 mL of 0.04 M

hydroxylamine hydrochloride in 25% acetic acid for 5 hours at 96 °C with occasional agitation. The Oxidizable form was obtained extracting the residue of the previous extraction with 2 mL of 0.02 M HNO<sub>3</sub> and 5 mL of 30 % H<sub>2</sub>O<sub>2</sub> adjusted to pH 2, heating at 85 °C for 2 hours with occasional agitation, then adding a second 3 mL aliquot of H<sub>2</sub>O<sub>2</sub>, and heating again for 3 hours agitating once in a while. After cooling 5 mL of 3 M ammonium acetate in 25 % HNO<sub>3</sub> was added, the sample was diluted to 20 mL and shaken continuously for 30 minutes. The residual form was obtained by treating the residue from the above fraction with HNO<sub>3</sub>, HF, and H<sub>2</sub>O<sub>2</sub> and digesting in a Milestone microwave oven. After cooling, HCl was added and the sample was evaporated to near dryness. The residue was dissolved in 1 M HCl and diluted to 25 mL.

After each treatment the mixture was centrifuged, the phases separated, and the residue was then washed by centrifugation with 8 mL of water. The washings were discarded.

To obtain Cu-amended soil samples, 5.593 mmol Cu kg<sup>-1</sup> of Soil 1 and 5.495 mmol Cu kg<sup>-1</sup> of Soil 2 were added to the surface layer of each soil and the Cu-treated soil was then stored in stoppered polyethylene wide mouth bottles at 20 °C. Samples were extracted from each Cu-treated specimen after 1 hour, 24 hours and 32 days of incubation and sequentially extracted as described above.

Sorption of Cu and Zn was studied treating 1 g dry weight samples of soils with 20 mL aliquots of solutions containing a range of the respective metal perchlorate. The suspension was then shaken for 24 hours at constant temperature (20°C), centrifuged and the metal determined in the supernatant solution by AAS. Metal adsorption was calculated "by difference" by the decrease of Cu or Zn, respectively, from the initial value obtained for the supernatant solution after equilibration. The two-surface Langmuir equation was used to calculate adsorption parameters (Sposito, 1982):

$$q = \frac{b_1 k_1 C}{1 + k_1 C} + \frac{b_2 k_2 C}{1 + k_2 C}$$

where:  $q$  = amount sorbed ( $\text{mmol kg}^{-1}$ )  
 $C$  = amount in equilibrium solution ( $\text{mmol L}^{-1}$ )  
 $b_1, b_2$  = Adsorption maxima  
 $k_1, k_2$  = Constants related to bonding energy

## RESULTS

The soils, of a sandy clay loam texture, have a rather similar pH which increases with depth (Table 1) from 6.9 to 7.6. Organic-C content of Soil 1 (irrigated with untreated sewage waters) is high, with a value of 9.4% at the surface and 2.4 % C at the subsurface level. This high organic carbon content of the surface layer had not been observed before by the authors working with somewhat similar soils (Schalscha et al., 1986 ) and might be due not only to fecal matter deposited by exclusive irrigation with untreated sewage water over a period of more than 50 years, but also from some other, and unknown to us, source. The values obtained were checked several times and on different samples of the same soil. In Soil 2, a control soil, organic-C content was found to be 2.8 and 1.4 %, respectively. No Cd was detected in these soil samples. Total Cu ( $470 \text{ mg kg}^{-1}$ ) and Zn ( $473 \text{ mg kg}^{-1}$ ) in the surface layer of Soil 1 was found to be more than twice as high as in Soil 2 (control). In the sub-surface layer, Cu ( $296 \text{ mg kg}^{-1}$ ) is still nearly twice as high as in the control soil , and Zn ( $250 \text{ mg kg}^{-1}$ ) is half as high.

### Partitioning of metals in soils

The sequential extraction of metals in the soils studied is based, as already described, on the fractionation procedure of Tessier et al. (1979) that partitions metals into the exchangeable, bound to carbonate(Carbonate), bound to Fe,Mn-oxide(Reducible), bound to organic matter(Oxidable) and Residual forms or fractions.

**COPPER:** The proportion of Cu recovered (i.e. the sum of the amount extracted in the five steps divided by the total amount) was about 80% in Soil 1 and 92 to 105% in Soil 2. These low values are probably due to the incomplete destruction of the mineral matrix in the last step of extraction (Keller et al., 1994). In the surface soil of the waste-water irrigated soil, the greatest amount of Cu was found in the Oxidizable fraction (bound to organic matter) which accounts for 62% of the fractional sum of Cu, followed by the Residual fraction (22.2% of fractional sum). Moderate amounts of Cu (11.8 %) are extracted in the Reducible fraction (associated with Fe, Mn-oxide forms) and in the Carbonate one (3%), and less than 1% in the Exchangeable form. In the sub-surface of Soil 1 the highest proportion of Cu was found in the Residual fraction (49.7%), followed by 32.4% in the Oxidizable form, 14% in the reducible one and very little in the Exchangeable and Carbonate forms.

In Soil 2 - the control soil - the Oxidizable fraction of the surface soil accounted for 30% and the Residual fraction for 46% of the extractable Cu. The Reducible form accounted for 7% of the sum of extractable Cu, Carbonate for 2% and the Exchangeable form for less than 1%.

In the sub-surface layer of Soil 2 Exchangeable and Carbonate forms are present in the same proportion as in the surface soil. The Reducible (Fe, Mn-oxide associated) form is higher (15.6%) and the proportion of Oxidizable (bound to organic matter) form decreases noticeably to 23.2%. The Residual fraction increases to 58.4% of the fractional sum.

**ZINC :** The fractional sum of Zn in Soil 1 is above 90% of total Zn in both horizons. The highest proportion of Zn is present in the Reducible form in the topsoil (43.6%) followed by the Residual fraction (25.8%). In the subsoil, values are 17.6 % Reducible and 63.5 % Residual fraction Zn. Exchangeable Zn is less than 1% but Carbonate bound Zn accounts for 16.5 % in the top soil and 7.2 % in the subsoil. Organic matter-bound metal was found to be 13 % and 11.4% respectively.

In the control, Soil 2, Zn was differently distributed since 47.1% in the top soil and 78.3 % in the subsoil were found in the Residual fraction. The Reducible fraction accounted for 26.6% and 13.7% of Zn in the top and subsoil respectively and the Oxidizable fraction for 19% and 6.1%.

### Distribution of copper in Cu-amended soils

Results obtained when sequentially extracting Cu-forms from copper-amended Soils 1 & 2 are shown in Table 3.

Copper added increased exchangeable Cu in both soils only slightly, however significant increases in the carbonate, reducible and oxidable fractions of both soils were observed. The reducible as well as the carbonate form increased initially even more than the oxidizable one, however the carbonate fraction in both soils decreased with time of incubation and the reducible form in Soil 1 tended to stabilize. In Soil 1 the oxidizable form increased more markedly after 24 hours of incubation and decreased slightly after 32 days. The increase of this fraction in Soil 2 was even more significant and no decrease with time was observable. Practically no increase was observed in the residual fraction after 1 and 24 hours of incubation, some increase occurring after 32 days.

After 32 days of incubation about 90% of the theoretically extractable Cu, in both soils, was accounted for.

### Adsorption of metals by soils

Adsorption curves show that copper adsorption by Soil 1 is higher than by Soil 2. Zinc adsorption is higher in the top layer of Soil 1 than in the same layer of Soil 2, however the lower layer (10-40 cm) of Soil 2 sorbed more Zn than the one of Soil 1. Copper and zinc retention can be interpreted by the Langmuir isotherm equation, and examples of the results obtained applying the "one-surface" or, respectively, the "two-surface" Langmuir equation model (Sposito, 1982) are shown in Fig. 1 and 2.

Copper adsorption at both depths of Soil 1 conforms to the "one-surface" Langmuir equation model, while in Soil 2 Cu-sorption can be described by the "two-surface" model. Zinc sorption can be interpreted by the "two-surface" Langmuir equation model at both depths of the two soils and parameters calculated (Table 4). Maximum sorption capacity, "b", for Cu was found to be higher in the surface layer of both soils (about 200 for the topsoil and 140 for the sub-soil) and is somewhat higher than the one for Zn (approximately 170 and 125, respectively).

Bonding energy values of the adsorbed ion, as described by the K values of the "one-surface" Langmuir equation for Cu, were 9.4 for the surface layer and 34.5 for the subsurface one. The bonding energy value in those cases where the "two-surface" Langmuir equation was applicable, suggested the presence of two different adsorption sites with different bonding energies.

## DISCUSSION

Copper and zinc distribution patterns in the soils under study are different as shown by the fractional extraction procedure applied. Organic matter plays an important role in copper retention by soils and this is quite obvious in the waste water-irrigated soil where the decrease in the organic-C content of the soil reduces the proportional amount of copper extracted in the "oxidizable fraction". Zinc distribution is not markedly affected by the organic matter content of the soil and is found predominantly in the "reducible" -or Mn,Fe,oxide-occluded fraction. The same pattern holds true in the control soil. However, the sum total of Cu fractions extracted accounted for about 80% of the total Cu in the sewage-irrigated soil while practically all Cu was accounted for by the sum of the fractions in the control soil. The fraction sum for zinc in the wastewater-irrigated soil was higher than in the control soil.

The data obtained clearly show that irrigation with untreated sewage water increased the reactivity of both elements under study, assuming that reactivity decreases with an increase in the number of extractants in the sequential procedure,



and that the reducible and oxidizable fractions constitute an important source of potentially bio-available Cu and Zn (Tessier et al., 1979).

In the copper-amended soils, incubated for 32 days, a marked increase occurred in the carbonate and also in the reducible forms of the waste water-irrigated soil while smaller increases were observable in the other forms extracted. The increase in the carbonate form indicates that a slight decrease in the pH of the soil will increase bio-available Cu, a reaction that should be expected at the root-soil interaction zone.

The surface horizons of the polluted and the control soil exhibit a higher Cu-adsorption capacity than the respective sub-soils. Copper sorption increases as organic-C content increases. The correlation coefficient between maximum adsorption capacity of Cu and organic C % of soil was found to be 0.98. Thus Cu-retention by organic matter appears to be the predominant mechanism involved, confirming results described by Ritchie and Jarvis (1986). In the subsurface horizon of the waste water-irrigated soil and in both horizons of the control soil, organic matter and manganese and iron oxides appear to be involved in copper retention.

Zinc sorption in all the samples can be described by the "two-surface" Langmuir model and therefore two sorption mechanisms, each with different bonding energy, are present. The surface horizon adsorbs more Zn than the sub-surface one. However, no correlation between adsorbed Zn and organic-C % was found. The  $b_2$  values are higher than the  $b_1$  ones and could be indicating that Zn is predominantly retained by the solid phase of the soil by weak bonding through a non-specific adsorption mechanism

## CONCLUSIONS

The results confirm the dependence of the distribution pattern of metal fractions in the soils on the metal type, copper and zinc having different affinities for the various constituents of the soil. Zinc predominates in the reducible (Fe, Mn-oxide occluded) fraction in the surface soil while the residual form predominates in the subsurface one. Retention by organic matter is the most important mechanism in the case of copper.

Amending soils with copper sulfate and incubating for 32 days before sequentially extracting copper show that the distribution of copper in the wastewater-irrigated soil is very similar with and without added copper. In the control soil however the proportional distribution among fractions is different since in the copper-amended samples the oxidable form increases while the reducible and residual forms decrease.

The "two surface" Langmuir equation model interpreted Cu and Zn adsorption by soils, the exception being the surface horizon of the wastewater irrigated soil, where the "one-surface" Langmuir model applied. Maximum adsorption values for Cu were higher than those of zinc with one exception.

### ACKNOWLEDGEMENT

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**TABLE 1. Some characteristics of soils studied**

Depths, cm	Soil 1		Soil 2	
	0 - 10	10 - 40	0 - 10	10 - 40
pH	6.96	7.46	6.89	7.63
Organic-C, %	9.41	2.38	2.82	1.39
Cd, mmol kg <sup>-1</sup>	nd*	nd	nd	nd
Cu, mmol kg <sup>-1</sup>	7.48	4.71	3.68	2.56
Cr, mmol kg <sup>-1</sup>	4.43	0.71	0.73	0.63
Ni, mmol kg <sup>-1</sup>	0.88	0.45	0.50	0.56
Pb, mmol kg <sup>-1</sup>	0.42	0.22	0.24	0.17
Zn, mmol kg <sup>-1</sup>	7.28	3.85	3.43	2.67

\* = not detected

**TABLE 2. Sequential extraction of Cu and Zn from two soils.**

Depth, cm	Soil 1		Soil 2	
	0 - 10	10 - 40	0 - 10	10 - 40
	----- <b>Copper</b> -----			
Exchangeable	0,05	0,03	0,03	0,02
Carbonates	0,19	0,1	0,08	0,05
Reducible	0,74	0,56	0,27	0,39
Oxidizable	3,87	1,25	1,71	0,58
Residual	1,39	1,92	1,79	1,46
SUM	6,24	3,86	3,88	2,5
	----- <b>Zinc</b> -----			
Exchangeable	0,07	0,01	0,04	0,01
Carbonates	1,09	0,27	0,16	0,03
Reducible	2,89	0,65	0,73	0,29
Oxidizable	0,86	0,42	0,52	0,13
Residual	1,71	2,35	1,29	1,66
SUM	6,62	3,7	2,74	2,12

TABLE 4. Values of Langmuir parameters for Cu and Zn sorption.

Depth, cm	Model	b	b <sub>1</sub>	b <sub>2</sub>	K	K <sub>1</sub>	K <sub>2</sub>
0-10	Langmuir	212.8	1.4	1.4	8.4	1.4	1.4
10-40	Langmuir	144.0	1.4	1.4	24.1	1.4	1.4

TABLE 3. Sequential extraction of copper from the 0-10 cm depth of soils to which Cu has been added.

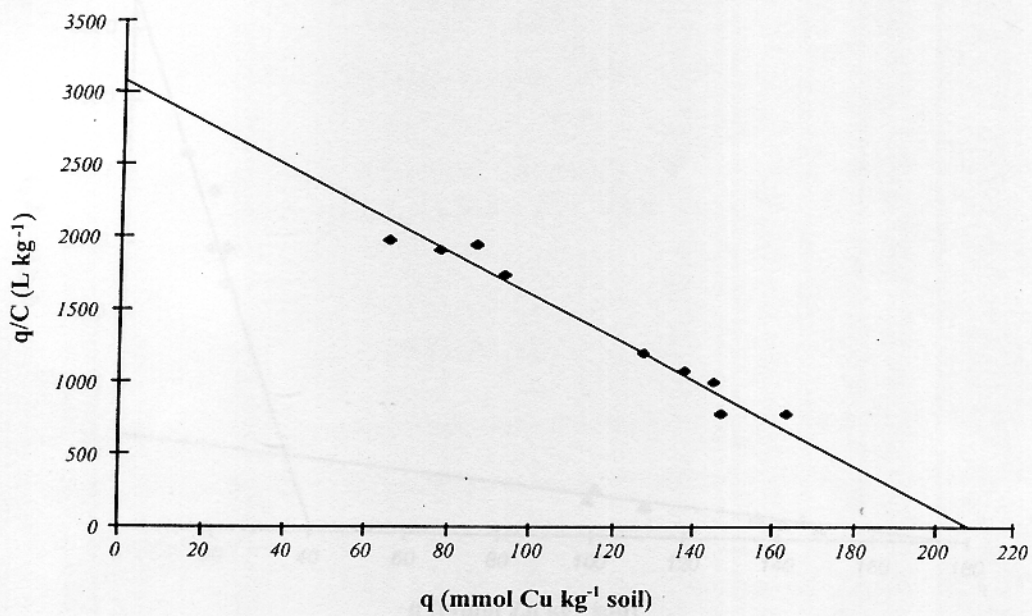
Fraction	1 hour		24 hours		32 days		No Cu added	
	Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2	Soil 1	Soil 2
	----- mmol kg <sup>-1</sup> -----							
Exchangeable	0.14	0.09	0.07	0.06	0.06	0.04	0.05	0.03
Carbonate	0.72	0.42	0.43	0.31	0.48	0.32	0.19	0.08
Reducible	1.47	0.89	1.61	0.84	1.56	1.03	0.74	0.27
Oxidizable	6.25	4.23	7.11	4.41	6.09	5.13	3.87	1.71
Residual	1.86	1.24	1.95	1.31	2.81	1.56	1.39	1.79

TABLE 4. Values of Langmuir parameters for Cu and Zn sorption.

Depth, cm	Model	mmol/kg			L/mmol		
		b	b <sub>1</sub>	b <sub>2</sub>	K	k <sub>1</sub>	k <sub>2</sub>
Copper							
Soil 1	0 - 10	*	212.8			9.4	
	10 - 40	*	144.9			34.5	
Soil 2	0 - 10	**	200.9	70.3	130.6		39.7 5.4
	10 - 40	**	139.5	93.3	46.2		117.6 3.8
Zinc							
Soil 1	0 - 10	**	173.2	32.1	141.1		103.9 3.1
	10 - 40	**	124.8	24.7	100.1		202.4 1.2
Soil 2	0 - 10	**	172.4	25.3	147.1		127.9 1.2
	10 - 40	**	171.8	23.7	148.1		238.9 1.1

\*\* = two-surface Langmuir equation

\* = one-surface Langmuir equation



**FIGURE 1 :** Langmuir "one-surface" isotherm for copper adsorption on top-Soil 1



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IN SOILS OF CENTRAL CHILE

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ABSTRACT

Soil samples contaminated with untreated industrial and municipal wastewater  
for several months and a field not treated soil (control) were analyzed  
for total Zn and Cu. The Zn and Cu forms were determined by sequential  
extractions with weak  $\text{NiOAc}$ ,  $\text{HNO}_3$ ,  $\text{NH}_4\text{OAc}$ , and  $\text{HNO}_3$ -  
 $\text{HF}$ .

Organically-bound Cu forms predominated in the wastewater-affected soil while  
the control soil both residual and organic forms yielded the same proportion of Cu.  
Distributions of Zn was different in the diverse fractions, and in the polluted soil the  
residual and the residual forms predominated while in the control soil the residual  
form accounted for the highest proportion of recovered Zn.

Sequential extraction of Cu from a copper sulfate-amended soil incubated for 32  
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forms in the polluted soil. In the control soil the oxidizable form decreased and the  
residual one increased noticeably.

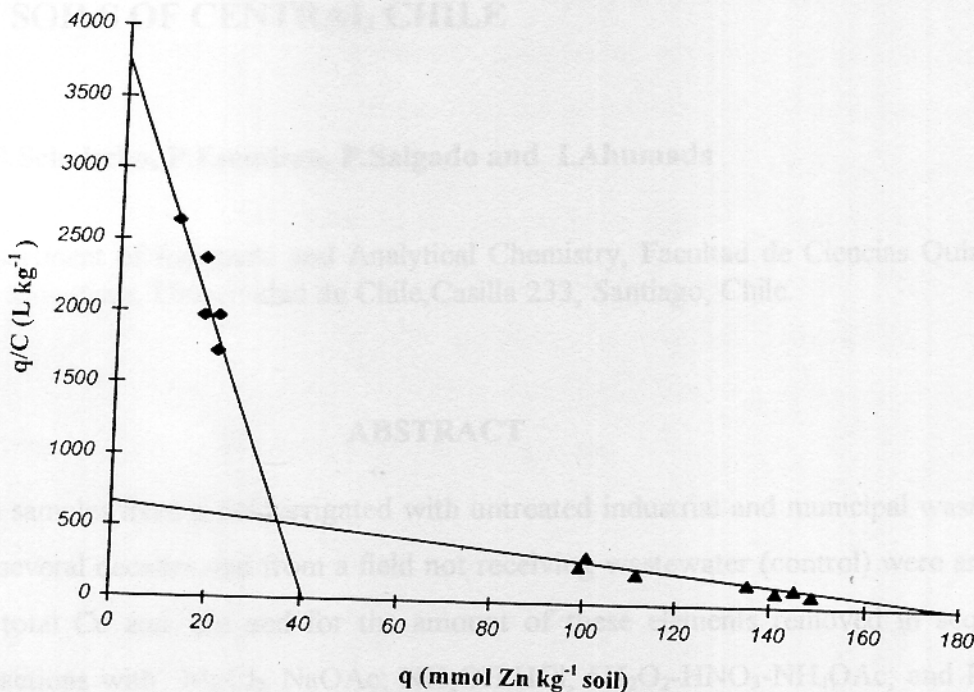


FIGURE 2 : Langmuir "two-surface" isotherm for zinc adsorption on top-Soil 1